DEVELOPMENT OF MONOLITHIC CATALYSTS FOR STORAGE AND REDUCTION OF NITROGEN OXIDE (NOX) IN DIESEL ENGINE EXHAUST

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UNIVERSITI SAINS MALAYSIA
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Laporan Akhir Projek Penyelidikan Jangka Pendek

Development of Monolithic Catalysts for Storage and Reduction of Nitrogen Oxide (NOx) in Diesel Engine Exhaust

by

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PEJABAT PENGURUSAN & KREATIVITI PENYELIDIKAN
RESEARCH CREATIVITY AND MANAGEMENT OFFICE [RCMO]

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*
FINAL REPORT OF SHORT TERM RESEARCH PROJECTS

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1) **Nama Ketua Penyelidik :**
Name of Research Leader :

Ketua Penyelidik *Research Leader*	PTJ *School/Centre*
DR AHMAD ZUHAIRI BIN ABDULLAH	**KEJURUTERAAN KIMIA**

Nama Penyelidik Bersama
(Jika berkaitan) :
Name/s of Co-Researcher/s
(if applicable)

Penyelidik Bersama *Co-Researcher*	PTJ *School/Centre*
PROFESOR SUBHASH BHATIA	**KEJURUTERAAN KIMIA**

2) **Tajuk Projek :**
Title of Project:

DEVELOPMENT OF MONOLITHIC CATALYSTS FOR STORAGE AND REDUCTION OF NITROGEN OXIDE (NOx) IN DIESEL ENGINE EXHAUST

3) **Abstrak untuk penyelidikan anda**

(Perlu disediakan di antara 100 – 200 perkataan di dalam **Bahasa Malaysia dan Bahasa Inggeris**. Ini kemudiannya akan dimuatkan ke dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & luar).

Pembangunan mangkin monolit bagi penstoran dan seterusnya penurunan NOx dalam gas ekzos injin diesel telah dikaji. Zeolit ZSM-5 telah digunakan sebagai sokongan berluas permukaan tinggi untuk disalut ke atas monolit seramik. Reaktor alas tetap yang dioperasikan antara 200 dan 500°C, pada halaju ruang per jam gas (GHSV) 13,000 h^{-1} dan disuap dengan 1,000 ppm NO telah digunakan untuk peringkat penstoran NO. semasa penurunan NO yang terserap, 1,000 ppm i-C_4H_{10} telah disuap kepada reaktor tersebut. Mangkin telah dicirikan sebelum dan selepas tindakbalas bagi mengkaji perubahan-perubahan fizik/kimia yang berlaku kepada bahan tersebut. Komponen aktif bagi pengoksidaan jelaga juga turut dikaji. Mangkin K_2O/Al_2O_3 didapati paling aktif bagi penstoran NO dengan kapasiti penstoran menurun mengikut turutan: K_2O/Al_2O_3 > BaO/Al_2O_3. > CaO/Al_2O_3. Kapasiti penstoran NO bagi $K_2O(10)/Al_2O_3$ juga menurun dengan peningkatan suhu, terutamanya selepas 300°C. Proses penstoran NO mencapai nilai maksimum pada suhu 250°C bagi $K_2O(10)/Al_2O_3$. Cu/ZSM-5 menunjukkan activiti yang paling tinggi bagi penurunan NO, diikuti dengan Fe/ZSM-5 dan Mn/ZSM-5. Suhu optimum bagi penurunan NO ialah 350°C. Pada suhu yang lebih tinggi, penukaran NO merosot atas pelbagai sebab. Substrat monolit dengan makroliang yang mencukupi telah berjaya dihasilkan dan apabila disalut dengan Cu-K_2O-BaO/ZSM-5, suatu mangkin yang aktif untuk penstoran dan penurunan NO telah dihasilkan. Bahan ini memberikan penyingkiran NO melebihi 95 % pada suhu 300°C.

Abstract of Research

(Must be prepared in 100 – 200 words in Bahasa Malaysia as well as in English. This abstract will later be included in the Annual Report of the Research and Innovation Section as a means of presenting the project findings of the researcher/s to the university and the outside community)

The development of monolithic catalysts for the storage and subsequently reduction of NOx in diesel engine exhaust gas was studied. ZSM-5 zeolite was used as the high surface area support to be washcoated onto ceramic monolith. A packed bed reactor operated between 200 and 500°C, at gas hourly space velocity (GHSV) of 13,000 h^{-1} and fed with 1,000 ppm of NO was used for the NO storage stage. During the reduction of stored NO, 1,000 ppm of i-C_4H_{10} was fed to the reactor. The catalysts were characterized before and after the reaction to elucidate physicochemical changes occurred on the materials. Active components for the oxidation of diesel soot were also investigated. K_2O/Al_2O_3 catalyst was found to be the most active for the NO storage process with storage capacity decreased in the order: K_2O/Al_2O_3 > BaO/Al_2O_3. > CaO/Al_2O_3. The NO storage capacity for $K_2O(10)/Al_2O_3$ also decreased with increasing temperature, especially at above 300°C. The NO storage process achieved its maximum at an intermediate temperature (250°C) for $K_2O(10)/Al_2O_3$. Cu/ZSM-5 showed the highest activity for the reduction of NO, followed by Fe/ZSM-5 and Mn/ZSM-5. The optimum temperature for NO reduction was observed at 350°C. At higher temperatures, the conversion of NO would decrease due to various reasons. Monolith substrate with sufficient macroporousity was successfully produced and upon washcoating with Cu-K_2O-BaO/ZSM-5, an active catalyst for NO storage and reduction was produced. With this material, a NO removal of above 95 % was achieved at 300°C.

4) Sila sediakan Laporan teknikal lengkap yang menerangkan keseluruhan projek ini. [Sila gunakan kertas berasingan]

Kindly prepare a comprehensive technical report explaining the project
(Prepare report separately as attachment)

SILA RUJUK KEPADA LAMPIRAN

Senaraikan Kata Kunci yang boleh menggambarkan penyelidikan anda :
List a glosssary that explains or reflects your research:

Bahasa Malaysia	Bahasa Inggeris
OKSIDA NITROGEN (NOx)	**OXIDES OF NITROGEN (NOx)**
MANGKIN	**CATALYST**
PENSTORAN DAN PENURUNAN	**STORAGE AND REDUCTION**
MONOLIT	**MONOLITH**
GAS EKZOS	**EXHAUST GAS**
ENJIN DIESEL	**DIESEL ENGINE**
JELAGA	**SOOT**
ZEOLITE ZSM-5	**ZSM-5 ZEOLITE**
SILIKA MESOLIANG	**MESOPOROUS SILICA**

5) **Output Dan Faedah Projek**
Output and Benefits of Project

(a) * Penerbitan *(termasuk laporan/kertas seminar)*
Publications (including reports/seminar papers)
(Sila nyatakan jenis, tajuk, pengarang, tahun terbitan dan di mana telah diterbit/dibentangkan).
(Kindly state each type, title, author/editor, publication year and journal/s containing publication)

1. Hamidah Abdullah, Subhash Bhatia and Ahmad Zuhairi Abdullah (2007). High performance catalysts for storage and selective catalytic reduction of nitrogen oxides (NOx) in diesel engine exhaust, *AEESEAP Journal of Engineering Education* (Penerbit: Association of Engineering Education in South East Asia and the Pacific (AEESEAP)), diterima untuk penerbitan.
2. A.Z. Abdullah, Y.W. Cheng, H. Abdullah and S. Bhatia (2007). Temperature-programmed analysis of diesel soot oxidation assisted by K_2O-V_2O_5/ZSM-5 catalysts, *Reaction Kinetics and Catalysis Letters,* dalam penilaian.
3. Ahmad Zuhairi Abdullah and Subhash Bhatia (2005). A review of high performance catalyst for storage and reduction of nitrogen oxides (NOx) in diesel engine exhaust, *Proceedings of The AEESEAP Conference 2005*, 7-9 June, Kuala Lumpur.
4. Ahmad Zuhairi Abdullah, Mohamad Zailani Abu Bakar and Subhash Bhatia (2005). Synthesis and characterization of mesoporous SBA-15: A material evaluation for roles in catalysis, *Proceedings of the 2nd International Conference on Chemical and Bioprocess Engineering (ICCBPE 2005)*, in conjunction with *the 19th Symposium of Malaysian Chemical Engineers (SOMChE 2005),* 8-10 December, Kota Kinabalu, Sabah. pp. 858-862.
5. Khor Li San, Noor Shamira Kamaruddin, Subhash Bhatia and Ahmad Zuhairi Abdullah (2006). Development of mixed metal oxides for storage of NOx in diesel engine exhaust, *Proceedings of the International Conference on Green Chemistry (MCC 2006)*, Petaling Jaya, 19-21 September,
6. Phan Wei Loon, Hamidah Abdullah, Subhash Bhatia and Ahmad Zuhairi Abdullah (2006). Performance of Cu-, Fe- and Mn/ZSM-5 in selective catalytic reduction of NOx in diesel engine exhaust gas, *Proceedings of the International Conference on Energy and Environment (ICEE 2006)*, 28-29 August, Kajang, pp. 71-74.
7. Hamidah Abdullah, Cheng Yoong Wah, Subhash Bhatia and Ahmad Zuhairi Abdullah (2006). Development of soot-resistant catalyst for the removal of NOx in diesel engine exhaust gas, *Proceedings of the International Conference on Environment (ICENV 2006)*, Penang, 13-15 November 2006.

(b) **Faedah-Faedah Lain Seperti Perkembangan Produk, Prospek Komersialisasi Dan Pendaftaran Paten atau impak kepada dasar dan masyakarat.**
Other benefits such as product development, product commercialisation/patent registration or impact on source and society

Penyelidikan ini dilihat sebagai telah menyumbang terhadap penilaian aspek-aspek teknikal dalam teknologi penyingkiran NOx dari gas ekzos injin diesel. Pembangunan teknologi yang praktikal, berkesan dan berkos rendah untuk tujuan ini akan menyumbang terhadap penjagaan alam sekitar amnya, dan kesihatan manusia khususnya. Dengan itu, sektor penjanaan tenaga dan penjagaan alam sekitar mampu bergerak selari ke arah mencapai kemajuan negara menerusi pembangunan lestari.

* Sila berikan salinan
* *Kindly provide copies*

(c) **Latihan Gunatenaga Manusia**
Training in Human Resources

i) Pelajar Siswazah :
Postgraduate students:
(perincikan nama, ijazah dan status)
(Provide names, degrees and status)

1. **HAMIDAH ABDULLAH (MSc, 2005-SEKARANG). TAJUK PENYELIDIKAN: *DEVELOPMENT OF MONOLITHIC CATALYST FOR STORAGE AND REDUCTION OF NOx IN DIESEL ENGINE EXHAUST GAS.***

ii) Pelajar Prasiswazah *:*
Undergraduate students:
(Nyatakan bilangan)
(Provide number)

1. **KHOR LI SAN (TAMAT PADA 2006). TAJUK PENYELIDIKAN: *DEVELOPMENT OF MIXED METAL OXIDES FOR STORAGE OF NOx INI DIESEL ENGINE EXHAUST GAS.***
2. **PHAN WEI LOON (TAMAT PADA 2006). TAJUK PENYELIDIKAN: *DEVELOPMENT OF CATALYST FOR SELECTIVE REDUCTION OF NOx IN DIESEL ENGINE EXHAUST.***
3. **CHENG YOONG WAH (TAMAT PADA 2006). TAJUK PENYELIDIKAN: *DEVELOPMENT OF CATALYST FOR THE OXIDATION OF SOOT IN DIESEL ENGINE EXHAUST.***

iii) Lain-Lain :
Others:

6. **Peralatan Yang Telah Dibeli :**
Equipment that has been purchased:

1. Bag pensampelan gas 150 ml.
2. Meter aliran gas nitrogen (0-100 ml/min).
3. Tubing dan fitting keluli tahan karat.
4. Reaktor mikro keluli tahan karat (difabrikasi).

KOMEN JAWATANKUASA PENYELIDIKAN PUSAT PENGAJIAN
Comments of the Research Committees of Schools/Centres

Penyelidikan telah dijalankan
dalam jangka seperti perancangan
dalam cadangan asal penyelidikan

18/6

TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN PUSAT PENGAJIAN
Signature of Chairman
[Research Committee of School/Centre]

PROFESOR ABDUL LATIF AHMAD, CEng FIChemE
Dekan
Pusat Pengajian Kejuruteraan Kimia
Kampus Kejuruteraan
Universiti Sains Malaysia, Seri Ampangan
14300 Nibong Tebal, Seberang Perai Selatan
Pulau Pinang

TARIKH
Date

Updated : 16MAC2006

LAPORAN TEKNIKAL LENGKAP PROJEK GERAN JANGKA PENDEK USM

DEVELOPMENT OF MONOLITHIC CATALYSTS FOR STORAGE AND REDUCTION OF NITROGEN OXIDE (NOx) IN DIESEL ENGINE EXHAUST

Secara keseluruhannya, projek ini boleh dibahagikan kepada beberapa peringkat aktiviti seperti yang disenaraikan di bawah.

1) Pengubahsuaian sistem reaktor yang sedia ada di Pusat Pengajian Kejuruteraan Kimia.

Beberapa pengubahsuaian telah dilakukan untuk menyesuaikan rig reaktor ini bagi menjalankan penyelidikan semasa. Ia termasuklah fabrikasi kolum reaktor pada saiz dan dimensi yang sesuai. Pengubahsuaian juga dilakukan terhadap tubing logam serta kedudukan injap-injap. Reaktor keluli tahan karat telah difabrikasi untuk kegunaan penyelidikan ini. Selain itu, proses penentusahan kadar alir mass flow controller juga dilakukan untuk setiap gas yang terlibat dengan menggunakan meter aliran gas piawai. Gas-gas yang diperlukan (N_2 dan O_2) juga telah dibeli untuk kegunaan penyelidikan ini. Sebuah meter aliran bagi gas nitrogen juga telah ditambah kepada rig tersebut.

Bagi tujuan analisis gas masukan dan juga gas hasilan, proses pembaikan kecil telah dilakukan terhadap alat kromatografi gas (GC) (Shimadzu, model 8A) memandangkan terdapat kebocoran kecil pada bahagian kolumnya. Berikutnya, proses penentusahan, pengenalpastian keadaan-keadaan operasi yang sesuai serta penentuan kepekatan NOx telah dilakukan menggunakan alat GC tersebut. Satu silinder gas helium juga telah dibeli untuk tujuan pengoperasian alat GC tersebut.

Larian pendahuluan rig reaktor juga telah dilakukan untuk mengenalpasti kadar-kadar alir yang sesuai bagi setiap gas yang terlibat untuk memberikan nisbah komposisi yang diingini bagi masukan (feed) ke reaktor. Kestabilan komposisi gas masukan yang diperolehi telah dinilai untuk menjamin keputusan yang bakal diperolehi adalah tepat dan boleh dipercayai. Umumnya, proses penstoran NO (sebagai nitrat logam) dilakukan dengan suapan gas yang mengandungi 1,000 ppm NO, 16 % O_2 dan bakinya ialah nitrogen. Proses ini dilakukan pada suhu antara 200 dan 450 °C. Bagi penurunan nitrat logam pula, suapan tersebut mengandungi 1,000 ppm i-C_4H_{10} sebagai agen penurunan. Kualiti suapan ini digunakan kerana dalam keadaan ini, sistem bermangkin tersebut didapati beroperasi tanpa melibatkan kesan penghadan pemindahan jisim iaitu kadar tindakbalas merupakan langkah pengawalan proses.

2) Proses sintesis dan penilaian kesesuaian bahan sokongan mangkin bermesoliang (mesoporous).

Kajian bertujuan untuk menilai kesesuaian bahan silika bermesoliang (mesoporous silica) untuk bertindak sebagai bahan sokongan mangkin untuk proses penurunan NOx. Penghasilan bahan silika bermesoliang (mesoporous silica) telah dilakukan dengan menggunakan polyethylene glycol-polypropylene glycol-polyethylene glycol (jisim molekul=5800) sebagai triblock co-polymer (TCP) (agen pentemplatan). Reagen-reagen lain ialah seperti tetraethyl orthosilicate (TEOS) sebagai sumber silika serta asid HCl. Suatu siri bahan bermesoliang telah dihasilkan dengan mengubah komposisi gel serta suhu tindakbalas. Faktor-faktor yang dikaji ialah seperti kesan keasidan, kandungan TEOS, kandungan TCP serta suhu peringkat pengelan. Bahan bermesoliang yang diperolehi dikaji menggunakan kaedah-kaedah pencirian biasa seperti TEM, XRD, ciri-ciri permukaan dan sebagainya.

Kestabilan bahan bermesoliang tersebut terhadap pengolahan termal, hidrotermal serta mekanikal juga turut dikaji. Ini dilakukan dengan cara melihat perubahan dalam ciri-ciri utama bahan bermesoliang selepas pengolahan-pengolahan tersebut. Objektf utama kajian ini ialah untuk menilai kesesuaian bahan tersebut untuk bertindak sebagai bahan sokongan mangkin dalam aplikasi penyingkiran NOx dari gas ekszos diesel.

Oleh sebab hidrolisis TEOS dan kondensasi silica yang cepat, peningkatan keasidan menggalakkan pembentukan mesoliang. Suatu bahan yang mempunyai luas permukaan sebanyak 760 m^2/g, kebanyakannya dalalm julat meso, telah disentesis menggunakan komposisi gel 1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O pada pH 2.1. Kepekatan cmc TCP ini sedikit rendah berbanding nilai yang dilaporkan untuk poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) lain. Pembentukan mesoliang sangat dipengaruhi oleh nisbah TEOS:TCP. Peningkatan nisbah dari 1.56:1 ke 2.09:1 menggalakan pembentukan mesoliang manakala peningkatan selanjutnya ke 2.61:1 adalah disebaliknya. Peningkatan kandungan TCP ke 3.5 % berat/berat menggalakan pemiselan. Namun, peningkatan seterunya ke 4.6 % patut dielak. Keasidan lemah silica mesoliang disumbangkan oleh kumpulan silanol pada dinding dalaman bahan tersebut.

Pengolahan termal dan hidrotermal mengurangkan kemesoliangan sebanyak 19.2 % dan 32.6 %, masing-masing dengan pembentukan nanoliang sekunder yang lebih besar sebagaimana yang dicirikan oleh isoterma penjerapan-penyahjerapan. Pada 75 MPa, silica mesoliang mampu mengekalkan lebih dari 80 % luas permukaannya. Kestabilan ini dikaitkan susunan heksagonal bagi liang-liang lurusnya serta ketebalan dinding liang.

3) Kajian proses penstoran NOx pada bahan mangkin pada kepekatan NOx yang rendah untuk suatu jangkamasa yang panjang.

Kajian ini meliputi pelbagai peringkat seperti berikut.

i) Analisis bebolehulangan data eksperimen. Analisis ini dilakukan untuk menilai kebolehulangan data pada keadaan eksperimen yang sama bagi tindakbalas tersebut. Hasilnya, kebolehulangan data penukaran sebanyak 2 % telah diperolehi dan dianggap memadai untuk tujuan kajian ini.

ii) Pengukuran Keberkesan penstoran NOx. Kajian ini dilakukan pada kepekatan NO 1,000 ppm, kepekatan oksigen 16 % dan selebihnya ialah nitrogen. Jumlah kadar aliran bagi gas masukan ialah 50 ml/min. Eksperimen ini dilakukan pada suhu 350°C selama 20 min. Komponen aktif yang dikaji ialah 10 % berat K_2O dan CaO dengan bahan sokongan alumina (Al_2O_3).

iii) Kajian kesan suhu operasi. Kajian ini dilakukan pada suhu 200-450°C untuk menilai kesan suhu terhadap keberkesanan proses penstoran NOx dalam K_2O/Al_2O_3 dan CaO/Al_2O_3.

iv) Kajian kesan kandungan logam. Kajian ini dilakukan menggunakan K_2O/Al_2O_3 pada kandungan K_2O antara 0-25 % berat. Objektifnya ialah untuk menilai kesan kandungan logam tersebut terhadap keberkesanan serta kelakuan proses penstoran NOx dalam bahan mangkin tersebut.

v) Kajian kesan komposisi logam. Kandungan logam barium dalam $BaO(x)K_2O(y)/Al_2O_3$ juga turut dikaji.

vi) Proses pencirian bahan mangkin seperti sifat permukaan, imej SEM dan juga telah dilakukan untuk mencirikan perubahan-perubahan yang telah berlaku ke atas bahan mangkin tersebut.

Amaun NO yang distorkan dalam mangkin didapati bergantung kepada kebesan komponen storan. Mangkin K_2O/Al_2O_3 didapati paling aktif untuk proses storan NO dengan kapasiti storan menurun mengikut turutan: K_2O/Al_2O_3 > BaO/Al_2O_3. > CaO/Al_2O_3. Kapasiti storan NO bagi $K_2O(10)/Al_2O_3$ juga menurun dengan peningkatan suhu, terutamanya selepas 300°C. Proses penstoran NO mencapai nilai maksimumnya pada suhu 250°C for $K_2O(10)/Al_2O_3$. Bagi $BaO(10)/Al_2O_3$ pula, kapasiti penstoran NO meningkat dengan peningkatan suhu. Kesan kandungan K 0-25 % (berat/berat) bagi penstoran oleh K_2O/Al_2O_3 menunjukkan bahawa penambahan K_2O mempunyai kesan negatif terhadap sifat-sifat morfologi pada kandungan melebihi 15 %. Namun, peningkatan kandungan K_2O mengakibatkan peningkatan ketara dalam NO penyerapan semasa titik bulus. Dalam keadaan ini, penstoran maksimum NO sebanyak 60 % telah diperolehi bagi sampel $K(15)/Al_2O_3$. Kombinasi Ba dan K (masing-masing 5 % berat) dalam mangkin didapati meningkatkan aktiviti mangkin berbanding mangkin logam tunggal.

4) Kajian proses penurunan bermangkin terpilih (SCR) bagi NOx pada kepekatan agen penurunan (butane) yang tinggi.

Kajian ini meliputi pelbagai peringkat seperti berikut.

i) Larian kosong. Peringkat ini dilakukan untuk menilai keberkesanan penurunan bermangkin terpilih (SCR) bagi NOx tanpa kehadiran bahan mangkin. Ia dilakukan pada kepekatan gas masukan NO 1000 ppm, kepekatan butana 1000 ppm, kepekatan oksigen 3 % dan selebihnya ialah nitrogen. Kadar alir yang digunakan ialah 50 ml/min.

ii) Proses SCR bagi NOx. Kajian ini melibatkan penggunaan 0.2 g Cu, Fe dan Mn/ZSM-5 pada komposisi 10 % berat. Saiz partikel mangkin yang digunakan ialah 475-600 μm. Perbandingan keberkesanan bagi setiap mangkin dalam penyingkiran NOx telah dilakukan.

iii) Kajian kesan suhu terhadap keberkesanan penyingkiran NOx menggunakan Cu/ZSM-5. Kajian ini dilakukan pada suhu tindakbalas antara 200-450 °C.

iv) Kajian kesan kandungan Cu dalam Cu/ZSM-5 terhadap keberkesanan penyingkiran NOx. Kajian ini dilakukan mengunakan Cu/ZSM-5 pada % kandungan Cu antara 5-25 % berat.

v) Pencirian mangkin sebelum dan selepas tindakbalas juga telah dilakukan bagi mencirikan perubahan fizikal/kimia yang telah berlaku akibat tindakbalas tersebut.

Di antara 3 jenis mangkin zeolit yang diuji, Cu/ZSM-5 menunjukkan aktiviti yang paling tinggi (sehingga 55 %) bagi proses penurunan NO, diikuti dengan Fe/ZSM-5 dan Mn/ZSM-5. suhu optimum bagi penurunan NO telah diperhatikan pada 350°C. Penyingkiran yang paling tinggi bagi Fe/ZSM-5 (45 %) berlaku pada 300°C. Pada suhu yang lebih tinggi, penukaran NO akan menurun akibat pengoksidaan agen penurunan (i-C_4H_{10}) yang keterlaluan. Pada kandungan Cu yang rendah, aktiviti penurunan NO meningkat dengan peningkatan kandungan Cu dalam mangkin. Kandungan Cu melebihi 15 % tidak membawa peningkatan ketara dalam penurunan NO kerana faktor halangan bagi sebilangan liang dalam zeolit tersebut.

5) Kajian pengenalpastian komponen mangkin yang berperanan dalam pengoksidaan jelaga (soot) yang terhasil dalam pembakaran diesel.

Kajian ini meliputi pelbagai peringkat seperti berikut.

i) Kajian pengoksidaan berprogramkan suhu (TPO). Kajian ini bertujuan menyelidiki keupayaan mangkin untuk mengoksidakan jelaga hasil pembakaran diesel. Eksperimen dilakukan pada suhu antara 60-600°C dalam udara pada kadar aliran 50 ml/min menggunakan mangkin V_2O_5/HZSM-5 dan K/V_2O_5/HZSM-5. Nisbah mangkin kepada jelaga ialah 9:1 dengan berat keseluruhannya 0.5 g. Gas produk dianalisis menggunakan GC yang dilengkapi dengan kolum Porapak Q untuk pemisahan gas CO_2.

ii) Kajian kesan kandungan K dalam K_2O/HZSM-5. Kajian ini dilakukan menggunakan kandungan K antara 1.5-7.5 % berat.

ii) Kajian kesan SO_2 dalam gas masukan terhadap pengoksidaan jelaga. Kajian ini dilakukan untuk mengkaji kesan pembentukan sulfat pada mangkin. Mangkin yang telah digunakan ialah V_2O_5/HZSM-5 dan kesan kehadiran SO_2 dinilai dari segi perubahan dalam penghasilan CO_2 dari pengoksidaan jelaga.

iv) Kajian kesan penggunaan logam-logam berlainan. Kajian ini telah dilakukan menggunakan V_2O_5/HZSM-5, CuO/HZSM-5 dan Fe_3O_4/HZSM-5 sebagai perbandingan.

v) Pencirian mangkin sebelum dan selepas tindakbalas juga telah dilakukan bagi mencirikan perubahan fizikal/kimia yang telah berlaku akibat tindakbalas tersebut.

Aktiviti mangkin bagi pembakaran jelaga diesel dipengaruhi oleh sentuhan antara jelaga dan mangkin. Mangkin dengan Catalyst dengan mobiliti atom permukaan akan mempertingkatkan sentuhan antara jelaga dan mangkin kerana titik cairnya yang rendah. Oleh itu, ia mampu menurunkan suhu bagi pembakaran jelaga. Pendopan kalium ke dalam mangkin vanadium mampu meningkatkan kereaktifan ikatan V-O dan seterusnya mempertingkatkan sentuhan antara mankin dan jelaga. Jadi, kalium mampu pempertingkatkan aktiviti bagi pengoksidaan jelaga. Antara mangkin yang dikaji dengan kandungan kalium yang berbeza (1.5%, 4.5% dan 7.5%), yang pertengahan itu mempamerkan aktiviti yang paling tinggi bagi pembakaran jelaga manakala mengkin dengan kandungan kalium yang paling tinggi didapati paling stabil. Kalium mampu memainkan peranan yang berbeza dalam kelakuan mangkin-mangkin ini iaitu i) meningkat sentuhan mangkin-jelaga dengan memberikan mobiliti permukaan, ii) memelihara kapasiti redoks bagi V_2O_5, iii) menggalakkan pengoksidaan jelaga dengan cara menggunakan karbon bagi membentuk spesis karbonat semasa pembakaran jelaga.

6) Penyediaan substrat monolit seramik

Substrat monolit seramik dengan berbagai komposisi juga telah disediakan. Keliangan makro juga telah ditingkatkan dengan cara mencampurkan metil selulosa dalam campuran bahan seramik. Pes bagi seramik itu dikeringkan pada suhu 105 °C selama 2 jam dan seterusnya dikalsinkan pada suhu 900 °C selama 4 jam. Ciri-ciri permukaan bahan monolit seramik itu seterusnya dikaji menggunakan kaedah SEM. Substrat monolit seramik terbaik telah diperolehi dengan komposisi pes seperti berikut: kaolin (70 %), sodium lignosulfate (10%) and magnesium hydroxide (20 %). Penambahan metil selulosa sebanyak 3 % berat didapati telah meningkatkan kemakroliangan substrat tersebut dengan ketara. Kandungan metil selulosa yang lebih tinggi menyebabkan struktur seramik yang lemah terhasil.

7) Penstoran dan penurunan NO menggunakan mangkin monolit seramik

Mangkin monolit telah disediakan dengan menyalut (washcoat) monolit seramik dengan silika mesoliang dan ZSM-5 yang kemudiannya diimpregnasikan dengan 10 % Cu, 5 % K_2O dan 5 % BaO secara kaedah impregnasi bersama (co-impregnation). Umumnya, proses penstoran NO (sebagai nitrat logam) dilakukan dengan suapan gas yang mengandungi 1,000 ppm NO, 16 % O_2 dan bakinya ialah nitrogen. Proses ini dilakukan pada suhu antara 200 dan 450 °C. Bagi penurunan nitrat logam pula, suapan tersebut mengandungi 1,000 ppm i-C_4H_{10} sebagai agen penurunan. Mangkin monolit dengan ZSM-5 didapati lebih aktif dalam aktiviti penstoran dan penurunan NO. Ia dikaitkan dengan faktor penyebaran komponen aktif pada permukaan substrat monolit seramik tersebut. Penyingkiran melebihi 95 % mampu dicapai dengan mangkin ini pada suhu 300 °C. Kestabilan dalam aktiviti ini diperolehi sehingga 4 kitaran penggunaannya. Ujian kestabilan terhadap kitaran suhu tinggi (700 °C) dan penyejukan kepada suhu bilik menunjukkan bahawa mangkin seramik ini adalah stabil and tidak mengalami perubahan struktur yang ketara.

High Performance Catalysts for Storage and Reduction of NOx in Diesel Engine Exhaust

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ABSTRACT

Despite offering fuel efficiency and reliability its operation, diesel engines also cause adverse environmental effects, especially due to the emission of nitrogen oxides (NOx) and soot. Selective catalytic reduction of NOx is a practical method to get rid of NOx in diesel engine exhaust gases. A number of catalysts have been developed in which the active phases are different metallic oxides such as oxides of Mn, Co, Cu and noble metals. The common catalyst supports being employed are such as vanadia, titania, ceria, zirconia and lanthana. The reduction of NOx generally takes place over a fairly narrow temperature range. The innovative NOx storage and reduction (NSR) concept offers few advantages for NOx removal process. NOx will first be stored in the catalyst followed by the reduction when spikes of reductant are introduced into the feed. The catalysts used for NSR comprise combinations alkali oxides (barium or potassium) to store NOx as surface nitrates. Combinations of noble and/or transition metals then play the role in reducing nitrates to benign gaseous nitrogen. The second stage is carried out in a shorter lean periods in which very rich purges of reductant such as ammonia or hydrocarbons are fed. Potassium–loaded catalysts promoted by barium have been found to show high activity in soot combustion due to their high mobility to consequently increase the effective contact between the catalyst and the soot particle. Thus, the reaction rate soot combustion reaction rate is accelerated. By a proper combination of active metals, a catalyst suitable for the NSR process, while showing lower tendency to be deactivated by soot can be obtained. Structured NSR catalyst can offer added advantages in terms of low pressure drop and resistance to thermal shock.

Keywords: Diesel exhaust, NOx, selective catalytic, reduction, storage, soot oxidation.

1 Introduction

The diesel engine owes its popularity to its fuel efficiency that results from its lean-burn operation, reliability, durability and relatively low fuel price (Solis *et al.,* 2001, Milt *et al.,* 2003, Kabin *et al.,* 2004). However, diesel engine exhaust also has many adverse environmental effects, particularly due to the high concentration of nitrogen oxides (NOx), particulate matter in the form of soot and sulfur dioxide (SO_2). The emission of nitrogen oxides (NOx) and particulate matter (soot) from diesel engine vehicles is of major environmental concern, especially in view of the increasingly stringent limits worldwide. Legal limits for emissions of carbon monoxide, unburned hydrocarbons and nitrogen oxides (NOx) in automotive and stationary sources exhaust gases are becoming more and more strict. Emission standards for heavy duty vehicles in 2007 and beyond will require a 90 % reduction in total particulate matter and NOx from 2003 levels (Kabin *et al.,* 2004). These standards place new demands for an improvement in engine performance, as well as on the development of suitable catalytic converter technology to minimize the discharge of those pollutants. At the same time, there is a strong pressure to lower the fuel consumption for economic purposes and to lower the production of carbon dioxide, which is an important greenhouse gas (Odenbrand *et al.,* 1999, Koci *et al.,* 2004). This objective can be achieved by running the engine with oxygen excess, known as 'lean burn' that can reduce fuel consumption by 20-30 % (Kabin *et al.*, 2004). Unfortunately, this measure will often result in an increase in NOx emission as the high oxygen in such engine exhausts means that the three-way catalyst (TWC) technology conventionally used to remove NOx can no longer be used. Thus, alternative catalytic method to remove NOx in such engines is very much demanded.

2 Selective catalytic reduction (SCR) of NOx

2.1 SCR process and reaction

Conventional process for deNOx of exhaust gases is by converting NOx via a reduction process mainly by ammonia or hydrocarbon (HC) component that present in the gas, to nitrogen (N_2) which is safe to the environment. In recent years, hydrocarbons have been studied in order to replace the current best control technology for reducing NOx emission stationary sources that usually employ ammonia as reducing agent (Blanco *et al.,* 1998, Seijger *et al.,* 2001). NH_3-SCR is a well-known process, which can remove NOx in oxygen-rich conditions. It is, however, difficult to employ ammonia as the reducing agent for mobile NOx sources because of its toxicity and corrodibility (Blanco *et al.*, 1998). The main advantage of the reaction between NOx and hydrocarbons in post-combustion processes is the use of gas mixture similar to that found in the exhaust. The lean-burn conditions of diesel combustion, which yield higher combustion temperature and improved efficiency, produced an exhaust gas containing an excess of oxygen. This complicates conventional approaches to chemically reduce NOx to N_2 as the reducing components such as carbon monoxide (CO), hydrocarbon (HC) and hydrogen (H_2) are preferably oxidized by oxygen (Koci *et al.,* 2004). Therefore, selective catalytic reduction using a hydrocarbon as a reducing agent has been widely proposed as one of the promising techniques to get rid of NOx in the exhaust gas. The reaction involves is;

$$a\,\mathrm{NO} + b\,\mathrm{HC} + c\,\mathrm{O_2} \rightarrow d\,\mathrm{N_2} + e\,\mathrm{CO_2} + f\,\mathrm{H_2O} \qquad (1)$$

The catalytic reduction of NOx has been generally found to take place over a fairly narrow temperature range. However, diesel exhaust temperature varies from 200°C to 600°C (Seijger *et al.*, 2001). Thus, to obtain the needed reduction over a wide range of operating temperatures, more than one catalyst could be used (Kabin *et al.* 2004).

2.2 Active catalysts for SCR of NOx

The reduction of NOx in oxygen rich-conditions using hydrocarbon (HC) as reductant is a well proven technique for the removal of NOx from stationary sources and has become of increasing interest in recent years (Solis *et al.*, 2001). A number of catalysts have been developed in which the active phases are different metallic oxide such as manganese oxide (Solis *et al.*, 2001), cobalt (Milt *et al.*, 2003 ; Pisarello *et al.*, 2002), copper (Odenbrand *et al.*, 1999 ; Seijger *et al.*, 2001) and noble metals (Odenbrand *et al.*, 1999 ; Blanco *et al.*, 1998 ; Bahamonde *et al.*, 2003). The common catalyst supports being evaluated for this application are such as vanadia (Makkee *et al.*, 2002), titania (Odenbrand *et al.*, 1999), ceria (Pisarello *et al.*, 2002), zirconia (Bahamonde *et al.*, 2003) and lanthana (Pisarello *et al.*, 2002 ; Milt *et al.*, 2003). Several other catalyst systems and the observation in their application are summarized in Table 1. Bearing in mind the narrow operating window for NOx reduction, more than one catalyst has to be used to obtain the needed reduction over a wide range of operating temperatures. The combinations of catalysts have been recently reviewed by Blanco *et al.* (1998). They distinguished two main types of systems: bifunctional catalysts, in which there is a cooperation of two catalytic species, and staging of two or more catalysts in line. In short, the development of a multimetallic catalyst for improved performance over a wider temperature range is a current research trend in this area and is definitely a worthwhile effort.

Table 1. Performance of few catalyst systems tested for NOx reduction.

Ref	Catalyst	Conditions	Remarks
Odenbrand *et al*, (1999)	Cu & Pt/TiO_2	Real exhaust gas 1000 ppm NOx 260 ppm HC	Active for NOx reduction with diesel fuel as reductant. Stable with slight deactivation after 50 h in operation.
Bagnasco *et al*., (2000)	$[Fe(H_2O)]_{0.2}(VO)_{0.8}PO_4$	250-450°C $t=9x10^{-3}$ s 500 ppm CH_4	NO conversion by CH_4 reached up to 60 % with small N_2O production. H_2O could suppress N_2O formation
Ohtsuka *et al*. (2000)	Pd & Pt/ sulfated ZrO_2	350-500°C 150 ppm NOx 2,000 ppm CH_4	Reached over 50 % conversion over 100 h operation in 9 % water vapor and 3 ppm SO_2
Seijger *et al*. (2001)	Cu-ZSM-5	200°-350°C 500 ppm NOx NH_3/NOx < 2.5	Active catalyst for SCR of NOx with NH_3. Slight deactivation after 100 h of operation.
Bahamonde *et al*. (2003)	Pd/ZrO_2	300-600°C 500 ppm NO 5,000 ppm CH_4	High activity for NO conversion with CH_4. Amorphous zirkonium hydroxide was a more suitable as the starting material than crystalline ZrO_2.
Deeng *et al*. (2004)	Cu-ZSM-5	375°C 1730 ppm NOx 1280 ppm i-C_4H_{10}	94 % reduction of NO and 4.6 % SCR-HC selectivity. No structural changes in the catalyst after 48 h of continuous operation.
He *et al*. (2005)	Ag /Al_2O_3	300-400°C C_2H_5OH/ NOx=3:1	The highest NOx conversion reached 92.3 % Extremely effective in the NOx reduction even in the presence of water vapor.

3 NOx storage and reduction (NSR)

3.1 NOx storage and reduction mechanism.

One novel approach of deNOx process is the so called NOx storage and reduction (NSR) concept based on storage of NOx in the catalyst for relatively long lean periods until saturation, followed by interruption by rich spikes of reductant (Pisarello *et al.*, 2002 ; Bahamonde *et al.*, 2003). During the rich periods, the NOx stored in the catalyst during the lean periods is decomposed and subsequently reduced to nitrogen. The NOx storage and reduction process over a noble metal catalyst is schematically shown in Figure 1 (Takahashi *et al.*, 1996).

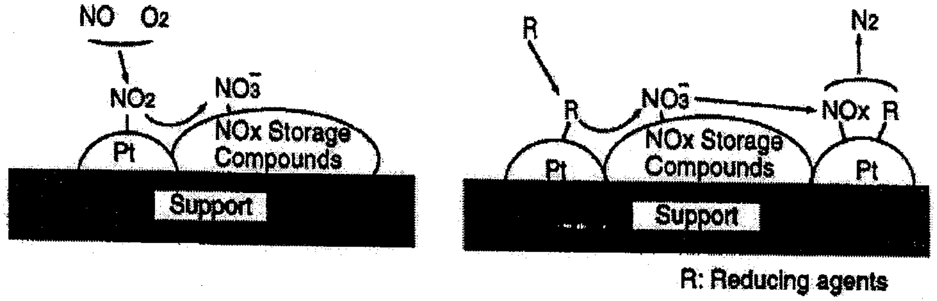

Figure 1. NOx storage and reduction process.

3.1.1 NOx storage mechanism

The most commonly used active components of the catalyst for NOx storage applications comprise combinations of noble metals for oxidation and reduction purposes and barium oxide/carbonate as the storage materials (Amberntsson *et al.*, 2003). It has been reported that the nitrogen oxides are chemically bound as surface nitrates (Bahamonde *et al.*, 2003). It is generally assumed that the oxidation of NO to NO_2 is a necessary initial step before NOx storage can actually take place during lean conditions (Amberntsson *et al.*, 2003). The storage would then take place by the formation of nitrate.

$$2\,NO_2 + \tfrac{1}{2}\,O_2 + BaO \rightarrow Ba(NO_3)_2 \qquad (2)$$

The high absorption rate and capacity are generally attained using more basic components. The alkaline earth and rare earth are effective components in this respect. However, the use of bulk alkaline or rare earth compounds implies degradation by the formation of stable carbonate in the presence of CO_2 (Eguchi *et al.*, 1996).

3.1.2 NOx reduction mechanism

Nitrates formed under oxidizing conditions are supposed to be decomposed into NOx by the reducing agent (HC, CO, H_2, NH_3, etc.). Then, the emitted NOx is immediately reduced by the reducing agent to nitrogen. This process is catalyzedd by the active metal components in the catalyst (Takahashi *et al.*, 1996). The reduction process proceeds as the following,

$$2\,NOx + HC + a\,O_2 \rightarrow N_2 + b\,CO_2 + c\,H_2O \quad (3)$$

3.2 The deactivation of NSR catalysts

The affinity for nitrate formation also entails the affinity for sulphation, which will lead to deactivation of the NOx storage capacity if sulfur is present in the exhaust gas (Park *et al.*, 2005). Two pathways of catalyst deactivation by SO_2 are generally discriminated. Under lean conditions (exposure to SO_2 and O_2), the storage component forms barium sulfides, which are transformed from surface to hardly reducible bulk sulphates species. The irreversible blocking of the Ba sites led a decrease in NOx storage capacity. Under rich condition (SO_2 / HC), evidence for the formation of sulfides on the oxidation/reduction component of the catalyst was found, which blocks the metal surface and thus, hinders the further reduction of the sulfides (Sedlmair *et al.*, 2002). Recently, the performance of the catalysts is improved through sulfur tolerance studies. It is achieved by the incorporation of suitable metals into the NSR catalyst. Encouraging results have been reported with the addition of iron (Fanson *et al.*, 2003), zinc (Hasegawa *et al.*, 2005) and silver (Park *et al.*, 2005). The addition of iron improves the long term stability of the catalyst by supporting the formation of unobserved bulk nitrate species that are resistant to the effects of SO_2 (Fanson *et al.*, 2003). The silver catalysts also show enhanced NOx reduction performance in the presence of SO_2 (Park *et al.*, 2005). They discovered that the enhancement was attributed to the formation of Ag_2SO_4 phase from silver oxide. Silver sulfate phase was found to be more active and selective for the reduction of NOx than silver oxide.

Water vapor is one of the gaseous components that generally present in diesel exhaust. Its presence will also cause catalyst deactivation but the effect waas temporary and reversible (Deeng *et al.*, 2004). They observed that when the addition of water vapor was stopped, the NOx conversion recovered to its initial level. This observation is in contrast to the observation made when ethanol was used as the reductant. In this case, the presence of water vapor did not decrease the NOx conversion but in fact, enhanced the activity of Ag/Al_2O_3 (He *et al.*, 2005).

3.3 Factors affecting the performance of NSR catalyst.

The NOx storage capacity of model NSR catalysts is as a function of temperature, oxygen (O_2), carbon dioxide (CO_2) and reductant concentrations (Kabin *et al.*, 2004). The influences of O_2 and CO_2 on the NOx release step have been investigated and they concluded that O_2 inhibits the NOx release process by rising the desorption temperature. In contrast, CO_2 promotes NOx release by forming barium carbonate ($Ba(CO_3)$) as also concluded by Amberntsson *et al.* (2003). The NOx release process is also minimized when shorter lean periods are used (translated as lower amount of NOx stored) and when very rich purges are fed (translated as providing excess reductant) (Kabin *et al.*, 2004).

Water vapor also affects the performance of NSR catalysts. It has been reported that CO_2 and water both decrease the storage capacity of Pt/Ba based NSR catalysts, with H_2O having a stronger effect than CO_2 (Hendershot *et al.*, 2006). Water vapor hinders the release of NO_2 and thus decreases the regeneration rate, resulting in less NOx storage

(Cant *et al.*, 2003). The gas hourly space velocity (GHSV) is another important operating variable in assessing the performance of potential catalysts for reduction of NOx. It is associated with the engine load speed (rpm), which indirectly controls the exhaust gas flow rate. It reported that the NO reduction decreased with the increase in GHSV (Deeng *et al.*, 2004). Obviously, the performance of NSR catalysts is also strongly influenced by the catalysts composition. Encouraging results have been reported where the storage capacity are proportional to the Ba-loading (Mahzul *et al.*, 1999). Also, high Ba loading (25 wt %) is necessary for the adsorption of NO at elevated temperatures, suggesting the negative effect of increasing temperature on the NOx storage capacity (Fanson et al., 2003).

3.4 Roles of metal in NSR catalyst.

The most popular metals being investigated for NOx reduction process are noble metals, particularly platinum, palladium and rhodium (Pisarello *et al.*, 2002 ; Amberntsson *et al.*, 2003). The metals seem to play several roles in the NOx storage and reduction cycles as well as for sulfur deactivation and during catalyst regeneration process. Thus, it is of great importance to elucidate their roles in detail (Pisarello *et al.*, 2002). It is found that palladium containing catalysts have a slightly higher NOx storage ability at lower temperatures compared to the platinum loaded samples and that the NOx oxidation activity is much higher on platinum as compared to palladium (Pisarello *et al.*, 2002). The effect of the addition of noble metals to a calcium oxide based NOx storage and reduction catalyst was studied by Amberntsson *et al.* (2003). It is reported that rhodium provides better NOx storage ability for the catalyst compared to platinum based catalyst due to higher formation of NO_2 prior to the formation of nitrates. However, the thermodynamic equilibrium concentration of NO_2 can hardly be reached due to the reduction of NOx with the hydrocarbon.

The main function of the active metals in a NSR catalyst during the rich period of the NOx storage reduction cycle is the ability to reduce NO. The main drawback for the successful and practical use of noble metals is their high cost, that will limit its use, especially in this waste abatement process. Thus, efforts toward finding alternative and potential metals among transition metals that are available at lower cost should be further explored. Encouraging results have been reported by using cobalt (Co) (Pisarello *et al.*, 2002), copper (Seijger *et al.*, 2001) and manganese (Blanco *et al.*, 1998). Complementary studies in this area should be focused on the understanding of the roles and interaction of the metals during the rich and lean periods of NOx storage and reduction processes. Recently, effects of metal additives on the catalytic performance are investigated. It has been reported that two kinds of roles of metal additive (dopant) are prevention of catalyst deactivation and promotion of a reaction step. For example, the catalytic activity for NO reduction is significantly improved when Li, Mg, Ba, Cu, and Zn are doped to Rh/SiO_2 (Hasegawa *et al.*, 2005). This finding opens a new area in the development of high performance catalyst for the NSR process.

4 Particulate matter (soot) removal

In diesel engines, soot particles are formed in the cylinder of the engines due to local shortage of oxygen (Makkee *et al.*, 2002, Nhon *et al.*, 2004). The composition of diesel particulate depends on several factors such as engine load, speed and temperature (Nhon *et al.*, 2004). Since NOx are formed in an oxygen rich atmosphere at high temperatures and pressures, measures to reduce particulate mass emission will result in an increase in NOx emissions, and vice versa. This phenomenon is known as NOx-PM trade-off (Seijger *et al.*, 2001). In a NSR catalytic application, soot is expected to cause serious deactivation to the catalyst. However, removing of soot from diesel engine exhaust gas is a challenging topic. The combination of a filter filled with oxidation catalysts appears to be the most plausible after-treatment technique to eliminate soot particles (Pisarello *et al.*, 2002). The soot is separated on the filters and later oxidized by NO_2 to CO_2 (Equation 4) whereby the nitrogen dioxide, NO_2 is reduced into nitric oxide, NO. In this process, NO_2 is produced by oxidation of NO in the feed gas over a Pt catalyst. Considering the overall NOx reactions, there is no removal of nitrogen oxides.

$$\text{“C”} + 2\,NO_2 \rightarrow CO_2 + 2\,NO \tag{4}$$

A possible way for removal of NOx and soot from diesel exhaust gas is simultaneous catalytic conversion of both the components (5-6). In these reactions, NOx is reduced by soot forming N_2 and CO_2 according to the overall Equations 5-6, in which soot is considered to be pure carbon for simplicity

$$\text{“C”} + 2\,NO \rightarrow CO_2 + N_2 \tag{5}$$

$$\text{“C”} + NO_2 \rightarrow CO_2 + \tfrac{1}{2}N_2 \tag{6}$$

In this application, the soot-catalyst contact appears to be one of the most important problems to overcome (Querini *et al.*, 1998). Thus, it is of utmost importance in the catalyst formulation to include active components with high mobility (Milt *et al.*, 2003). Any catalyst placed over the soot filter should possess high thermo-chemical stability and intrinsic oxidative properties to reliably ignite the soot as early as possible (Nhon *et al.*, 2004). Potassium–loaded catalysts have been found to show high activity in soot combustion (Milt *et al.*, 2003, Pisarello *et al.*, 2002). This metal can play the role due to its high mobility to consequently increase the effective contact between the oxidation catalyst and the soot particle (Milt *et al.*, 2003). The activity can be further improved by the introduction of barium as the promoter (Pisarello *et al.*, 2002). Encouraging results have been reported with $Pt\text{-}Ba/Al_2O_3$ which is able to simultaneously remove both soot and NOx. In contrast, a Pt/Al_2O_3 catalyst which effectively performs the soot oxidation is not able to remove gas phase NOx to a significant extent (Castoldi *et al.*, 2005).

In the soot oxidation process, the contact between the soot and the catalyst critically affects the reaction rate. Comparison between the soot sample and soot-free sample indicates that the presence of soot reduces the amount of NOx which could be stored at NOx breakthrough (Castoldi *et al.*, 2005). Therefore, the incorporation of metals that can play active roles in the oxidation of soot seems to be crucial in the quest for development of high performance catalyst for NSR application. In this respect, the identification of suitable components and their composition should be seriously investigated. Other issues could be the method of preparation and synergistic interactions between the active components. In conclusion, by a proper combination of active metals, a catalyst suitable for the NSR process, while showing lower tendency to be deactivated by soot can be developed.

5 Structured catalysts

For a deNOx unit, pressure drop is the key issue (Odenbrand *et al.*, 1999, Makkee *et al.*, 2002). In a car exhaust or a power plant flue gas system, the pressure drop should typically be below 10-20 mbar (Seijger *et al.*, 2001). Additional demands comprise low sensitivity to dust and resistance to thermal shock. A suitable solution can therefore be provided by the implementation of a low pressure drop structured catalyst packing. The pressure drop in structured catalysts is significantly lower than the randomly packed bed of particles (Cybulski *et al.*, 1998). Usually, structured catalytic bed reactors have large void fraction ranging from 0.7 to more than 0.9, compared to 0.5 in packed bed reactors. Structured packings, like ceramic and metal honeycombs, and ceramic foams are gaining attention for application in low pressure drop reactors, membrane reactors and catalytic distillation units. With ceramic monoliths (Figure 2), the support structure is made of non-catalytic, thermally resistant material, typically cordierite, onto which a catalytic layer, typically γ-alumina, zeolites or mesoporous materials can be deposited (Ulla *et al.*, 2003).

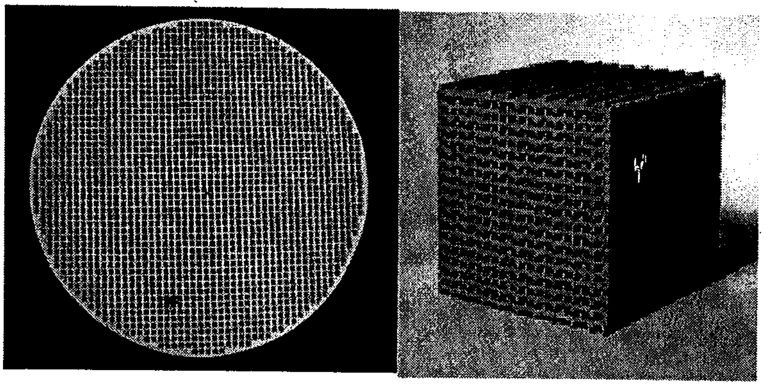

Figure 2. Examples of ceramic monoliths for catalyst support.

Typical advantages of open macroporous structures of structured catalyst follow from their good internal accessibility due to their high porosity and low accumulation of dust due to the large size of the pores. These materials are also generally more abrasion resistant and have a high axial crushing strength. The specific surface area of most structured supports is below 1 m^2/g, which is too low for catalytic purposes. By washcoating with suitable microporous or mesoporous materials, the specific surface area can be enhanced up to about 40 m^2/g (Seijger *et al.*, 2001). Apart from low pressure drop, monolith reactors offer the advantage of thinner walls, high geometric surface area and good mass transfer performance (Williams *et al.*, 2001). Thus, an active and stable NSR monolithic catalyst with soot oxidizing ability and low pressure drop should appear to be an ideal catalyst for the deNOx of a diesel exhaust gas.

6 Conclusions

Despite providing fuel combustion efficiency and reliability in operation, diesel engine has adverse environmental effects, particularly due to the emission of NOx and soot. Selective catalytic reduction (SCR) of NOx is a practical and efficient method to remove NOx in diesel engine exhaust gases. The active phases for SCR catalysts are different metallic oxides such as oxides of Mn, Co, Cu and noble metals, supported over vanadia, titania, ceria, zirconia or lanthana. The reduction of NOx generally takes place over a narrow temperature window. An innovative method to treat NOx using a so-called NOx storage and reduction (NSR) has been recently introduced. The catalysts used for NOx storage step comprise combinations of noble metals for oxidation and reduction purposes and barium oxide/carbonate as the storage materials as the nitrogen oxides are chemically bound as surface nitrates. The NOx is then released from the catalyst when spikes of reductant such as ammonia or hydrocarbons are introduced. During this stage, the NOx will be reduced to environmentally benign nitrogen gas. Catalysts can rapidly deactivate in presence of water vapor and sulfur. Potassium–loaded catalysts generally show high activity in soot combustion due to its high mobility to consequently increase the effective contact between the oxidation catalyst and the soot particle. The activity of the catalyst can be improved when promoted by barium. The contact between the soot and the catalyst strongly affects the reaction rate. By proper combinations of active metals, catalysts suitable for the NSR process, while showing lower tendency to be deactivated by soot can be obtained. Structured NSR catalyst can offer added advantages in this application as they cause low pressure drop while showing high resistance to thermal shock.

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TEMPERATURE-PROGRAMMED ANALYSIS OF DIESEL SOOT OXIDATION ASSISTED BY K_2O-V_2O_5/ZSM-5 CATALYSTS

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Abstract

Temperature-programmed oxidation of diesel soot on 15 wt. % CuO/, V_2O_5/, Fe_2O_3/ and K_2O-V_2O_5/ZSM-5 catalysts was studied. V_2O_5/ZSM-5 showed the highest activity and further improved by 4.5 wt. % K_2O.

Keywords: Diesel soot, oxidation, K_2O-V_2O_5/ZSM-5, loose.

INTRODUCTION

Diesel engines usually emit polluting soot and nitrogen oxides (NOx). While NOx can be removed by catalytic reduction processes [1], soot particulates are commonly collected on a catalytic filter and periodically oxidized to CO_2 [2]. The catalyst in the trap must be sufficiently active to oxidize the soot within the exhaust gas temperatures (300-400°C) [3].

Catalysts investigated for soot filter are such as noble metals [2], perovskites [1], transition metals [4] and alkali metals [5]. However, reports on transition metal-alkali metal are quite rare in the literature despite promising results reported by Liu et al. [3]. Zeolites support provides advantages of having high surface area and small pores to avoid clogging by soot particles while active metals in the pores can proceed with the oxidation of smaller oxidation intermediates to form CO_2. This paper focuses on the loose contact soot oxidation by combined transition metal-alkali metal/ZSM-5 catalysts.

EXPERIMENTAL

The soot was obtained by burning diesel fuel [6]. 15 wt. % CuO, V_2O_5 and Fe_2O_3 on H-ZSM-5 (Si/Al=90) catalysts were prepared by impregnation method using of $Cu(NO_3)_2$, NH_4VO_3 and $Fe(NO_3)_3$ as precursors followed by drying (8 h at 105°C) and calcinations (500°C for 3 h). KOH was also used as co-solution to give K_2O loadings of up to 7.5 wt. %, while maintaining total metal loading at 15 wt. %. The reactor set up as described in Saaid et al. [7] was used for soot oxidation study. 500 mg of mortar-mixed soot-catalyst mixtures (1:9) were used for temperature-programmed oxidation (60°-660 °C). The experiment was conducted in 50 ml/min of O_2 at 10 °C/min. The CO_2 concentration in the outlet was measured using a GC unit (Shimadzu 8A) and the SEM image was taken using a Leica Cambridge S-360 system. The elemental analysis of soot sample was obtained by means of a Perkin Elmer 2400 system.

RESULTS AND DISCUSSION

Elemental analysis of the diesel soot sample proved its carbonaceous nature with 77.5 wt. % and 2.0 wt. % for carbon and hydrogen, respectively. Small amounts of nitrogen and sulfur were also detected (0.1 wt. % and 0.6 wt. %, respectively). This soot composition was quite similar to those used in reported literatures [1, 2, 4]. The low H:C ratio caused the low thermal oxidizability of the soot to justify the use of a certain catalyst to catalytically oxidize it at lower temperature.

Fig. 1 typically shows the relatively larger soot particles (marked with arrows) embedded in catalyst particles (in this case V_2O_5/ZSM-5). It is noted in the micrograph that a loose contact formed between the soot and the catalyst with clearly discernable inter-particle spaces. The loose contact was intended in this study to simulate the actual operating condition of the catalytic filter in which mostly loose contact predominates [8].

In a typical solid-solid-gas phase reaction, good contact between the carbon and the catalyst is required to achieve high catalytic oxidation. This contact will involve in various pathways for the local transport of reactive oxygen species from the active catalytic species to the soot agglomerate [9]. The nature of the contact (loose or tight) can therefore affect the relative effectiveness of a catalyst in promoting soot oxidation. Loose contact always shows reduced activity compared to tight contact for all compositions, but the degree of degradation varies from compound to compound [5]. Hinot et al. [2] stressed that soot particles could not be effectively oxidized unless the catalyst is deposited uniformly in the soot clusters. However, some benefit could also be obtained from loose contact as oxygen diffusion is facilitated.

In Fig. 2, the evolution of CO_2 with temperature in soot oxidation for three different metal oxides deposited on ZSM-5 is plotted. The profile for ZSM-5 that indicates thermal oxidation of soot is also shown for comparison. The thermal oxidation of the soot started at around 400 °C and peaked at 500 °C. Almost all the soot was completely oxidized at 660 °C when no more CO_2 was detected in the outlet stream.

When the catalysts were impregnated with metal oxides, the oxidation of soot proceeded at significantly lower temperatures. V_2O_5/ZSM-5 produced the best result with the most active oxidation occurred at about 450 °C. The actual peak temperature could be lower but with the measurement interval used in the present study (40 °C), it was not able to be determined. With CuO/ZSM-5 and V_2O_5/ZSM-5 catalysts, the oxidation of soot completed at around 600 °C. The oxidation peaked at about the same temperature (500 °C) for CuO/ZSM-5 and Fe_2O_3/ZSM-5 catalysts but with a more intense oxidation at that temperature (indicated by higher CO_2 concentration). Between the two catalysts, the completion of the reaction with CuO/ZSM-5 was achieved at a relatively lower temperature. The higher oxidation activity of V_2O_5/ZSM-5 was ascribed to the ability of V to present at more oxidation states to make it more efficient in generating reactive oxygen species.

Fig. 3 shows the effect of increasing K_2O addition into the V_2O_5/ZSM-5 (maintaining 15 wt. % of total metal content) on the oxidation of soot. The addition of 1.5 wt. % K_2O resulted in minimal effect on the soot oxidation. When the K_2O content was increased to 4.5 wt. %, significant improvement in the activity of the catalyst was detected. This was consistent with conclusion by Laversin et al. [9] when investigating Cu-K/ZrO_2 catalysts. The soot oxidation started at about 40 °C lower and a reduction of as much as 80 °C was achieved in the temperature to reach the peak oxidation activity. This temperature was much lower that reported with Pt-based catalyst which occurred at about 560 °C [2]. Meanwhile, further addition of K_2O was found to be detrimental to the oxidation process. At 7.5 wt. % K_2O, the peak oxidation temperature shifted to be at about 500 °C with a significantly less intense oxidation (indicated by lower CO_2 concentration) at this peak temperature.

The minimal loss of soot oxidation activity for the catalyst with 1.5 wt. % K_2O suggested the lower activity of this oxide in catalyzing the oxidation process compared to V_2O_5. It was mainly due to the ability of V_2O_5 to present at multiple oxidation states rendering it more efficient in assisting the formation of reactive oxygen species [9]. At higher K_2O loading (4.5 wt. %), the effect of the V_2O_5 content was offset by the effect of additional reactive oxygen species resulting from the alkali metal-transition metals interactions [8].

With increasing K_2O content, the amount of reactive oxygen species generated increased accordingly. In addition, the presence of K_2O species improved the contact between the catalyst-soot as well as causing the facilitated transfer of reactive oxygen species to oxidize the soot [9]. Further increase in K_2O content to 7.5 wt. % meant the reduction in V_2O_5 content to 7.5 wt. % in the catalyst. As the redox activity of K_2O species was significantly lower than that of V_2O_5, a reduction in the oxidation activity resulted.

In the context of present study, the activity of the V_2O_5 in the soot oxidation reaction was closely related to the reactivity of the oxygen in the V-O or V=O bond [8]. The improvement in the presence of alkali metal oxide was ascribed to their electron-donating effect of the alkali metals which enhanced the reactivity of V-O bonds. Moreover, it was also observed that potassium could weaken the C-C bonds and promoted the formation of C-O bonds during catalytic oxidation [6]. Therefore, the catalytic activity after the addition of K should be attributed to the synergetic effect of alkali metals and V-O bonds, which were simultaneously present in the vanadyl structures. The role of electron-donating effect of potassium agreed with the experimental results. The oxidation results showed that the decrease of the oxidation temperature by the vanadium species in the presence of potassium, which suggested the weakening of the V=O bond.

In this study, the catalytic soot oxidation activity was successfully correlated with the redox ability of the K_2O-V_2O_5/ZSM-5 catalyst for the combustion reaction of soot. However, the promotional effect of potassium in the K_2O-V_2O_5/ZSM-5 catalyst was limited to below 4.5 wt. %, above which, detrimental effect to the soot oxidation resulted.

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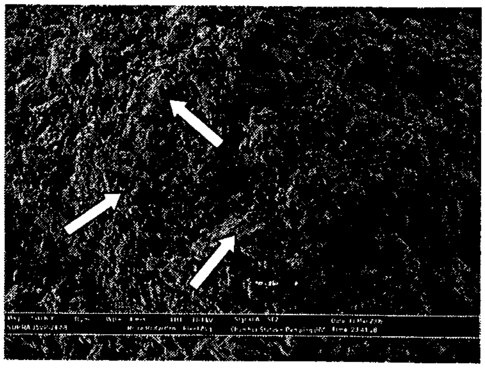

Fig. 1. SEM image showing soot particles embedded in V_2O_5/ZSM-5 catalyst particles.

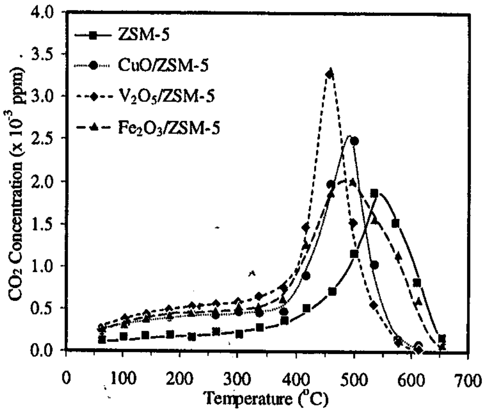

Fig. 2. Evolution of CO_2 with temperature for various catalysts.

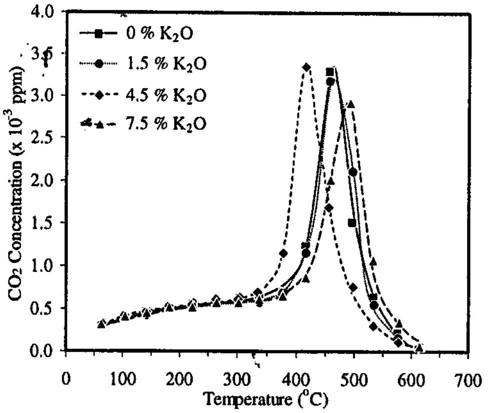

Fig. 3. Evolution of CO_2 with temperature for V_2O_5/ZSM-5 catalyst with various K_2O loadings.

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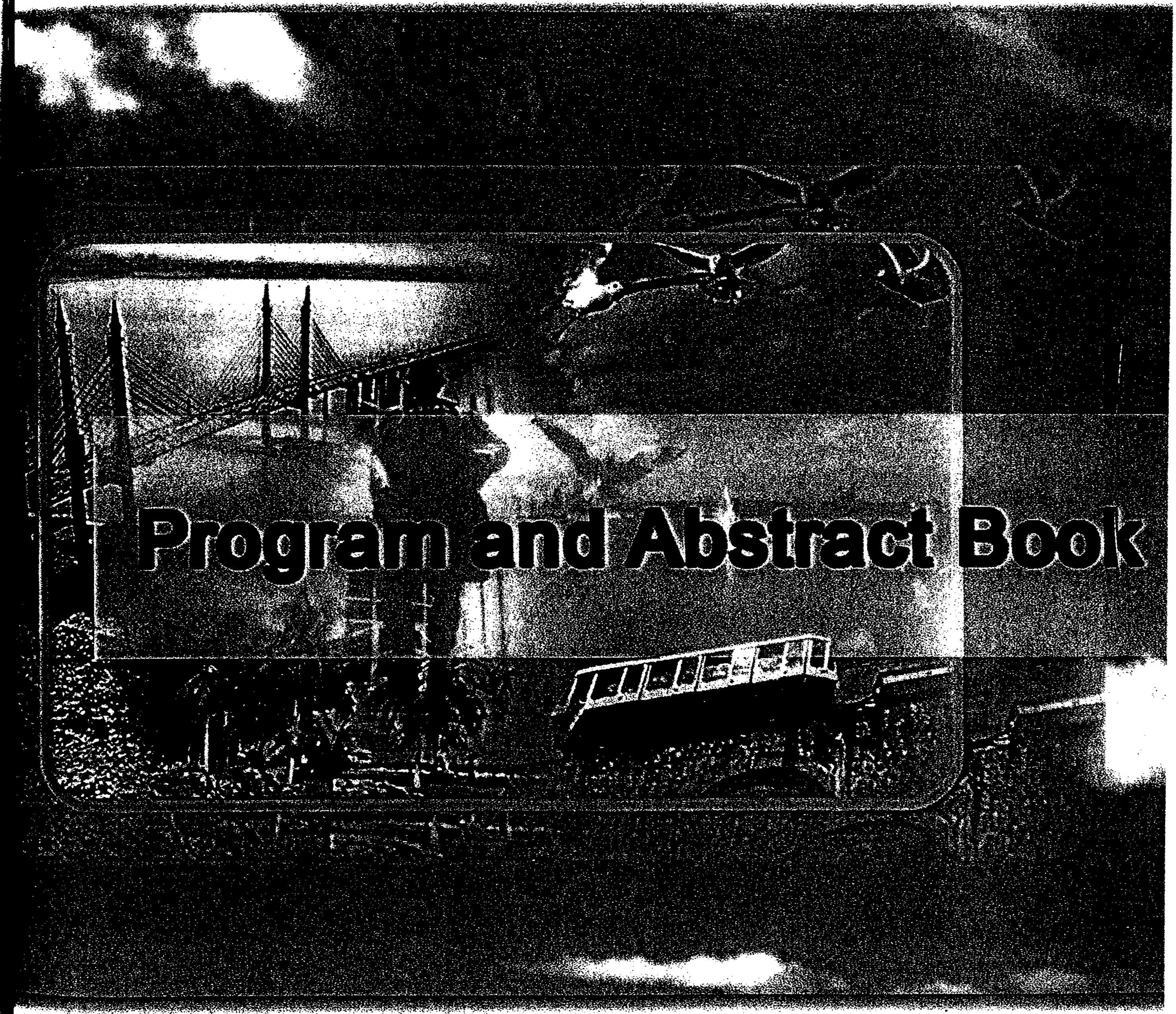

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DEVELOPMENT OF SOOT-RESISTANT CATALYST FOR THE REMOVAL OF NOx IN DIESEL ENGINE EXHAUST GAS

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ABSTRACT

Selective catalytic reduction (SCR) of NOx in diesel engine exhaust is a practical method for the removal this environmental pollutant from the exhaust gas. However, the catalyst tends to be deactivated rapidly by soot. Therefore, catalysts that are capable of oxidizing soot will be able to retain their high activity for a longer period of time. The identification of the type and composition of active catalytic components for soot oxidation is reported in this paper. The study was conducted using V_2O_5 and K_2O-V_2O_5 as active species deposited on H-ZSM-5 support. The performance of the catalyst was based on the temperature programmed oxidation (TPO) experiments in 50 ml/min of air at between 60-600°C. Results showed that the activity of soot combustion was affected by the contact between soot and the catalyst. Doping of 4.5 % w/w of K_2O into V_2O_5/H-ZSM-5 could enhance the reactivity of V-O bonds and improve the contact between the catalyst and soot. Higher K_2O content was found to improve the stability of the catalyst. The presence of K_2O in the catalyst would favor the oxidation of soot by consuming the carbon to form carbonate species.

Keywords: Soot; Diesel Exhaust; Oxidation; NOx; SCR; TPO; TGA

PHARMACEUTICAL COMPOUNDS IN THE ENVIRONMENT: OCCURRENCE, SOURCES, IMPACTS AND CONTROL

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ABSTRACT

Pharmaceutical Compounds (PCs) in the environment lately have been acknowledged to constitute a health risk for human, terrestrial and aquatic ecosystems. Human and veterinary applications are the main sources of PCs in the environment and the major pathways are excretion and discharge through sewage treatment plants (STPs). The reason why PCs may be interesting as environmental micropollutants, is that they are developed with the intention of performing a biological effect and they have many of the necessary properties to bioaccumulate and provoke effects in the aquatic or terrestrial ecosystems and potential human health risk. Sources of PCs in the environment are multiples including STPs, hospitals, irrigation with treated wastewater and some other sources. Intensive farming designed to concentrate a great number of animals in a limited area implies the use of feed additives or drugs for mass therapy. They may be found in animal ejects and can maintain significant activity and toxicity. As a result of normal practices, parts of these chemicals are released into the environment and may exert specific effects on the freshwater ecosystem. The presence of PCs in the sewage effluents can possibly pose significant environmental and health hazards to aquatic organisms. Feminization of male fish within STPs effluents, are attributed to the presence of endocrine disrupters. Drugs can alter the normal post-germinative development of the plants, the growth of roots, hypocotyls and leave. These pollutants also pose some potential health hazards such as the synergistic effects. Recent decades have brought increasing concerns for the potential adverse human and ecological health effects resulting from such pollutants. At least 60 PCs with concentrations up to ì g/L have been reported from aquatic matrices.

Key words: pharmaceutical compounds, environment, pollution, sources, impacts, control.

DEVELOPMENT OF SOOT-RESISTANT CATALYST FOR THE REMOVAL OF NOx IN DIESEL ENGINE EXHAUST GAS

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ABSTRACT

Selective catalytic reduction (SCR) of NOx in diesel engine exhaust is a practical method for the removal this environmental pollutant from the exhaust gas. However, the catalyst tends to be deactivated rapidly by soot. Therefore, catalysts that are capable of oxidizing soot will be able to retain their high activity for a longer period of time. The identification of the type and composition of active catalytic components for soot oxidation is reported in this paper. The study was conducted using V_2O_5 and K_2O-V_2O_5 as active species deposited on H-ZSM-5 support. The performance of the catalyst was based on the temperature programmed oxidation (TPO) experiments in 50 ml/min of air at between 60-600°C. Results showed that the activity of soot combustion was affected by the contact between soot and the catalyst. Doping of 4.5 % w/w of K_2O into V_2O_5/H-ZSM-5 could enhance the reactivity of V-O bonds and improve the contact between the catalyst and soot. Higher K_2O content was found to improve the stability of the catalyst. The presence of K_2O in the catalyst would favor the oxidation of soot by consuming the carbon to form carbonate species.

Keywords: Soot; Diesel Exhaust; Oxidation; Nox; SCR; TPO; TGA

INTRODUCTION

Despite better fuel economy than stoichiometric gasoline engines, diesel engine has adverse environmental problems. The main pollutants emitted for diesel engines are particulate matter particles (soot) and nitrogen oxides (NOx) which cause severe environmental and health problems. Catalytic processes have been widely investigated for NOx removal such as selective catalytic reduction (SCR) (Solis *et al.*, 2001; Pisarello *et al.*,2002 ; Milt *et al.*, 2003; Bennici *et al.*,2005; Castoldi *et al.*,2006) and NOx storage and reduction (NSR) (Bahamonde *et al.*,2003 Amberntsson *et al.*,2003 ; Piacenti *et al.*,2005 ; Krishna *et al.*,2006). In this catalytic system, soot is expected to cause serious deactivation to the catalyst. Therefore, catalysts that are capable of oxidizing soot to gaseous carbon dioxide will be able to retain their high activity for a longer period of time. Furthermore, the uncatalyzed combustion of soot occurs at 550°C-650°C whereas the temperature range of the exhausted gases from a diesel engine is generally 150°C-400°C (Neeft *et al.*, 1996). For oxidizing the soot at that temperature, it is necessary to have active oxidation catalyst to bring the ignition temperature of soot down to within this temperature range. Thus, the development of proper catalyst is needed for soot oxidation.

A number of supported metal oxide catalysts were screened for their catalytic performance for the oxidation of soot using oxygen as the oxidant as reported in literature (Caldeira *et al.*, 2004; Bueno-Lopez *et al.*, 2004; Liu *et al.*, 2000). The aim of this work was to develop the soot oxidation catalyst by study the effects of doping the potassium into supported vanadium catalyst and the potassium amount to improve the stability of the catalyst. Before selecting this type of catalyst, the performance of various catalysts using different metals and supports had been tested.

MATERIALS AND METHODS

Soot Preparation. The soot was obtained by burning commercial diesel fuel in a glass vessel at a temperature around 55°C. The hot plate stirrer (PMC 502 series) was used to increase the temperature from 25°C (room temperature) to 55°C (flash point of commercial diesel). After being collected from the vessel walls, it was dried in an oven for 24 h at 120°C.

Catalyst Preparation. The catalyst were prepared by incipient wetness impregnation from a H-ZSM5 (Unilab) support suspension in water, to which NH_4VO_3 (BDH) solution and KOH (Merck, Germany) was added to obtain desired amount of K_2O and V_2O_5.The mixture was evaporated while being vigorously stirred on a hot plate stirrer until achieving a paste which was dried in an oven for 24 h at 120°C, and calcined at 500°C for 2 h. The powder samples were then pressed at 500 kg/cm^2 into pellets and crushed to granules with sizes ranging from 0.25 mm to 0.5 mm.

Experimental Set up. The experiment set up used for catalytic activity measurement is shown in the schematic diagram in Figure 1. The experimental rig consisted of 3 major parts i.e (1) gas flow system, (2) catalytic reactor and (3) gas analysis system.

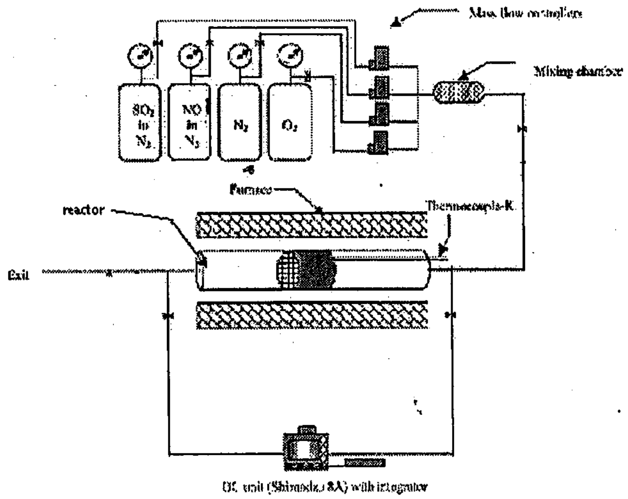

Figure 1: Schematic Diagram of Experimental Set Up for Catalytic Measurement.

TPO experiment. Soot /catalyst mixtures were prepared at 1/9 ratio with a final total sample weight of 500 mg (50 mg soot, 450 mg catalyst).The mixtures were mounted at the centre of the reactor, placed horizontally in the tubular furnace (Linberg-TF 55035C). The reaction was carried out in the temperature range of 60°C to 600°C in flowing of oxygen which was 99.80 % purity (Malaysian Oxygen Bhd) at 50 ml/min. The concentration of carbon dioxide after soot had been oxidized was measured at the outlet of the reactor using GC unit (Shimadzu 8A). The effect of SO_2 over the activity of the catalyst was studied by added the sulphur dioxide gas which concentration is 2000 ppm in nitrogen (Malaysian Oxygen Bhd).

RESULT AND DISCUSSION

The role of the potassium loading on activity and stability. Based on data shown in Figure 2, both of the profiles showed a low and constant concentration of CO_2 initially. It is shown that not much soot was oxidized at lower temperature but at higher temperature (600°C), all soot was able to be oxidized thus no more CO_2 can be detected. V_2O_5/H-ZSM5 catalyst showed a T_p of around 460°C. The soot oxidation was started at 340°C (T_i) and completed at about 600°C (T_f). When potassium was added into V_2O_5/H-ZSM5 catalyst, T_p, T_i and T_f were at 440°C, 330°C and 600°C, lowered by 10°C, 20°C and 0°C, respectively.

It is well known that the activity of the vanadium oxide in oxidation reaction was closely related to the reactivity of the oxygen in the V-O or V=O bond. The oxygen rate of catalyst based on transition metal oxides was found to be improved by doping with potassium. The improvement was ascribed to their electron-donating effect of the alkali metals which enhanced the reactivity of V-O bonds. Moreover, it was also observed that potassium could weaken the C-C bonds and promoted the formation of C-O bonds during catalytic oxidation. Therefore, the catalytic activity after the addition of K should be attributed to the synergetic effect of alkali metals and V-O bonds, which were simultaneously present in the vanadyl structures. The role of electron-donating effect of potassium agreed with the experimental results. TPO results showed that the decrease of the oxidation temperature by the vanadium species in the presence of potassium, which suggested the weakening of the V=O bond. The catalytic activity had been successfully correlated with the redox ability of the K_2O-V_2O_5/H-ZSM5 catalyst for the combustion reaction of soot (Liu *et.al.*, 2005).

Besides that, the positive influence of potassium on the activity by the stabilization of H-ZSM5 support texture which increased the specific surface area of the catalyst which could favor the formation of the catalyst/soot interface during combustion process. On the other hand, it also explained the high activity of the catalyst through the mobility and volatility of these compounds.

In Figure 3, there is an optimum in the potassium content since the catalyst containing 4.5 % of K presented a combustion peak at 380°C and the CO_2 concentration increased substantially, whereas those containing 1.5% and 7.5% of K presented it at temperatures over 400°C and slightly increased for the catalyst with 1.5% and 7.5% of K. Hence, the role of this alkaline metal was clearly, to some extent, promoted the activity of the catalyst and 4.5% was the optimum loading of the metal.

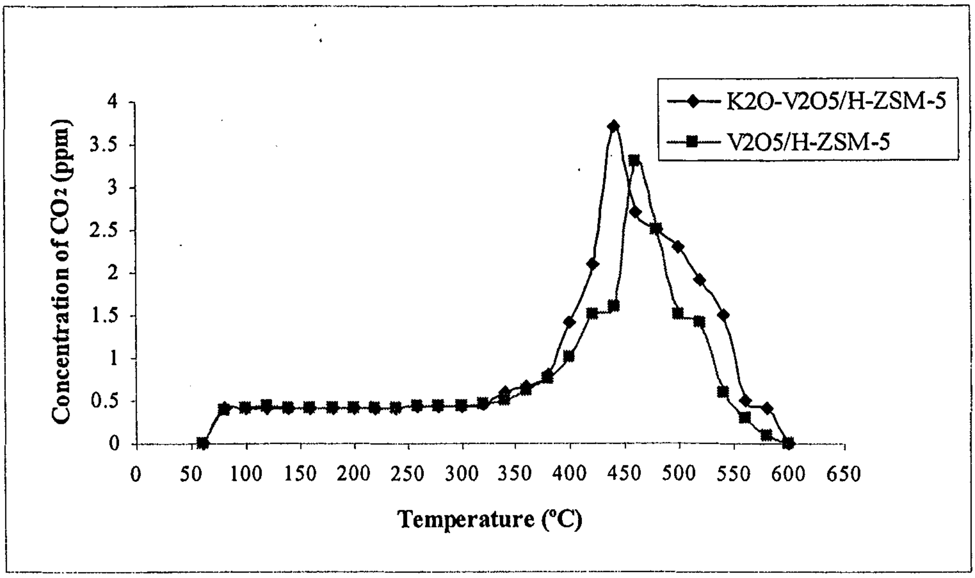

Figure 2: The TPO Plots Of V_2O_5/H-ZSM5 and K_2O-V_2O_5/H-ZSM5 (1.5% W/W K)

The behavior was correlated with the activity measurements for soot combustion, since the most active catalyst (with 4.5% of K), among all the catalyst studied, was the one presenting the highest surface concentration of K, thus favoring the soot-catalyst contact. On the other hand, the melting point of the catalyst decreased slowly with the increase in potassium amount, which promoted the contact between the catalyst and soot. However, excessive K presenting on the catalyst surface lowered the synergetic effect of alkali metals and V_2O_5 species (Liu *et.al.*, 2005). In the catalyst with 1.5% and 4.5% of K, this temperature increase caused the potassium migrated to the surface of the solid, thus increasing the K_2O-V_2O_5 ratio whereas, for the catalyst with 7.5% of K, it was vice versa.

The higher activity of promoted V_2O_5 catalyst could be related to the ability of K_2O favoring the redox cycle of the active V_2O_5 species. This synergy between good redox property and low melting point of the catalyst played a key role in promoting the soot combustion.

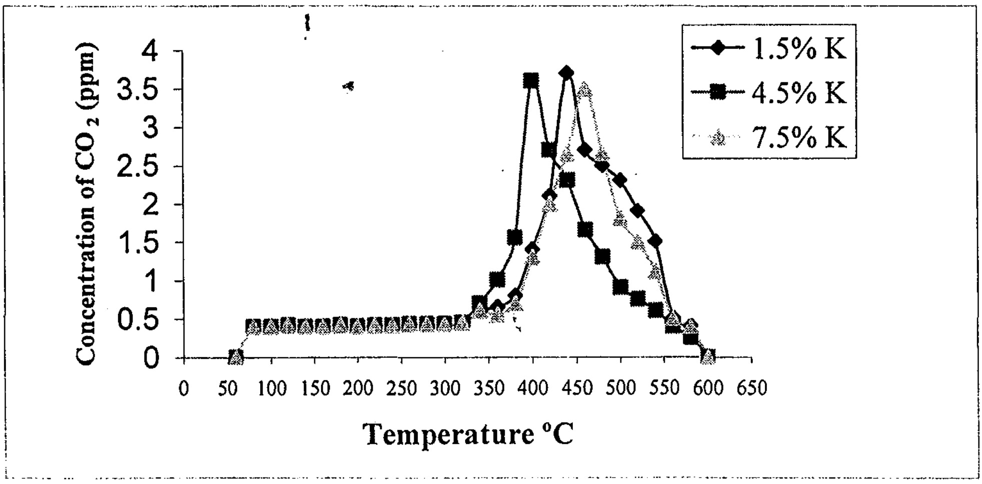

Figure 3: The TPO Profiles of Different Amount of K Loadings on Soot Oxidation Activity.

CONCLUSION

The catalytic activity for soot combustion was affected by the contact between soot and catalyst. Catalyst with the good mobility of surface atoms was able to increase the contact between soot and catalyst because of their melting points. Therefore, they could lower the temperature of soot combustion. Doping of potassium into supported vanadium catalyst could enhance the reactivity of V-O bonds and improved the contact between the catalyst and soot. So, potassium could remarkably improve the catalytic activity for soot combustion. Among the catalyst studied with different potassium contents (1.5%, 4.5% and 7.5%), the intermediate one demonstrated highest activity for the combustion of diesel soot whereas the one with the highest potassium content was the most stable. Potassium probably played different roles in the behavior of these catalyst i.e. i) increasing the catalyst-soot contact by conferring surface mobility, ii) preserving the redox capacity of V_2O_5, iii) favoring the oxidation of soot by consuming the carbon to form carbonate species during soot combustion.

ACKNOWLEDGEMENTS

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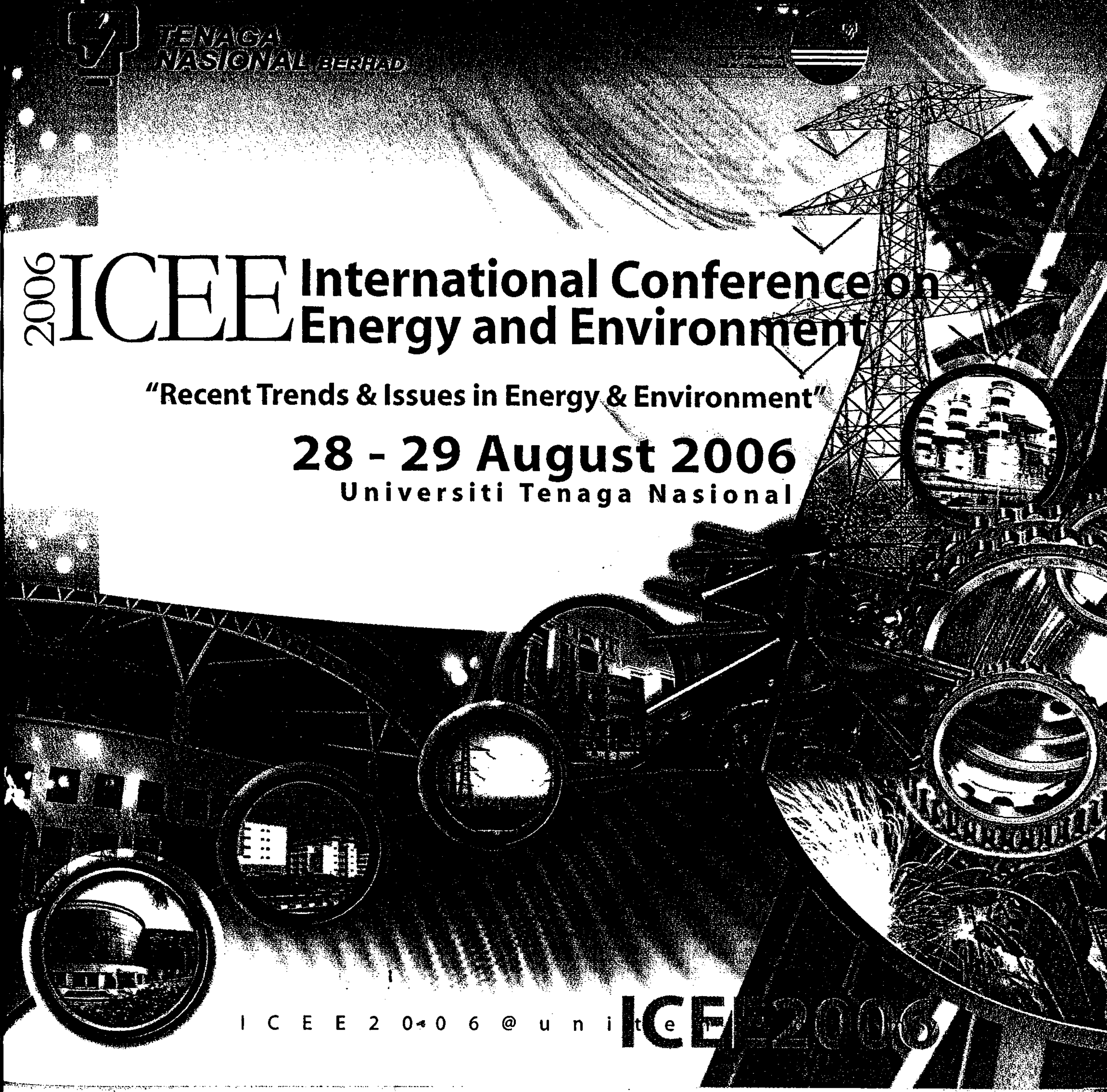

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Performance of Cu-, Fe- and Mn/ZSM-5 in Selective Catalytic Reduction (SCR) of NO in Diesel Engine Exhaust Gas

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Keywords: NOx, selective catalytic reduction (SCR), diesel exhaust, reductant, oxidation.

Abstract

The selective catalytic reduction (SCR) of of NOx with hydrocarbon as the reducing agent has attracted a lot of interest and is the most promising way to eliminate NOx from the oxygen-rich stream of diesel exhaust gas. The use of Cu/ZSM-5, Fe/ZSM-5 and Mn/ZSM-5 catalysts to selectively reduce nitric oxide (NO) to environmentally benign N_2 in the presence of iso-butane (iC_4H_{10}) as the reductant is reported. The catalyst were prepared by impregnation method at a metal loading of 10 wt. % using ZSM-5 (Si/Al=50) as the support material. They were then characterized and tested for selective catalytic reduction of 1,000 ppm of NOx with 1,000 ppm of iC_4H_{10} in 3 % oxygen. The process was carried out at a gas hourly space velocity (GHSV) of 13,000 h^{-1} with reaction temperatures varied between 200 and 450°C. Under the test condition, Cu/ZSM-5 catalyst showed the highest efficiency in selective catalytic reduction of NOx with the maximum removal efficiency of 56 %, followed by Fe/ZSM-5 (45 %) and Mn/ZSM-5 (20 %). The optimum reaction temperature of NOx reduction over Cu/ZSM-5 was observed at 350° C. At higher reaction temperatures, the conversion of NO tended to decrease for various reasons. At low Cu content, NO removal efficiency by Cu/ZSM-5 increased with an increase in the Cu content in the catalyst. But at higher Cu loading in ZSM-5, the removal efficiency of NO stabilized at around 45 %.

1 Introduction

Nitrogen oxides, or NOx, are the generic term for a group of highly reactive gases, all of which contain nitrogen and oxygen in varying amounts [1]. Many of the nitrogen oxides are colorless and odorless. However, one common pollutant, nitrogen dioxide (NO_2), along with particles in the air can often be seen as a reddish-brown layer over many urban areas. Nitrogen oxides form when fuel is burned at high temperatures, as in a combustion process. The primary sources of NOx are motor vehicles, electric utilities and other industrial, commercial and residential sources that burn fuels [2].

The catalytic methods for removing NOx from diesel engine exhaust gases are usually classified into non-selective reduction, selective reduction and decomposition. Selective catalytic reduction (SCR) is a proven and effective method to reduce nitrogen oxides which are air pollutant associated with the power generation process. Nitrogen oxides are contributors to ground level ozone [2].

The interest in developing new catalytic processes for the reduction of NOx under oxygen of excess oxygen such as that needed for stationary sources, diesel engines and lean burn Otto engines is currently very high [3]. Conventional process for deNOx of exhaust gases is by converting NOx via a reduction process by mainly hydrocarbon (HC) component present in the gas to nitrogen (N_2) which is safe to the environment. The lean-burn conditions of diesel combustion, which yielded high combustion temperature and improved efficiency, produced an exhaust gas containing excess oxygen. This complicates conventional approaches to chemically reduce NOx to N_2 as the reducing components such as carbon monoxide (CO), hydrocarbon (HC) and hydrogen (H_2) are preferably oxidized by oxygen [4]. Thus, the use of hydrocarbons as alternative reductants is being intensively investigated [2,5].

The reduction of NOx in oxygen-rich conditions using hydrocarbon (HC) as reductant is a well proven technique for the removal of NOx from stationary sources and has become of increasing interest in recent years [6]. A number of catalysts have been developed in which the active phases are different metallic oxide such as manganese oxide [6], cobalt [7], copper [8,9] and noble metals [8, 10, 11]. The common catalyst supports being evaluated for this application are such as vanadia [12], titania [8], ceria [7], zirconia [10] and lanthana [10, 13]. The reduction of NOx has been generally found to take place over a fairly narrow temperature range. However, the temperature of diesel engine exhaust varies from 200° to 600°C. In this study, the performance of impregnated Cu, Fe and Mn on ZSM-5 as catalysts for NO removal in synthetic diesel engine exhaust was comparatively evaluated. iso-butane (iC_4H_{10}) was used as the reductant.

2 Materials and methods

2.1 Catalyst preparation and characterization

ZSM-5 zeolite (Si/Al=50) samples was obtained from Zeolyst Inc. and was used as received. The Cu/ZSM-5, Fe/ZSM-5 and Mn/ZSM-5 catalysts were prepared using a conventional impregnation method. After drying in an oven at 60°C for 24 h, the powder was calcined in a furnace at 500°C for 6 h followed by pressing, crushing and sieving to diameters between 475-600 µm. The finish catalyst samples were characterized for surface characteristics using SEM and surface analyzer.

2.2 NO reduction process

The set up for the NO reduction process consisted of component gases, mass flow controllers, a tubular reactor and the gas analysis equipment. N_2, O_2, 5,000 ppm NO in N_2 and 5,000 iC_4H_{10} in N_2 were mixed at desired flow rates to give 100 ml/min of feed at a composition of 1,000 ppm of NO, 1,000 ppm of iC_4H_{10}, 3 % O_2 and balance N_2. This feed gas composition was comparable with the reported result where the concentration of NO and hydrocarbon were in the range of of 500-2,000 ppm [1, 14]. Oxygen in the feed was fixed at 3 %, which is the optimum concentration in the selective catalytic reduction of NO with hydrocarbon [1]. The reaction temperature were in the optimum range of 200-450°C for selective catalytic reduction of NO with hydrocarbon as the reductant as reported in the literature [5].The reaction was carried out in a 20 mm i.d. stainless steel reactor packed with 0.2 g of catalyst to give the corresponding gas hourly space velocity (GHSV) of 13,000 h^{-1}. The feed and product gasses were analyzed using a Shimadzu 8A gas chromatograph equipped with a thermal conductivity detector, a Porapak Q and MS5A columns.

3 Results and Discussion

3.1 Blank experiment

To demonstrate the performance of the particular zeolite catalyst in the selective catalytic reduction of NO with hydrocarbon, a blank experiment was carried out earlier o measure its activity for selective catalytic of nitric oxide (NO) with iso-butane (iC_4H_{10}). Table 1 shows the result obtained from the blank experiment. There was insignificant reduction of NO observed when 50 ml/min of synthetic diesel exhaust (1,000 ppm NO, 1,000 ppm iC_4H_{10}, 3 % O_2 and balance N_2) passed through an empty tubular fixed bed reactor at the temperature range of 200°C-450°C. Zeolite catalyst without any metal loading was also tested under similar conditions. The results showed that minimal NO reduction occurred when the synthetic diesel exhaust was passed through the particulate zeolite in the fixed bed reactor. This result was attributed to thermal reduction on the surface of the zeolite.

Table 1: NO conversion in blank experiment.

Catalyst	NO Reduction (%)		
	200°C	300°C	400°C
No catalyst	0.5	1.2	1.5
ZSM-5	1.8	2.2	2.9

3.2 Comparative performance study

Figure 1 shows the NO reduction profile at a duration time of 15 min over all three catalysts tested. The result shows that the Cu/ZSM-5 catalyst gave the highest NO reduction among these three tested metals. Fe/ZSM-5 gave better result compared to Mn/ZSM-5 catalyst. At low reaction temperatures (200-300°C), NO reduction of Cu/ZSM-5 catalyst and Fe/ZSM-5 catalyst showed almost similar values. However, at higher temperatures (350-450°C), NO reduction of Fe/ZSM-5 catalyst started to drop and gave lower NO conversion than Cu/ZSM-5 catalyst. Optimum NO reduction for Cu/ZSM-5 catalyst was observed at a reaction temperature of 350°C while the maximum NO conversion by Fe/ZSM-5 catalyst was about 50 % at the reaction temperature of 300°C.

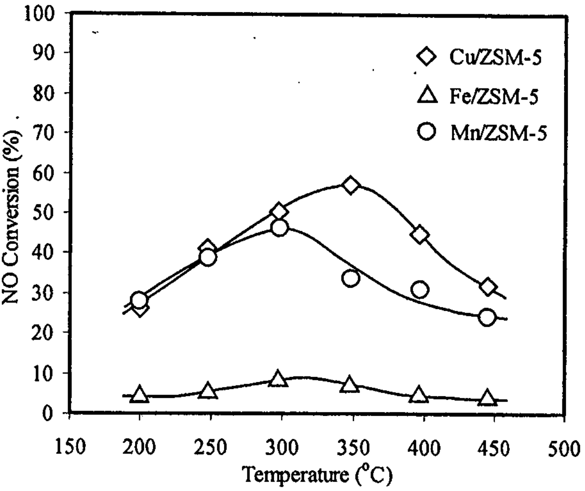

Figure 1: NO conversion as a function of temperature for various zeolite catalysts

The trend of NO reduction of Cu/ZSM-5 catalyst in Figure 1 shows that the NO reduction dropped at higher temperature. The temperature at which the NO conversion reaches its maximum corresponds to the temperature value (nearly) maximum oxidation of the hydrocarbon was achieved. The decline at higher reaction temperature was primarily attributed to the direct oxidation of the iC_4H_{10} by excess oxygen. The drop in NO conversion at higher reaction temperature was most probably due to the more rapid oxidation of the hydrocarbon. The temperature of the maximum NO conversion is dependent on the nature of the catalyst, the type and the concentration of the hydrocarbon, the time on stream and the space velocity. The characteristic behavior was also observed during the study of the direct NO decomposition reaction over similar catalyst by Koci et al. [4] where it was attributed to a decrease in the surface coverage of the proposed gem-dinitrosyl $Cu(NO)_2$ reaction intermediate with increasing temperature. During the lean NOx reaction itself, this behavior may also be a consequence of similar adsorption/desorption effects, or it may be related to the more rapid oxidation of the hydrocarbons at higher reaction temperature.

For fresh catalysts, the temperature at which the peak NO conversion occurs was dependent on a number of factors, including the nature of hydrocarbon reductant, the concentration of the hydrocarbon, the space velocity and the exact specification of the catalyst (Cu loading, method of preparation etc.) [1, 2, 11]. Whereas the decomposition of NO into elements was inhibited by oxygen, the selective NO reduction was promoted by the presence of oxygen. In the absence of oxygen, the NO conversion was negligible. Adding 3 % O_2 affected maximum NO conversion. At higher concentration of oxygen, the NO conversion decrease again [5].

3.3 Iso-butane conversion

Figure 2 shows the concentration of iC_4H_{10} in percentage (relative to its initial concentration) and CO_2 formation during selective catalytic reduction of NO process over particulate catalyst Cu/ZSM-5 at the reaction temperatures between 200 and 450°C. It shows that at higher reaction temperature, higher fraction of the hydrocarbon was converted to CO_2. This suggested that at higher reaction temperature, the oxidation of hydrocarbon becomes dominant resulting in the drop of NO reduction.

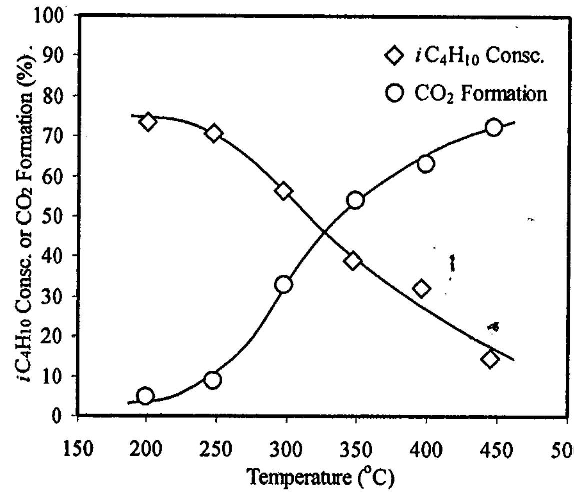

Figure 2: iC_4H_{10} relative concentration and the CO_2 formation in the outlet stream with Cu/ZSM-5 catalyst at 350°C.

3.4 Effect of copper loading in Cu/ZSM-5

Another parameter with considerable impact on the NO conversion is the metal loading. It was observed that Cu/ZSM-5 gave highest NO decomposition at a reaction temperature of 350°C, experiment was run under this reaction temperature with weight percent of Cu in catalyst varied from 5-20 wt %. The total mass of catalyst used in each run was fixed at 0.2 g and the particulate form of 475-600 μm in size. Figure 3 shows NO conversion for catalysts with different metal loadings. The catalytic activity increased with an increase in copper contents. But the NO conversion depends on copper concentration only up to 15 %, after that the NO conversion was almost the same although increase in the copper content. The result obtained was of almost similar trend with that reported by Makkee et al. [12] except the optimum was observed to occur at higher Cu content.

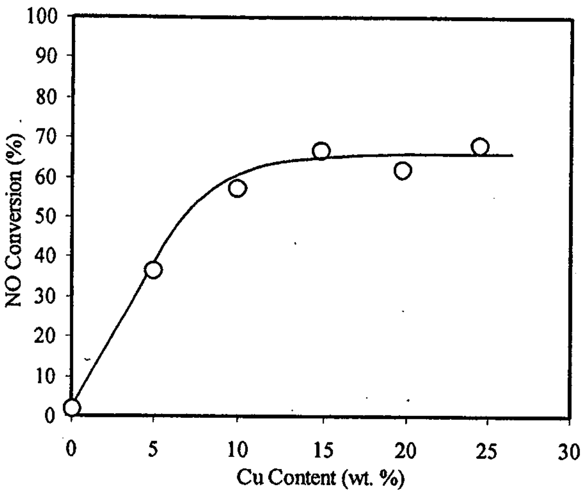

Figure 3: Effect of copper content on NO conversion of Cu-ZSM-5 catalyst at 350°C.

4 Conclusions

Among the three zeolite catalysts tested, Cu/ZSM-5 showed the highest activity (up to 55 %) for the reduction of NO, followed by Fe/ZSM-5 and Mn/ZSM-5. The optimum temperature for NO reduction was observed at 350°C. The highest removal for Fe/ZSM-5 (45 %) occurred at 300°C. At higher temperatures, the conversion of NO would decrease due to excessive oxidation of the hydrocarbon reductant. At low copper content, NO reduction activity increased with an increase in the copper content in the catalyst. Copper content higher than 15 % did not result in significant increase in the NO reduction due to the blockage of some zeolitic pores.

Acknowledgement: Financial assistance from Universiti Sains Malaysia in the form of short term research grant (A/C : 6012533) is gratefully acknowledged.

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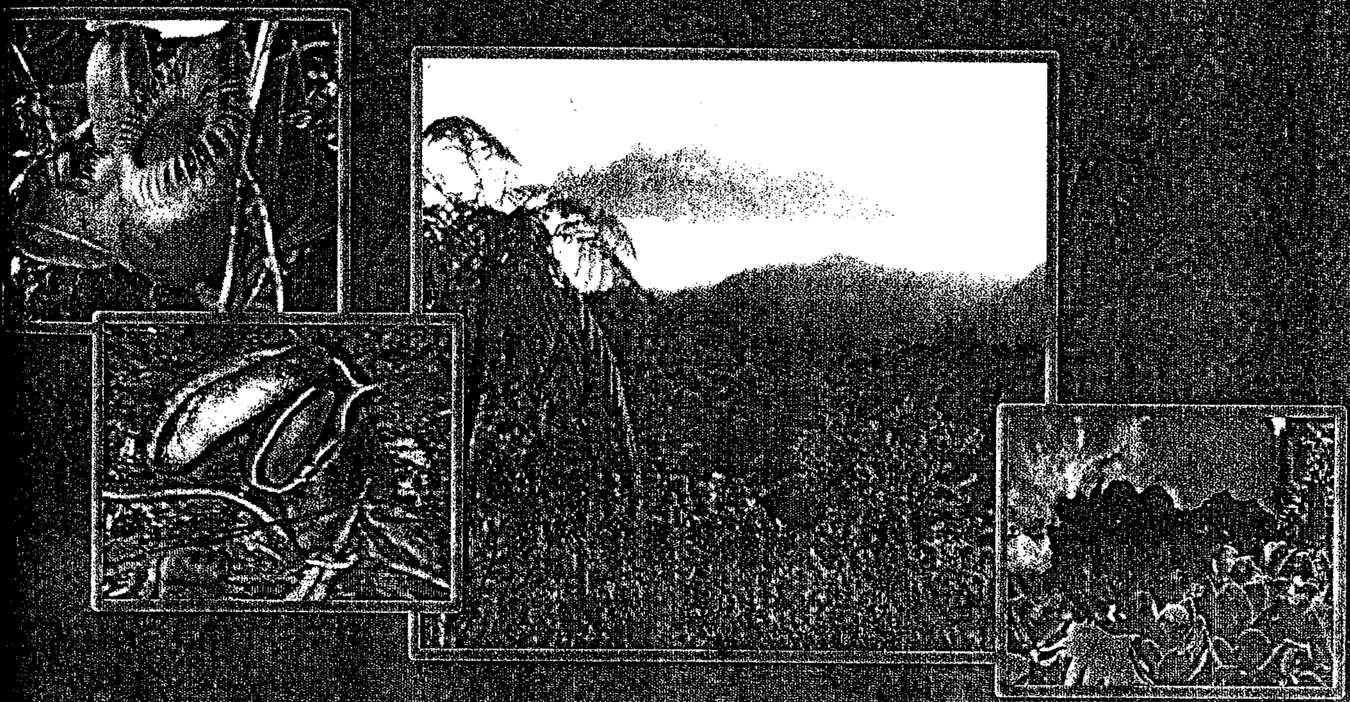

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TECHNICAL PAPERS

Development of Mixed Metal Oxides for Storage of NOx in Diesel Engine Exhaust

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NOx storage and reduction (NSR) is an effective approach for achieving high NOx conversion for a lead feed. There is a need to develop a catalyst that has high efficiency and storage capacity as well as sufficiently active at wide operating temperature for the deNOx of a diesel engine exhaust. In this report, a transient study on the nitrous oxide (NO) storage process over 10 % mixed metal oxide impregnated on alumina (K_2O/Al_2O_3, CaO/Al_2O_3 and BaO/Al_2O_3) was performed by using a synthetic exhaust gas containing 1,000 ppm of NO, 1,000 ppm of C_4H_{10}, 3 % O_2 and N_2 balance.

The reactor was operated at temperature between 250° C and 450°C with 0.20 g of catalyst and for duration of 1200 s for activity study. Scanning electron microscope (SEM) results showed that there was no structural change of the catalyst after subjected to the NO storage process. The data indicated that in the presence of oxygen, NO was effectively absorbed. The NOx storage capacity decreases in the order : $K_2O/Al_2O_3 > CaO/Al_2O_3$ and BaO/Al_2O_3. The NO storage capacity of K_2O/Al_2O_3 decreased with increasing temperature and achieved its maximum at 250°C.

The addition of the Ba and K loading in the catalyst was fund to improve the activity of the material. However, the addition of potassium at higher than 15 wt. % negatively affected the morphological properties and consequently the storage capacity of the material.

NMR and FT-IR Investigations of Low Density Polyethylene (grade FD 0374)

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In today's market, there is a need to study the structural and morphological changes of low density polyethylene (LDPE) and know what would be is the spontaneous effects of the thermal parameters since LDPE is a very important industrial production for many sectors due to its several advantages compared to other plastic polymers.

The main interest of our present work concern of the morphological and structural changes of low density polyethylene (LDPE), of grade FD 0374 which is produced by QAPCO (Qatar Petrochemical Corporation). The other commercial polymeric products that have been investigated parallel to LDPE are: polystyrene (PS) and acrylic styrene acrylonitrile (ASA) provided by the same company. The investigations of these polymeric products were made using different techniques at various temperatures such as:

1. Differential Scanning Calorimetry (DSC) technique within the temperature range: 10°C-500 °C. The results obtained existence of endothermic and exothermic peaks like: i) the melting point of LDPE (of grade FD 0374) was estimated at 111 °C, which is in a good agreement with reported values; ii) the melting point of ASA was estimated at 410 °C; iii) the melting point of PS was estimated at 420°C. The exothermic processes could be due to crystallization or the decomposition of the products at high temperatures.
2. X-Rays Diffraction (XRD) technique at ambient temperature has confirmed a partial crystalline character of LDPE, while PS and ASA are found to be amorphous polymers.
3. Helium Pycnometry technique to measure density at specific temperatures ranged from 15°C to 35°C. The general behavior of the density of these products decreases as temperature increases. This could be due to the expansion in volume due to normal thermal effect.
4. High-resolution cross-polarization magic angle spinning Carbon 13 solid state Nuclear Magnetic Resonance (CP/MAS ^{13}C solid state NMR) technique was applied, at ambient temperature, to investigate the

Development of Mixed Metal Oxides Catalysts For Storage of NOx in Diesel Engine Exhaust Gas

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Abstract

NOx storage and reduction (NSR) is an innovative approach for achieving high NOx conversion for a lean feed diesel engine exhaust gas. There is a need to develop a catalyst that has high storage capacity and active within wide operating temperature. A study on the NOx storage process over metal oxide catalysts (K_2O/Al_2O_3, CaO/Al_2O_3 and BaO/Al_2O_3) was performed by using a synthetic exhaust gas containing 1,000 ppm NO, 1,000 ppm i-C_4H_{10}, 8 % O_2 and N_2 balance. The reactor operated at temperatures between 250°C and 450°C duration of 20 min for activity study. Scanning electron microscope (SEM) results showed that there was no structured change of the sample catalyst after subjected to the NOx storage process. The data of studied suggested that in the presence of oxygen, NO was effectively adsorbed. The NOx storage capacity decreased in the order: $K_2O/Al_2O_3 > BaO/Al_2O_3 > CaO/Al_2O_3$. The NO storage capacity for K_2O/Al_2O_3 decreased with increasing temperature and achieved a maximum at 250°C. The potassium loading higher than 15% in the catalyst negatively affected the morphological properties. The combination of Ba and K loading in catalyst led to an improvement in the catalytic activity compared to its single metal catalysts. As a conclusion, mixed metal oxide was a potential catalyst for deNOx process in meeting the stringent diesel engine exhaust emissions regulations.

Keyword : Diesel exhaust; NOx storage; Lean deNOx; Exhaust catalyst; Mixed metal oxide.

Introduction

Diesel-powered engines have better fuel economy than stoichiometric gasoline engines. However, they have many adverse environmental effects, particularly due to the emission of excessive nitrogen oxides (NOx) in its gas emission. Due to the lean burn combustion in the engine, the exhaust gas also contains an excess of oxygen that complicates conventional approaches to chemically reduce NOx to environmentally benign nitrogen gas. Therefore, there is an urgent need to develop diesel emission control technology to take full advantage of the fuel efficiency and durability of diesel vehicles [1].

NOx storage and reduction (NSR) catalysts, which are also sometimes referred to as NOx adsorption catalysts and lean NOx trap have been developed as a promising alternative method to remove NOx from diesel engine emission [2, 3]. These catalysts operate in a cyclic manner where during the lean reductant (conventionally NH_3, CO or hydrocarbons) period of operation, the catalyst stores or traps NOx as nitrate species. A periodic and short rich pulse of reductant is then introduced so that the trapped NOx is released and reduced to N_2 and the catalyst is regenerated [3]. The NOx trapping materials can be found among the alkali (K, Mg, Ca) and alkaline earth metal (Ba, Li) oxides, where BaO has been most extensively studied experimentally [4]. In general, these metals show different efficiencies in storing NOx as nitrates that eventually have different stabilities in the catalysts. Therefore, efforts to determine the right types and content of oxides, or possibly a combination of oxides in the catalyst should be explored.

This study reports the efficiency of NOx to be stored by oxides of K, Ba and Ca supported on Al_2O_3 catalyst. The efficiency of the process was studied with single and combined oxide systems. The behavior of the process was characterized and elucidated with the final aims of identifying the active and efficient mixed metal oxides to store NOx from diesel engine exhaust gas.

Materials and Methods

Catalyst Preparation

Several metal oxides i.e. oxides of barium (Ba), calcium (Ca) and potassium (K) were studied for their effectiveness in the storage of NOx during lean reductant stage of the deNOx process. Alumina (Al_2O_3) was used as the catalyst supports in this study. The introduction of active metals was carried out through a wet impregnation method using respective metal nitrates as the precursors. In a typical procedure, for the preparation of BaO/Al_2O_3 (10 wt. %), 3.5 ml of deionized water was added under stirring to 4.5 g of the supporting oxide. 10 ml of an aqueous solution containing 0.96 g of $Ba(NO_3)_2$ was mixed with the paste and stirred for 2 h at room temperature. After evaporating the solvent at ≈ 100°C, the sample was dried at 110°C overnight and finally calcined in air at 500°C for 2 h. A fraction with particle sizes between 425 and 600μm was obtained by pressing, crushing and then sieving. The catalysts synthesized are denoted $MO(x)/Al_2O_3$ where x represent the weight composition of the metal oxide in the catalyst. The fresh and aged catalyst samples obtained in this study were be characterized for the surface analysis and imaging using a scanning electron microscope (SEM) and an elemental analyzer (EA).

Experimental Set up

The experimental set up used for activity study consisted of N_2, O_2, 5,000 ppm NO in N_2 and 5,000 ppm isobutene (i-C_4H_{10}) in N_2 gasses the flow rate of which were controlled by means of mass flow controllers (MKS). The reactor was made of 20 mm i.d. stainless steel tubing and was designed as cross sectional detachable type with a center joint, where the catalyst packing could be mounted and removed easily from the reactor. There pressure drop across the reactor was negligible under the normal operating conditions. A thermocouple type K (Cole-Palmer-88500-10) connected to a multi-channel digital temperature scanner (Cole-Palmer- 92000-05) was used to measure the temperature inside the reactor. The reaction temperatures (200° to 450°C) were achieved by means of a horizontal tubular furnace (Linberg-TF-55035C). The feed gas components comprising of 1,000 ppm NO, 1,000 ppm C_4H_{10}, 8 % O_2 and balanced N_2 were mixed to give the feed gas.

Catalyst Activity Study

The NO storage activity of the catalysts was evaluated at atmospheric pressure with a total feed flow rate of 50 ml/min. Lean NO presented in feed was reacted and chemically stored in the catalyst storage component for a duration of 20 min. The packing of 200 mg of catalyst was mounted at the center of the catalytic reactor. The furnace was allowed to cool down and the tubing system was flushed with nitrogen for about 30 min to remove excess oxygen. The feed gas mixture was fed into the system at 50 ml/min and the reactor was heated to the desired reaction temperature before measuring concentration of gases. The feed gas mixture was allowed run for about 10 min to ensure steady state and uniform mixture before measuring concentration of gases at the reactor outlet.

Gas Analysis System

An in-line gas chromatography (GC) (Shimadzu GC 8A) was used for the analysis of the feed and product gases. The GC unit was operated in an isothermal condition (80°C) with helium as the carrier gas. The GC used was equipped with a thermal conductivity detector, two separating columns and an integrator. A Molecular Sieve 5A column (Supelco) was used for separating N_2, O_2 and i-C_4H_{10} while Porapak Q column (Supelco) was used for the analysis of NO and CO_2.

Results and Discussion

Process Studies

This section presents and discusses experimental results obtained from a series of catalytic test on NO storage by mixed metal oxide catalysts. Experiments was carried out to determine the effect of the important independent process variables (i.e. storage compounds, reaction temperature, percentage of metal loading and metal composition) at fixed amount of catalyst, reaction duration and feed composition. The experiment was performed at a temperature of 350°C with reaction duration of 20 min. In order to examine the performance of different storage components, 20 mg of different catalysts i.e. $BaO(10)/Al_2O_3$, $K_2O(10)/Al_2O_3$ and $CaO(10)/Al_2O_3$ were investigated. Table 1 compares the activities of three catalysts in NOx storage at 350°C.

Table 1 : Amount of NO storage by different catalysts.

Catalyst	NO Concentration (ppm)		Amount of NO stored (%)
	$(C_{NO})_{in}$	$(C_{NO})_{out}$	
$BaO(10)/Al_2O_3$	1014	638.3	39.0
$K_2O(10)/Al_2O_3$	1009	450.4	55.4
$CaO(10)/Al_2O_3$	1010	616.0	37.1

For each experiment, the concentration of NO in the outlet gas measured was lower than that in the inlet gas. These results indicated that, NO was stored on the catalyst under the lean conditions. In the presence of 8 % O_2, K_2O/Al_2O_3 was the most active for the storage of NO and CaO/Al_2O_3 gave the lowest performance. The sequence of basicity strength are K>Ca>Ba. Therefore, the result suggested that the stronger the basicity of the NOx storage compound, the larger the quantity of the NO stored. The similar observation was reported by Takahashi *et al.* [5]. It was attributed to the higher stability of nitrates formed by oxides of stronger basicity [5]. Potassium also favored the surface mobility, and had higher surface basicity [6]. On the other hand it was found that CaO/Al_2O_3 was not efficient to catalyze the oxidation of NO to NO_2 and therefore, could not efficiently store NO to a significant extent even in the presence of oxygen [7].

It is generally reported in the literature that the formation of NO_2 from NO and O_2 is a necessary initial step before NOx storage can take place during lean conditions [8, 9]. However, this simple step already included several uncertainties and further, may be the sum of several elementary reaction steps [9]. NOx storage process for lean conditions can be assumed to comprise the following steps with M as storage component in the catalyst:

$$NO^{g} \rightarrow NO^{a} \quad (1)$$

$$O_2^{g} \rightarrow 2O^{a} \quad (2)$$

$$NO^{a} + O^{a} \rightarrow NO_2 \quad (3)$$

$$2NO + 3O + MO \rightarrow M(NO_3)_2 \quad (4)$$

$$2NO_2 + O + MO \rightarrow M(NO_3)_2 \quad (5)$$

The superscript g refers to gas from while superscript a refers to absorbed form of the chemical compound. This is a somewhat simplified reaction scheme. For example, NO_2 adsorption and desorption are not included [9]. A key role of the catalyst surface was found to be the oxidation of NO to NO_2 [10].

Effect of Operating Temperature

In order to determine the parameters for NOx storage process, the temperature dependence of the reaction at constant feed gas composition was investigated. For this purpose, catalyst $BaO(10)/Al_2O_3$ and $K_2O(10)/Al_2O_3$ had been evaluated on a catalytic reactor rig to determine its properties as a function of temperature for the range 200°-450 °C. Both metal oxide catalysts were tested under the same reaction conditions. Figure 1 shows the result of the temperature dependence of the catalytic activity under lean conditions. The difference between inlet and outlet NO concentration indicated the NOx storage.

The maximum NO storage for $K_2O(10)/Al_2O_3$ of around 58 % occurred at 250°C. After this, the NO storage reaction decreased with increasing temperature. As reported by Fridell *et al.* [9], the decrease in NO storage at higher temperature was associated with the stability of metal nitrate. In contrast to the $K_2O(10)/Al_2O_3$ catalyst, the $BaO(10)/Al_2O_3$ catalyst showed higher conversions at higher temperature. For $BaO(10)/Al_2O_3$, the lean feed shows peak steady-state NOx storage approximately 47 % at 450°C. As indicated by Figure 5, the $BaO(10)/Al_2O_3$ catalyst had higher NO storage activity than the $K_2O(10)/Al_2O_3$ catalyst at higher temperatures, particularly above 400°C. This suggested that the ionic bonding character of Ba nitrates increased with increasing temperatures [11].

As shown in Figure 1, the NO storage for both catalysts exceeded 40 % at 200°C. It was because of Al_2O_3 catalysts that were capable to play an important role as the storage site at temperatures below 300°C [12]. Contrary to the literature, a maximum NOx storage was not seen around 380°C for both cases. The similar behavior was also reported by Fridell *et al.* [9].

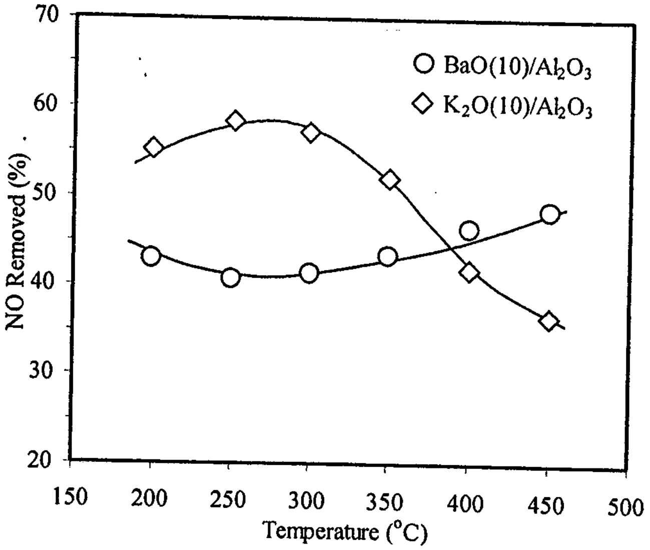


Figure 1: Percentage of NO storage onto $BaO(10)/Al_2O_3$ and $K_2O(10)/Al_2O_3$ as a function of reaction temperature.

Effect of Percentage Metal Loading in Catalyst

A series of K_2O/Al_2O_3 catalysts containing different K loadings (in the range 0-25 wt. %) had been prepared and tested for the NO storage under laboratory operating conditions. The objective was to investigate the effect of metal loading on the storage process. Accordingly, the role of the K loading on the storage of NOx could be analyzed. Figure 2 shows the NO storage performance of the catalyst as a function of K_2O loading.

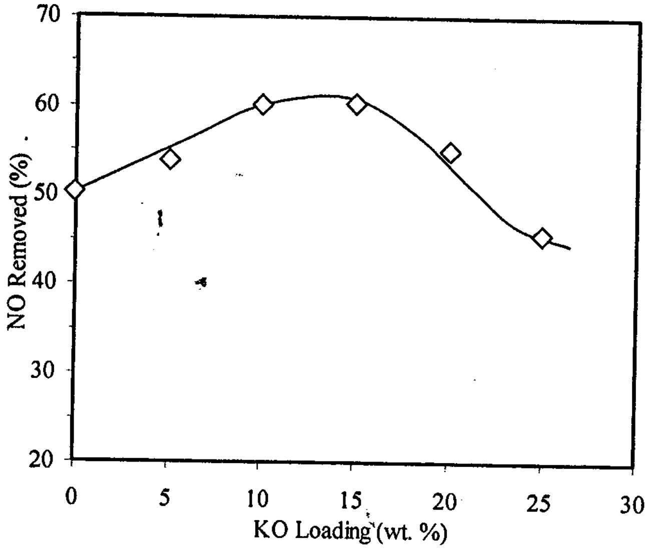


Figure 2: Amount of NO storage for different K_2O loadings in K_2O/Al_2O_3 catalyst.

Supporting 5-10 wt % of K_2O on Al_2O_3 was found to improve the lean NO storage activity of Al_2O_3, but the incorporation of 15 wt % K showed no significant improvement inn the storage activity. Further addition of K_2O proved to be detrimental to the performance of the catalyst. Westerberg *et al.* [12] proposed that K_2O could play an important role as a storage site at temperatures below 300°C.

As the loading of the catalysts increased, the activity increased as indicated by percentage of NO storage. The highest NO storage over K_2O/Al_2O_3 occurred when K contents were between 10-15 wt %. However, beyond that, the percentage of NO storage started to decreased, probably due to the diffusion limitations at higher loading. These data was in agreement with some literature reported [6, 8, 13]. The decrease in activity for the higher loading samples was also attributed to the dissolution of some amount of $K(NO_3)$ during the impregnation and cause higher K coverage of the alumina surface [13, 14]. Both potassium and alumina were able to react with NO_2 forming nitrates species. Both $K_2O(5)/Al_2O_3$ and K_2O $(20)/Al_2O_3$ produce NO retentions lower than, or similar to, pure Al_2O_3. In this way, K_2O $(10)/Al_2O_3$ showed the highest stability for nitrate species among the $K(x)/Al_2O_3$ formulations studied.

Effect of Metal Composition in Catalyst

The effect of the addition of BaO to $K_2O(x)/Al_2O_3$ system was studied with the objective of improving the interaction with NO molecules and to improve the catalytic activity for the NO storage reaction by increasing the formation of surface NO intermediates. Activity studies were performed on $K_2O(3)BaO(7)/Al_2O_3$, $K_2O(5)BaO(5)/Al_2O_3$ and $K_2O(7)BaO(3)/Al_2O_3$. Amount of NO stored are shown in Table 2.

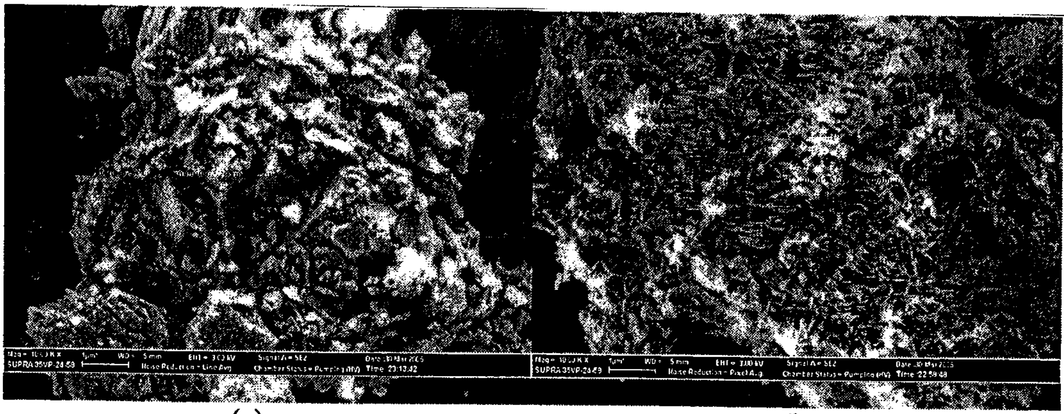
Table 2: Amount of NO storage over different storage composition in lean phase.

Catalyst	NO Concentration (ppm)		Amount of NO stored (%)
	$(C_{NO})_{in}$	$(C_{NO})_{out}$	
$K_2O(3)BaO(7)/Al_2O_3$	988	514.1	48.0
$K_2O(5)BaO(5)/Al_2O_3$	996	339.2	65.9
$K_2O(7)BaO(3)/Al_2O_3$	1012	422.6	58.2

First, the presence of Ba led to a lower NO storage activity for $K_2O(3)BaO(7)/Al_2O_3$. By increasing the loading of potassium into these catalysts, an increase in the activity could be observed. The highest NO storage over $Ba,K/Al_2O_3$ occurred when the loading of both metal was equal (i.e. K_2O $(5)BaO(5)/Al_2O_3$). The K_2O $(7)BaO(3)/Al_2O_3$ catalyst presented an activity similar to K_2O $(10)/Al_2O_3$, which was in agreement with results reported by Matsumoto *et al.* [15]. The combination of the Ba and K loading in catalyst was capable to shown improvement in the catalytic activity compared to single metal loading, attributed to some synergistical effects between these two metal oxides.

Characterization of Fresh and Aged Catalyst

The structure and morphology of fresh and spent catalyst were also investigated. The topological information such as crystal structure and morphology of a fresh and spent $K_2O(10)/Al_2O_3$ and $K_2O(5)BaO(5)/Al_2O_3$ catalyst prepared were studied using scanning electron microscope. Figure 3(a) shows a SEM micrograph of fresh $K_2O(10)/Al_2O_3$ catalyst while Figure 3(b) shows the SEM micrograph of the fresh $K_2O(5)BaO(5)/Al_2O_3$ catalyst.

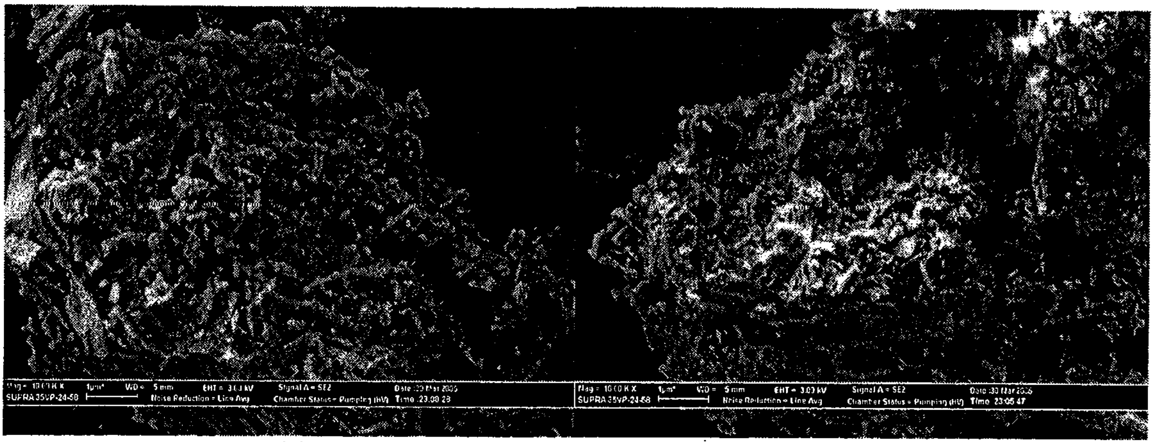


(a) (b)

Figure 3: SEM micrograph of a) fresh $K_2O(10)/Al_2O_3$ and, b) fresh $K_2O(5)Ba(5)/Al_2O_3$.

As shown in the Figure 3(a) and (b) above, the sample $K_2O(5)BaO(5)/Al_2O_3$ had clear crystalline shape compared to $K_2O(10)/Al_2O_3$. The micrograph of both samples suggested that the surface of alumina in sample $K_2O(5)BaO(5)/Al_2O_3$ was homogenously covered by metal as compared to sample $K_2O(10)/Al_2O_3$.

An analytical techniques were also carried out to characterize the structured of aged catalyst. The information about the structure and morphology of aged catalyst was investigated. The topological information of an aged $K_2O(10)/Al_2O_3$ and $(K_2O(5)BaO(5)/Al_2O_3$ catalyst were studied. This used sample was the catalyst that was previously subjected to NO storage condition for a duration of 1600 s under a reaction temperature of 350°C. Figure 4(a) and (b) show the SEM micrograph of $K_2O(10)/Al_2O_3$ and $K_2O(5)/Al_2O_3$ aged sample, respectively.



(a) (b)

Figure 4: SEM micrograph of aged (a) $K_2O(10)/Al_2O_3$ and (b) $K_2O(5)BaO(5)/Al_2O_3$ catalyst.

As shown in the micrograph, there was no structured change of both the sample after subjected to the NOx storage process if compared to the micrograph showed in Figure 3(a) and 3(b) respectively. As compared the fresh and aged sample, it could be concluded that as the coverage of metal in the surface increased, the capacity of storage also increased. Similar to observation was reported by Fanson *et al.* [16]. However, we are unable to unambiguously identify the species of the surface compound that exists and we are unsure of their exact origin.

The elemental analysis was also conducted on the spent catalysts. The composition of carbon, hydrogen and nitrogen content is shown in Table 3. The $K_2O(10)/Al_2O_3$ catalyst with notation a was tested under reaction temperature of 250°C while the catalyst with notation b was tested under reaction temperature of 350°C.

Table 3 : Composition of carbon, hydrogen, nitrogen and sulfur content in aged catalyst.

Element	Content (wt %)			
	$K_2O(10)/Al_2O_3$[a]	$K_2O(10)/Al_2O_3$[b]	$BaO(10)/Al_2O_3$	$CaO(10)/Al_2O_3$
Carbon	0.54	0.50	0.78	1.34
Hydrogen	0.66	0.57	0.50	0.98
Nitrogen	1.83	2.08	0.79	1.88

[a]Tested at 250°C; [b]Tested at 350°C

The percentages of carbon, hydrogen and nitrogen were found to increase from those of the fresh catalyst. The existence of the carbon and hydrogen was cause by the oxidation of the hydrocarbon (C_4H_{10}) in the feed gas by high temperature (> 250 °C) [17]. The clear evidence of nitrogen chemisorption could be observed with nitrogen content varied between 0.35-0.45 in the fresh sample. The decomposition process of NO to N_2 and O_2 inside the catalyst contributed to the growing of nitrogen content [8]. On the other hand it was found that BaO/Al_2O_3 was not efficient to catalyze the oxidation of NO to NO_2 and then to N_2 if compared to K_2O/Al_2O_3 and CaO/Al_2O_3. It was reported that BaO/Al_2O_3 did not store NO to a significant extent. Similar observation was reported by Lietti *et al.* [7].

Conclusion

The NO storage amount in a lean exhaust stream was dependent on the basicity of the storage compounds. K_2O/Al_2O_3 catalyst was found to be the most active for the NO storage process with storage capacity decreased in the order: K_2O/Al_2O_3 > BaO/Al_2O_3. > CaO/Al_2O_3. The NO storage capacity for $K_2O(10)/Al_2O_3$ also decreased with increasing temperature, especially at above 300°C. The NO storage process achieved its maximum at an intermediate temperature (250°C) for $K_2O(10)/Al_2O_3$. As for $BaO(10)/Al_2O_3$, the NO storage capacity increased with increasing of operating temperature. The effect of K loading 0-25 % (w/w) in the storage over K_2O/Al_2O_3 samples was investigated and the results indicated that the addition of K_2O negatively affected the morphological properties of the catalyst system at loading higher than 15 %. Nevertheless, the increase in the K_2O loading resulted in a strong increase of the NO adsorption at breakthrough. Under these conditions, a maximum value of NO storage of around 60 % was observed for the $K(15)/Al_2O_3$ sample. Significant amounts of NO were found to be stored in the catalysts containing $K(5)$-$Ba(5)/Al_2O_3$. The combination of Ba and K loading in catalyst led to an improvement in the catalytic activity compared to single metal catalyst.

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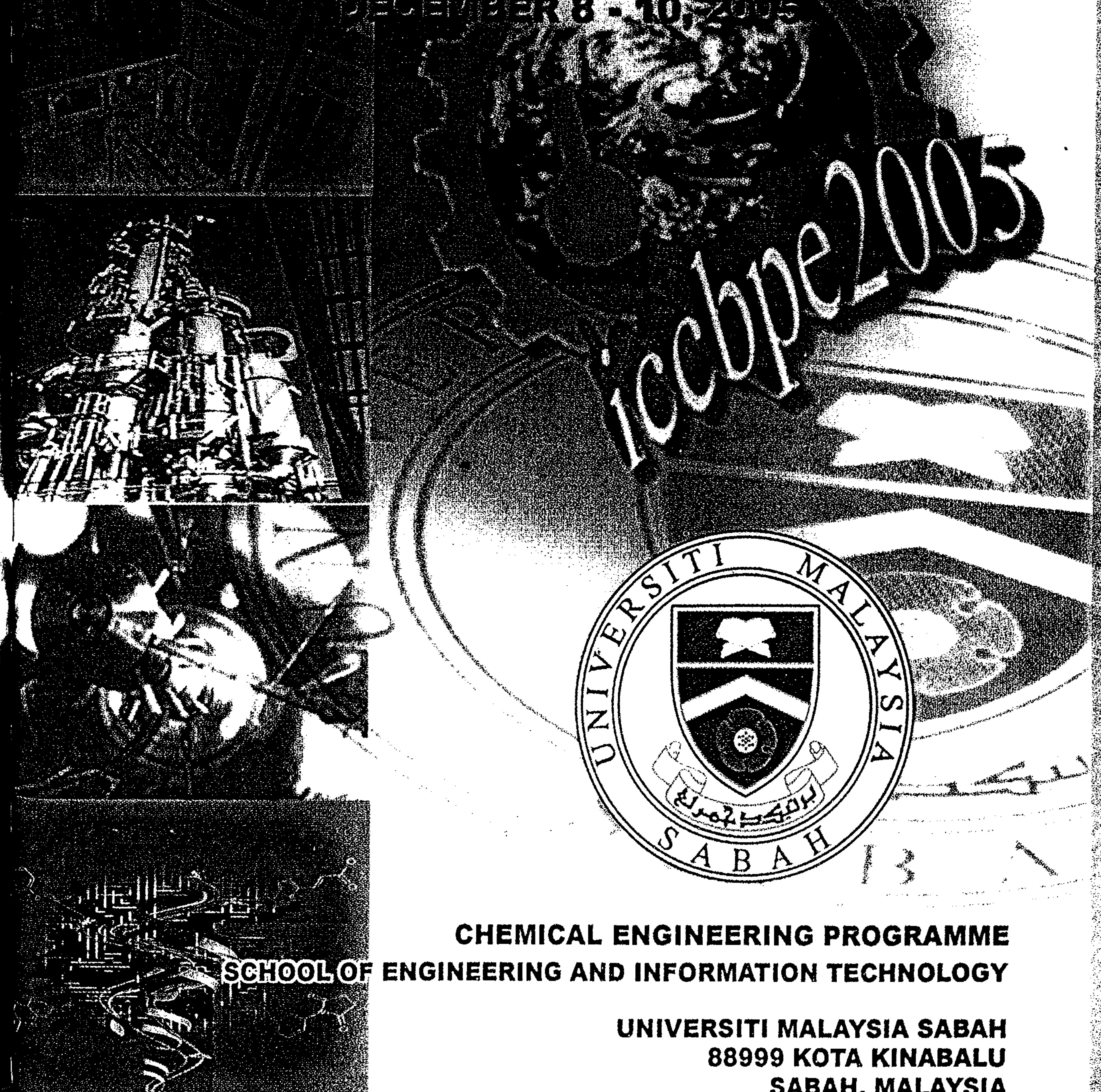

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MTE-15

Synthesis and Characterization of Mesoporous SBA-15 : A Material Evaluation for Roles in Catalysis

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Abstract

Mesoporous molecular sieve is a new class of materials that shows high potential in various applications, particularly catalysis. A series of mesoporous materials (SBA-15) were synthesized at different gel compositions using triblock copolymer (TCP) poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) as the surfactant. Gel compositions were varied to study the effect of acidity, the contents of tetraethyl orthosilicate (TEOS) and triblock copolymer(TCP) on the characteristics of the final material. Effect of synthesis temperature was also studied. Attributed to accelerated hydrolysis of TEOS, increasing acid content in the synthesis gel favored the formation of mesopores. The best material with total surface area of 760 m^2/g*, mostly in mesoporous size range was obtained at a gel composition of* $1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O$*.The controlling mechanisms for mesopores formation were predominately influenced by the right balance between the content of TEOS and TCP in the synthesis gel that appeared to be occurring in a very narrow range. All these materials showed low crystallinity as well as weak acidity, contributed by silanol groups terminating the Si-O-Si network.*

Keywords: SBA-15, Mesoporous, Catalyst, Synthesis, Characteristics.

Introduction

Despite successful application in many industrial processes, microporous materials such as zeolites become inadequate when reactants with sizes above the dimensions of the micropores (>1 nm) have to be processed [1,2]. Thus, mesoporous molecular sieves (MMSs) have introduced a new degree of freedom in the conception of catalysts. MMSs are very high surface area materials (up to 1600 m^2/g) having monodispersed pore diameters in the range 2-50 nm and a stereoregular arrangement of these channels [3]. Because of the size of their pores, they allow the processing of large molecules and the eventual accommodation of bulky intermediate transition states. This capability enables them to form catalysts or acting as catalytic supports in a wider range of industrial reactions. However, the basic understanding of the synthesis conditions is indispensable as mesoporous materials with desirable characteristics can only be obtained with properly controlled synthesis procedures [1,3]. Therefore, more research work is demanded to properly synthesize and subsequently manipulate the characteristics of these highly ordered materials towards their widest future potential applications in industrial processes [4].

Among the earliest MMSs developed are the M41S family that includes hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50. Their preparation involves ionic structure directing agents and occurs via liquid-crystal templating (LCT) mechanism. These materials have uniform pores which pore sizes can be tailored in the range of 16-100Å by changing the length of the alkyl chain of the surfactant, auxiliary chemicals and reaction conditions used in their synthesis [2]. However, the main drawback for successful application of M41S is its low thermal and hydrothermal stability [1,5]. Recently, mesoporous materials with larger pore size and better stability were synthesized with the template of nonionic block copolymers. These materials, exemplified by hexagonal (*p6mm*) SBA-15, have long range order, large monodispersed mesopores (up to 50 nm) and thicker walls (typically between 3 and 9 nm) which make them more thermally and hydrothermally stable than previous materials [5, 6]. The cubic phase mesoporous material SBA-16 (*Im 3m*) possesses three-dimensional channel system and uniform-sized pore of super large cage-like structure with a cubic symmetry [7,8]. The composition of the gel and the synthesis conditions are found to strongly determine the quality of the finished SBA-15 or SBA-16 [5,6]. By focusing on the SBA-15, the in-depth understanding of the correlation between synthesis conditions with the quality of the material obtained was investigated in this study towards designing a suitable material for catalytic purposes.

Approach and Methods

Synthesis of SBA-15

The siliceous SBA-15 mesoporous materials (MM) were synthesized using tetraethyl orthosilicate (TEOS) (Merck) as silica source, a triblock co-polymer (TCP) i.e. poly(ethylene glycol)-(propylene glycol)-poly(ethylene glycol) (Aldrich) with a molecular weight of 5800 as the structure directing agent, HCl and water. The gels molar compositions are given in Table 1. In a typical synthesis procedure, the TCP was first dissolved in a solution of water and HCl and the mixture was shaken in an orbital shaker at 30°C and 150 rpm for 2 h. Then, the required amount of TEOS was added to the above solution. As the gel started to develop, the mixture was quickly heated to desired temperatures (T) under shaking at 75 rpm for 24 h. The gel formed was then aged at 100°C for 6 h. The solid formed was then vacuum filtered, washed several times and calcined at 500°C for 6 h in a furnace. The mesoporous materials obtained were denoted as S-1 to S-9.

Table 1-Gel compositions and temperatures used in the synthesis of SBA-15 samples.

No	TEOS (g)	TCP (g)	HCl (g)	H_2O (g)	T (°C)	Molar ratio
1	24.0	11.5	21.9	300.0	60	1.0(TEOS):0.017(TCP):5.2HCl:144.7H_2O
2	24.0	11.5	26.4	270.0	60	1.0(TEOS):0.017(TCP):6.3HCl:130.2H_2O
3	24.0	11.5	30.7	240.0	60	1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O
4	18.0	11.5	26.4	270.0	60	1.0(TEOS):0.023(TCP):8.3HCl:173.6H_2O
5	30.0	11.5	26.4	270.0	60	1.0(TEOS):0.014(TCP):5.0HCl:104.2H_2O
6	24.0	7.5	26.4	270.0	60	1.0(TEOS):0.011(TCP):6.3HCl:130.2H_2O
7	24.0	15.5	26.4	270.0	60	1.0(TEOS):0.023(TCP):6.3HCl:130.2H_2O
8	24.0	11.5	26.4	270.0	40	1.0(TEOS):0.017(TCP):6.3HCl:130.2H_2O
9	24.0	11.5	26.4	270.0	50	1.0(TEOS):0.017(TCP):6.3HCl:130.2H_2O

Characterization of SBA-15

All SBA-15 samples were characterized for surface characteristics using a Quantachrome Autosorb-1 equipment with an outgassing temperature of 300°C. while X-ray diffraction patterns were obtained using a Siemens 2000X system. The acidity determination was made through a temperature programmed desorption of ammonia experiments using a Quantachrome Chembet 3000 system. In this test, the adsorption of NH_3 was carried out at 50°C. The Infrared spectroscopy characterization of the catalyst sample was carried out using a Perkin Elmer 2000 FT-IR system while the structure of the samples was also characterized using a Phillips CM 12 transmission electron microscope.

Results and Discussion

Surface characteristics of SBA-15

The surface area and pore characteristics of the nine SBA-15 samples produced in this study are summarized in Table 1. Bearing in mind the HCl acid content of the gel increased from S-1, S-2 to S-3, the total surface area was found to show corresponding increase. These surface areas were primarily contributed by mesopores that constituted between 62 to 73 % of the total surface area, depending on sample. The largest mesopore was demonstrated by S-3 with an average size of 6.92 nm. As a general trend in these three samples, more mesopores resulted in an increase in the pore volume. The highest pore volume was demonstrated by S-3 with a value of 0.98 cc/g. This value occurred in the normal pore volume range for SBA-15 as reported in literatures [2,4,5]. However, there was no clear correlation between the average pore width and the pore volume as they were strongly dependent on the distribution of micropores and mesopores in the sample.

The content of TEOS in the synthesis gel was increased sequentially in the preparation of S-4, S-2 and S-5 while maintaining the content of other components. Data in Table 1 suggest that with an increase in TEOS from S-4 to S-2, more mesopores formed in the SBA-15 sample. However, further increase resulted in a detrimental effect on pore formation. The decrease in the surface area and pore volume were quite drastic, suggesting the failure in the formation of mesopores in the samples at high TEOS concentration. This result suggested that in the synthesis of SBA-15, the content of the TEOS need to be neatly controlled to ensure the development of mesopores in the material. It is also noted that the average pore width failed to correlate with the formation of mesopores in the samples, suggesting the roles of macropores in between SiO_2 particles on the result of average pore widths measurement.
During the synthesis, the content of TCP in the gel was increased sequentially in the preparation of S-6, S-2 and S-7 while the proportion of other gel components fixed. With an increase in the TCP content in the preparation of S-2 compared to that of in the preparation of S-6, more mesopores developed, indicated by higher total surface area and mesopore area of the latter. However, further increase in the concentration of TCP resulted in severe failure in the development of mesopores. This conclusion was based on the characteristics of S-7 which showed little porosity with low surface area. The large value of the average pore width of this sample (6.88 Å) was therefore attributable to macropores of the SiO_2 particles which had little contribution to the total surface area.

S-8, S-9 and S-2 samples were synthesized with a gelling stage conducted at a temperature of 40°C, 50°C and 60°C, respectively. It is evident in Table 2 that mesopores did not satisfactorily form at low temperatures (40°C, 50°C) as S-8 and S-9 were characterized by lower surface area and lower pore volume as compared to S-2. However, the main contributor for surface area for the former two samples was still the mesopores that stood at between 54 to 61 % of the total surface area. This result suggested that at 40° and 50°C, synthesis of the orthosilane and the condensation of silica still can take place, although at lower rates. With an increase in temperature of the gelling stage, more ordered mesopores developed as clearly indicated by higher surface area and pore volume in the order of S-8, S-9 and S-2.

Table 2-Surface characteristics of the SBA-15 samples.

Sample	^{a}Total surface area (m^2/g)	^{b}Micropore area (m^2/g)	^{b}Mesopore area (m^2/g)	^{c}Average pore width (nm)	^{d}Pore volume (cc/g)
S-1	580	205	375	6.09	0.65
S-2	606	230	376	5.87	0.92
S-3	760	208	552	6.92	0.98
S-4	324	192	132	6.73	0.36
S-5	239	84	155	6.21	0.31
S-6	503	261	242	5.45	0.74
S-7	102	63	39	6.88	0.12
S-8	371	189	202	5.47	0.43
S-9	374	143	230	6.28	0.53

^{a}BET method, ^{b}*t*-method, ^{c}DR method, ^{d}MP method

Data in Table 2 suggested that among all the synthesis conditions studied, the content of TEOS and TCP in the synthesis gel were proven to more critical in the development of mesopores of the SBA-15. Despite the important roles in the successful synthesis of this mesoporous silica, the effect of content of HCl and gelling temperature in the range employed in this study was not that severe. Thus, controlling mechanisms for mesopores formation were predominately influenced by the right balance between the content of TEOS and TCP in the synthesis gel that appeared to be occurring in a very narrow range.

TEM study of the mesopores formed

Figures 1(a)-1(d) show different characteristics of mesopores formed in SBA-15 samples synthesized in this study. Generally, S-3 showed a relatively ordered mesopores, characterized by an array of straight and uniform sized pores as can be seen in Figure 1(a). The well formed mesopores correlated well with the high surface area and pore volume of this sample as indicated by data in Table 2. At low TCP content of the synthesis gel, mesopores also formed, but of less ordered manner as seen in Figure 1(b) for S-6. Meanwhile, at high TEOS content of the synthesis gel in the synthesis of S-5, satisfactory formation of mesopores also failed to occur as suggested by Figure 1(c). In Figure 1(d), it is noted that mesopores also failed to occur when the TCP content of the synthesis gel was beyond the critical limit for the formation of micelles.

XRD study of SBA-15 samples

The XRD patterns for different SBA-15 samples are shown in Figure 2. Generally, all samples were of amorphous or low crystallinity materials. Especially in samples S-1, S-2 and S-3, strong (100) peak (2θ between 1.8-1.9°), and very weak (110) (2θ between 2.4-2.5°) and (200) (2θ between 3.1-3.4°) signals were demonstrated, suggesting a high degree of hexagonal mesoscopic organization. S-3 showed the highest crystallinity among all samples synthesized in this study with an extra (210) signal occurring at 2θ=5.3°. No scattering signal was detectable for S-7, indicating this sample was of almost complete amorphous material. Samples S-4, S-5, S-8 and S-9 only exhibit very weak (100) diffraction peak that indicated the formation of poorly ordered mesoporous materials.

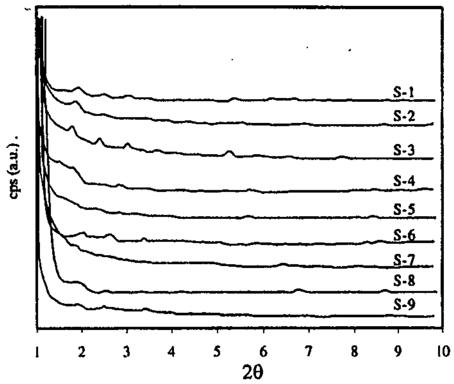

Figure 2-XRD patterns of SBA-15 samples.

Acidity study of SBA-15

All SBA-15 samples showed single and almost symmetrical desorption peak with low acidity as suggested by small desorption peak area (0.006-0.009 mmol NH_3/g) (Figure 3). Generally, the desorption started at as early as 70°C and peaked at temperatures below 110°C. This low temperature desorption suggested that the acidity in the SBA-15 was mainly contributed by weak acid sites. The single desorption peak in Figure 3 suggested that only one type of acid sites presented in all the samples. Many researchers attributed the acidity of SBA-15 to primarily the silanol groups (Si-OH) terminating the Si-O-Si network [3,4,6,7]. In the present study, the presence of silanol groups was confirmed by an infrared absorption peak at a wave number of 3,735 cm^{-1}, especially for S-1, S-2 and S-3. It s also noted that SBA-15 samples with relatively more mesopores such as S-1-S-2, S-3 and S-6 showed both shifted desorption peaks towards higher temperature and larger peak area. These observations indicated that more silanol groups presented in these samples, positively correlating the number of silanol groups and the occurrence of mesopores in the sample.

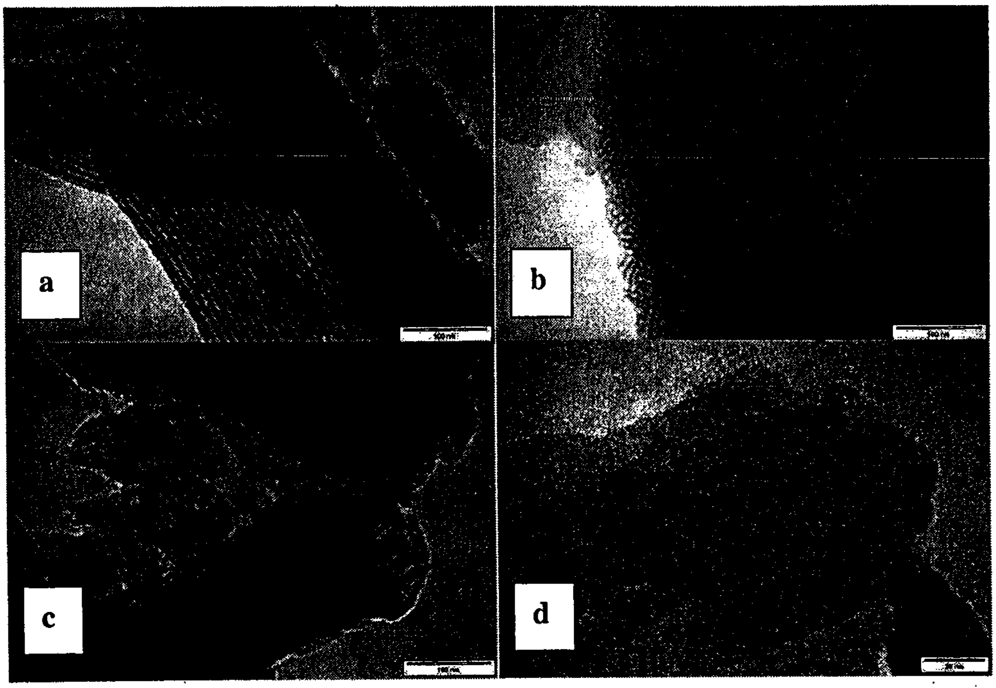

Figure 1-Different types of SBA-15 structures typically exemplified by (a) S-3 for ordered mesopores, (b) S-6 for randomly ordered mesopores, (c) S-5 for partially developed mesopores and (d) S-7 for undeveloped mesopores.

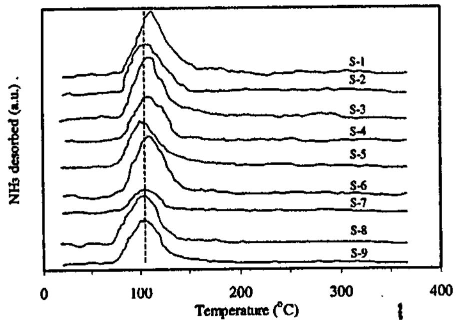

Figure 3-NH_3-TPD profiles of SBA-15 samples.

Conclusions

A series of mesoporous materials (SBA-15) were synthesized at different gel compositions using triblock copolymer (TCP) poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) as the surfactant. Attributed to accelerated hydrolysis of TEOS, increasing acid content in the synthesis gel favored the formation of mesopores. The best material with total surface area of 760 m^2/g, mostly in mesoporous size range was obtained at a gel composition of 1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O.The controlling mechanisms for mesopores formation were predominately influenced by the right balance between the content of TEOS and TCP in the synthesis gel that appeared to be occurring in a very narrow range. Successful development of SBA-15 resulted in a material with well ordered and straight array of pores of meso size range. All these materials showed low crystallinity as well as weak acidity, contributed by silanol groups terminating the Si-O-Si network.

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High Performance Catalysts for Storage and Reduction of NOx in Diesel Engine Exhaust

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ABSTRACT

Diesel engines offer fuel efficiency and reliability in its operation but they also cause many adverse environmental effects, especially due to the emission of nitrogen oxides (NOx) and particulate matter in the form of soot. Selective catalytic reduction of NOx is a well-proven method to get rid of NOx in diesel engine exhaust gases. A number of catalysts have been developed in which the active phases are different metallic oxide such as oxides of Mn, Co, Cu and noble metals. The common catalyst supports being evaluated for this application are such as vanadia, titania, ceria, zirconia and lanthana. The reduction of NOx has been generally found to take place over as fairly narrow temperature range. The catalysts used for NOx storage comprise combinations of noble meals for oxidation and reduction purposes and barium oxide/carbonate as the storage materials as the nitrogen oxides are chemically bound as surface nitrates. The NOx is then released from the catalyst when shorter lean periods were used while very rich purges of reductant is fed. Potassium–loaded catalysts have been found to show high activity in soot combustion. This metal can play the role due to its high mobility to consequently increase the effective contact between the oxidation catalyst and the soot particle. The activity can be further improved by introducing barium as the promoter. The contact between the soot and the catalyst strongly affects the reaction rate. By a proper combination of active metals, a catalyst suitable for the NSR process, while showing lower tendency to be deactivated by soot can be obtained.

Keywords: Diesel exhaust, NOx, selective catalytic reduction, storage, soot oxidation.

1 INTRODUCTION

The diesel engine owes its popularity to its fuel efficiency that results from its lean-burn operation, reliability, durability and relatively low fuel price [1-3]. However, diesel engine exhaust has many adverse environmental effects, due to the high concentration of nitrogen oxides (NOx), particulate matter in the form of soot and sulfur dioxide (SO_2). Emission of nitrogen oxides (NOx) and particulate matter (soot) from diesel engine vehicles is a major environmental concern, especially in view of the increasingly stringent limits worldwide. Legal limits for emissions of carbon monoxide, unburned hydrocarbons and nitrogen oxides (NOx) in automotive and stationary sources exhaust gases are becoming more and more strict. Emission standards for heavy duty vehicles in 2007 and beyond will require a 90 % reduction in total particulate matter and NOx from 2003 levels [3]. These standards place new demands on improved engine performance and catalytic converter technology. At the same time, there is a strong pressure to lower the fuel consumption for economic purposes and to lower the production of carbon dioxide, which is an important greenhouse gas [4,5]. Further developments of a diesel engine exhaust should be focused on the adverse effects on environment and health caused by NOx and sooth emissions. Unfortunately, measures to reduce particulate mass emission will often result in an increase in NOx emission and vice versa. This phenomenon is known as the NOx-PM trade-off.

2 SELECTIVE CATALYTIC REDUCTION (SCR) OF NOx

2.1 SCR Process and Reaction

Conventional process for deNOx of exhaust gases is by converting NOx via a reduction process by mainly ammonia or hydrocarbon (HC) component that present in the gas, to nitrogen (N_2) which is safe to the environment. In recent years, hydrocarbons have been studied in order to replace the current best control technology for reducing NOx emission stationary sources that employ ammonia as reducing agent [6,7]. The main advantage of the reaction between NOx and hydrocarbons in post-combustion processes is the use of gas mixture similar to that found in the exhaust. The lean-burn conditions of diesel combustion, which yielded higher combustion temperature and improved efficiency, produced an exhaust gas containing an excess of oxygen. This complicates conventional approaches to chemically reduce NOx to N_2 as the reducing components such as carbon monoxide (CO), hydrocarbon (HC) and hydrogen (H_2) are preferably oxidized by oxygen [5]. Selective catalytic reduction using a hydrocarbon as a reducing agent has been widely proposed as one of the promising techniques to get rid of NOx in the exhaust gas. The reaction involves is;

$a\mathrm{NO} + b\mathrm{HC} + c\mathrm{O_2} \qquad d\mathrm{N_2} + e\mathrm{CO_2} + f\mathrm{H_2O}$ (1)

The catalytic reduction of NOx has been generally found to take place over a fairly narrow temperature range. However, diesel exhaust temperature varies from 200°C to 600°C [7]. Thus, to obtain the needed reduction over a wide range of operating temperatures, more than one catalyst could be used.

2.2 Active Catalysts for SCR of NOx

The reduction of NOx in oxygen rich-conditions using hydrocarbon (HC) as reductant is a well proven technique for the removal of NOx from stationary sources and has become of increasing interest in recent years [1]. A number of catalysts have been developed in which the active phases are different metallic oxide such as manganese oxide [1], cobalt [2,8], copper [4,7] and noble metals [4,6,9]. The common catalyst supports being evaluated for this application are such as vanadia [10], titania [4], ceria [8], zirconia [9] and lanthana [2,8]. Several other catalyst systems and the observed results are summarized in Table 1. The reduction of NOx has been generally found to take place over as fairly narrow temperature range. However, the temperature of diesel exhaust varies from 200°C to 600°C. Thus, to obtain the needed reduction over a wide range of operating temperatures, more than one catalyst has to be used. The combinations of catalysts have been recently reviewed by Blanco *et al.* [6], who distinguishes two main types of systems: bifunctional catalysts, in which there is a cooperation of two catalytic species, and staging of two or more catalysts in line. Thus, the development of a multimetallic catalyst for improved performance over a wider temperature range is a worthwhile effort.

Table 1 Performance of Few Catalyst Systems Tested for NOx Reduction.

Ref	Catalyst	Conditions	Remarks
[4]	Cu & Pt/TiO_2	Real exhaust gas 1000 ppm NOx 260 ppm HC	Active for NOx reduction with diesel fuel as reductant. Stable with slight deactivation after 50 h in operation.
[11]	$[Fe(H_2O)]_{0.2}(VO)_{0.8}PO_4$	250-450°C $t=9x10^{-3}$ s 500 ppm CH_4	NO conversion by CH_4 reached up to 60 % with small N_2O production. H_2O could suppress N_2O formation.
[12]	Pd & Pt/ sulfated ZrO_2	350-500°C 150 ppm NOx 2,000 ppm CH_4	Reached over 50 % conversion over 100 h operation in 9 % water vapor and 3 ppm SO_2.
[7]	Cu-ZSM-5	200°-350°C 500 ppm NOx NH_3/NOx < 2.5	Active catalyst for SCR of NOx with NH_3. Slight deactivation after 100 h of operation.
[9]	Pd/ZrO_2	300-600°C 500 ppm NO 5,000 ppm CH_4	High activity for NO conversion with CH4. Amorphous zirkonium hydroxide was a more suitable starting material than crystalline ZrO_2.

3 NOx STORAGE AND REDUCTION CONCEPT (NSR)

One current approach of deNOx process is the so-called NOx storage and reduction (NSR) concept based on storage of NOx in the catalyst for relatively long lean periods until saturation followed by interruption by rich spikes [8,9]. During the rich periods, the NOx stored in the lean periods is decomposed and subsequently reduced to nitrogen. The catalysts most commonly used for NOx storage applications comprise combinations of noble meals for oxidation and reduction purposes and barium oxide/carbonate as the storage materials [13]. It has been reported that the nitrogen oxides are chemically bound as surface nitrates. Unfortunately, affinity for nitrate formation also entails affinity for sulphation, which will lead to deactivation of the NOx storage capacity if sulfur is present in the exhaust. Kabin *et al.* [3] found that the NOx storage capacity of model NSR catalysts was as a function of temperature, oxygen (O_2), carbon dioxide (CO_2) and reductant concentrations. Amberntsson *et al.* [13] examined the influence of O_2 and CO_2 on the NOx release step. They found that O_2 inhibits the NOx release process by raising the desorption temperature while CO_2 promotes NOx release by forming barium carbonate ($Ba(CO_3)$). The NOx release was also minimized when shorter lean periods were used (translated as reducing the amount of NOx stored) and when very rich purges were fed (translated as providing excess reductant) [3].

The most popular metals being investigated for NOx reduction process are noble metals particularly platinum, palladium and rhodium [8,13]. The metals seem to play several roles in the NOx storage and reduction cycles as well as for sulfur deactivation and for regeneration form the sulfur. Thus, it is of great importance to investigate their role in detail [8]. It was found that palladium-containing catalysts have a slightly higher NOx storage ability at lower temperatures compared to the platinum-loaded samples and that the NOx oxidation activity is much higher on platinum compared to palladium. The effect of addition of noble metals (palladium, platinum of rhodium) to a calcium oxide based NOx storage and reduction catalyst was studied by Amberntsson *et al.* [13]. It was reported that rhodium provides better NOx storage ability for a CaO/Al_2O_3 catalyst compared to platinum due to higher formation of NO_2. However, the thermodynamic equilibrium concentration of NO_2 was never reached due to reduction of NOx with the hydrocarbon. The main function of the metals during the rich period of the NOx storage reduction cycle is the ability to reduce NO. The main drawback for the successful and practical use for noble metals are their high cost, that will limit its use, especially in this waste abatement process. Thus, efforts toward finding alternative and potential metals among transition metals that are available at lower cost should be further explored. Encouraging results have been reported by Pisarello *et al.* [8] by using cobalt (Co), Seijger *et al.* [7] by using copper and Blanco et al. [6] by using manganese. Complementary studies in this area should be focused on the understanding of the roles and interaction of the metals during the rich and lean periods of NOx storage and reduction processes.

4 PARTICULATE MATTER (SOOT) REMOVAL

In diesel engines, soot particles are formed in the cylinder of the engines due to local shortage of oxygen [10,14]. The composition of diesel particulate depends on several factors such as engine load, speed and temperature [14]. Since NOx are formed in an oxygen-rich atmosphere at high temperatures and pressures, measures to reduce particulate mass emission will result in an increase in NOx emissions, and vice versa. This phenomenon is known as NOx-PM trade-off [7].

In a NSR application, soot is expected to cause serious deactivation to the catalyst. However, removing of soot from diesel engine exhaust gas is a challenging topic. The combination of a filter filled with oxidation catalysts appears to be the most plausible after-treatment technique to eliminate soot particles [8]. In this application, the soot-catalyst contact appears to be one of the most important problems to overcome [15]. Thus, something that is important in the catalyst formulation is to include active components with high mobility [2]. Any catalyst placed over the soot filter should possess high thermo-chemical stability and intrinsic oxidative properties to ignite reliably the soot as early as possible [14]. Potassium–loaded catalysts have been found to show high activity in soot combustion [2,8]. This metal can play the role due to its high mobility to consequently increase the effective contact between the oxidation catalyst and the soot particle [2]. The activity can be further improved by introducing barium as the promoter [8]. The contact between the soot and the catalyst strongly affects the reaction rate. By a proper combination of active metals, a catalyst suitable for the NSR process, while showing lower tendency to be deactivated by soot can be obtained.

5 STRUCTURED CATALYSTS

For a deNOx unit, pressure drop is a key issue [4,10]. In a car exhaust or a power plant flue gas system, the pressure drop should typically be below 10-20 mbar [7].

Additional demands comprise low sensitivity to dust and resistance to thermal shock. A suitable solution can therefore be provided by the implementation of a low-pressure drop structured catalyst packing. Structured packings, like ceramic and metal honeycombes and ceramic foams are gaining interest for application in low pressure drop reactors, membrane reactors and catalytic distillation units. Typical advantages of these open macroporous structures follow from their good internal accessibility due to their high porosity and low accumulation of dust due to the large size of the pores. These materials are also more abrasion resistant and have a high axial crushing strength. The specific surface area of most structured supports is below 1 m^2/g, which is too low for catalytic purposes. By washcoating with suitable microporous or mesoporous materials, the specific surface area can be enhanced up to about 40 m^2/g [7]. An active and stable NSR monolithic catalyst with soot oxidizing ability and low pressure drop should appear to be an ideal catalyst for the deNOx of a diesel exhaust gas. In fact, it is already close to a practical application for the pollution abatement in a real diesel exhaust system.

6 CONCLUSIONS

Despite providing fuel combustion efficiency and reliability in operation, diesel engine has many adverse environmental effects, particularly due to the emission of NOx and particulate matter in the form of soot. Selective catalytic reduction (SCR) of NOx is a practical and efficient method to remove NOx in diesel engine exhaust gases. The active phases for SCR catalysts are different metallic oxide such as oxides of Mn, Co, Cu and noble metals. The common catalyst supports being evaluated for this application are such as vanadia, titania, ceria, zirconia and lanthana. The reduction of NOx has been generally found to take place over as fairly narrow temperature range. An innovative method to treat NOx using a so-called NOx storage and reduction (NSR) has been recently introduced. The catalysts used for NOx storage step comprise combinations of noble meals for oxidation and reduction purposes and barium oxide/carbonate as the storage materials as the nitrogen oxides are chemically bound as surface nitrates. The NOx is then released from the catalyst when shorter lean periods were used while very rich purges of reductant is fed. During this stage, the NOx will be reduced to N_2. Potassium–loaded catalysts have been found to show high activity in soot combustion. This metal can play the role due to its high mobility to consequently increase the effective contact between the oxidation catalyst and the soot particle. The activity can be further improved by introducing barium as the promoter. The contact between the soot and the catalyst strongly affects the reaction rate. By a proper combination of active metals, a catalyst suitable for the NSR process, while showing lower tendency to be deactivated by soot can be obtained.

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UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
SERI AMPANGAN
PENYATA KUMPULAN WANG

TEMPOH BERAKHIR 30 APRIL 2007

DEV OF MONOLITHIC CATALYSTS FOR STORAGE & REDUCTION OF NITROGENT OXIDE (NOX

JUMLAH GERAN :-

NO PROJEK :-

PANEL :- J/PENDEK

PENAJA :- JANGKA PENDEK

Tempoh Projek:15/03/2005 - 14/03/2007

Vot	Peruntukan (a)	**Perbelanjaan sehingga 31/12/2006 (b)**	**Tanggungan semasa 2007 (c)**	**Perbelanjaan Semasa 2007 (d)**	**Jumlah Perbelanjaan 2007 (c + d)**	Jumlah Perbelanjaan Terkumpul (b+c+d)	**Baki Peruntukan Semasa 2007 (a-(b+c+d)**
11000: GAJI KAKITANGAN AWAM	3,083.10	2,764.15	0.00	0.00	0.00	2,764.15	318.95
21000: PERBELANJAAN PERJALANAN DAN SAR	2,000.00	2,861.40	0.00	0.00	0.00	2,861.40	(861.40)
23000: PERHUBUNGAN DAN UTILITI	200.00	0.00	0.00	0.00	0.00	0.00	200.00
24000: SEWAAN	500.00	0.00	0.00	0.00	0.00	0.00	500.00
26000: BAHAN MENTAH & BAHAN UNTUK PENY	3,000.00	0.00	0.00	0.00	0.00	0.00	3,000.00
27000: BEKALAN DAN ALAT PAKAI HABIS	6,000.00	8,837.93	2,000.00	0.00	2,000.00	10,837.93	(4,837.93)
29000: PERKHIDMATAN IKTISAS & HOSPITALITI	5,208.90	3,044.00	1,000.00	0.00	1,000.00	4,044.00	1,164.90
	19,992.00	17,507.48	3,000.00	0.00	3,000.00	20,507.48	(515.48)
Jumlah Besar	19,992.00	17,507.48	3,000.00	0.00	3,000.00	20,507.48	(515.48)

JABATAN BENDAHARI
UNIT KUMPULAN WANG AMANAH
UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
SERI AMPANGAN
PENYATA KUMPULAN WANG
TEMPOH BERAKHIR 31 JANUARI 2007

28 FEB 2007

DR AHMAD ZUHAIRI ABDULLAH

304.PJKIMIA.6035133

DEV OF MONOLITHIC CATALYSTS FOR STORAGE & REDUCTION OF NITROGENT OXIDE (NOX)

JUMLAH GERAN :-

Tempoh Projek:15/03/2005 - 14/03/2007

NO PROJEK :-

PANEL :- J/PENDEK

PENAJA :-

Vot		Peruntukan (a)	Perbelanjaan sehingga 31/12/2006 (b)	Tanggungan semasa 2007 (c)	Perbelanjaan Semasa 2007 (d)	Jumlah Perbelanjaan 2007 (c + d)	Jumlah Perbelanjaan Terkumpul (b+c+d)	Baki Peruntukan Semasa 2007 (a-(b+c+d)
11000	GAJI KAKITANGAN AWAM	3,083.10	2,764.15	0.00	0.00	0.00	2,764.15	318.95
21000	PERBELANJAAN PERJALANAN DAN SARAHI	2,000.00	2,861.40	0.00	0.00	0.00	2,861.40	(861.40)
23000	PERHUBUNGAN DAN UTILITI	200.00	0.00	0.00	0.00	0.00	0.00	200.00
24000	SEWAAN	500.00	0.00	0.00	0.00	0.00	0.00	500.00
26000	BAHAN MENTAH & BAHAN UNTUK PENYELE	3,000.00	0.00	0.00	0.00	0.00	0.00	3,000.00
27000	BEKALAN DAN ALAT PAKAI HABIS	6,000.00	8,837.93	2,000.00	0.00	2,000.00	10,837.93	(4,837.93)
29000	PERKHIDMATAN IKTISAS & HOSPITALITI	5,208.90	3,044.00	1,000.00	0.00	1,000.00	4,044.00	1,164.90
		19,992.00	17,507.48	3,000.00	0.00	3,000.00	20,507.48	(515.48)
	Jumlah Besar	19,992.00	17,507.48	3,000.00	0.00	3,000.00	20,507.48	(515.48)

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