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An investigation into catalysts to improve low temperature performance in the selective catalytic reduction of NO with NH₃

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Selective catalytic reduction with NH₃ is considered one of the most effective technologies controlling NO_x emission. Metal Fe-based catalysts were used in the investigation to improve low temperature performance of NO_x conversion. The temperature range studied was between 150°C and 350°C in increments of 50°C. The honeycomb catalysts were prepared by an impregnation method. The study also included characterisation of catalysts by BET, XRD, H₂-TPR and XPS methods.

It was found that an increase in metal Fe content from 2 to 6% wt offered an improvement in the catalytic performance. However, a further increase in Fe content resulted in a decrease in its performance. More than 90% NO_x conversion rate could be achieved over the Fe-based honeycomb catalyst at a low temperature by doping with different weights of Ni and Zr metals. Amongst all the catalysts studied, the mixed metal catalyst of Fe-Ni-Zr was the one with most potential. This was because of its higher NO_x conversion rate at a low temperature and also because of its wider operating temperature window. The effect of gas hourly space velocity (GHSV) was also investigated and the results showed that as GHSV increased, the reduction of NO_x decreased.

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Youhong Xiao is a PhD student in the Department of Naval Architecture & Marine Engineering at the Universities of Glasgow and Strathclyde. His researches have identified catalysts that offer improved performances in SCR to reduce NO_x from marine diesel engines. He is also a lecturer at Harbin Engineering University.

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INTRODUCTION

Since the 1970s, diesel engines have dominated the marine market for the provision of propulsion and electrical power. However, international shipping is considered to be a significant source of air pollution. NO_x emissions originating from shipping have been estimated to be about 10Mt per annum; approximately 14% of total global NO_x emissions from fossil fuels.¹ They contribute to the formation of photochemical smog and acid rain, which produces eutrophication (ie, acidification) of lakes and rivers.

There is worldwide interest in developing efficient catalysts for the removal of NO_x from diesel engine exhaust systems. Selective catalytic reduction (SCR) with ammonia is a well-proven technique for NO_x removal in diesel engines. The principal engine manufacturers provide SCR catalysts based on the TiO₂/V₂O₅ and urea solution with efficiencies above 95%.²

SCR catalysts used in industrial practice are based on TiO₂, with vanadium oxide as the catalytic active phase. WO₃ and MoO₃ have been reported to be used as promoters.^{2,3} The range of operating temperatures of these catalysts is 300°C to 400°C.

For large slow speed diesel engines, the exhaust gas temperatures are often below 300°C after the turbocharger especially at part load. Gas re-heating is often required to ensure high efficiency of the catalytic conversion.

Because of this, there has been a strong interest in developing SCR catalysts that activate at a temperature lower than 300°C. Some transition-metal-contained catalysts have been investigated to improve the low temperature performance of an SCR, such as chromic,⁴ NiSO₄/Al₂O₃,⁵ MnOx/Al₂O₃,⁶ V₂O₅/carbon-coated monoliths,⁷ iron-silica aerogels⁸ and MnOx/NaY.⁹ The use of these catalysts has shown some improvement in SCR activity at temperatures below 200°C.

Iron-based catalysts have been extensively used in several processes related to NO_x elimination, mainly due to their low cost compared with that of noble metals and their good performance with different reducing agents. It has been reported that Fe₂O₃,¹⁰⁻¹⁶ Fe containing oxides¹⁷⁻¹⁹ and Fe-exchanged materials²⁰⁻²⁴ have greater SCR activity than other types of catalyst. The process of selective catalytic reduction of NO_x at low temperature with ammonia has been investigated with metal Ni²⁵⁻²⁸ and the results show that Ni is efficient for the reduction of NO_x. ZrO₂ has better thermal stability and sulphur resistance.²⁹ can be very effective for NO_x reduction^{30,31} ZrO₂ is seldom used as the catalyst for SCR, but reports^{32,33} have shown that a Zr catalyst is durable and highly active for NO_x reduction.

With fixed-bed catalysts, large volumes of pellets, or granules, may cause high flow resistance and plugging problem due to particulates being carried over in flue gas

stream. In contrast, honeycomb catalysts produce low pressure drops, high surface areas, superior abrasive wear resistance and low tendency to fly ash plugging.⁴³⁻⁴⁵ For these reasons, the honeycomb vanadia-titania catalyst has been used in industry to remove NO_x from flue gas.⁴⁶ Based on their successful applications, the paper presents a study on the use of ceramic honeycomb structured catalysts. Fe, Fe-Ni, Fe-Ni-Zr catalysts are used to improve the low temperature conversion rate of NO_x.

EXPERIMENT

Catalyst preparation

In the laboratory test, a ceramic honeycomb substrate with a chemical composition of 2MgO-2Al₂O₃-5SiO₂ was cut into small columns 40mm in length and 8mm in diameter. After pre-treatment with a 40% nitric acid solution, the chosen nitrates were coated to the ceramic honeycomb substrates by an impregnation method. It has been reported that the acid treatment of the substrate exhibits an increased surface area and improved dispersion of active components.³⁴ The catalysts, eg, substrates coated with metal oxides were tested and analysed, including characterisation examination of the mixed oxides catalysts using X-Ray Diffraction (XRD), Temperature Programme Reduction-H₂ (TPR-H₂) and X-laboratory ray Photoelectron Spectroscopy (XPS) methods. The objective of these analyses was to establish the influence of meso-porosity on the performance of the catalysts prepared.

In this study, three types of catalyst – Fe, mixtures of Fe-Ni, and Fe-Ni-Zr were studied. The catalysts Fe, Ni and Zr were obtained from the mixture of the compounds of Fe(NO₃)₃, Ni(NO₃)₂ and Zr(NO₃)₄ solutions. Firstly, the ceramic honeycomb substrate was immersed in a nitric acid solution at a mass concentration of 40% for about 8 hours to clean its surface. Then the substrate was washed to pH = 7 with distilled water. The treated honeycomb substrate was then dried at 150°C for 8 hours before it was immersed into the aqueous solution of nitrates for a day. Finally, the substrate – saturated by catalyst – was dried at 250°C for 8 hours and calcined in the air at 600°C for 8 hours.

Catalytic activity tests

In the laboratory scale experiment, the honeycomb substrates – coated with different metallic oxides (shown in Table 1) – were tested in a selective reduction reactor under

Catalyst	BET (m ² /g)
Fe(4)Ni(0)Zr(0)	131.0
Fe(6)Ni(0)Zr(0)	134.6
Fe(8)Ni(0)Zr(0)	114.1
Fe(6)Ni(1)Zr(0)	185.3
Fe(6)Ni(2)Zr(0)	192.2
Fe(6)Ni(2)Zr(1)	256.2
Fe(6)Ni(2)Zr(2)	252.4

Table 1: BET Surface of catalysts

conditions close to an isothermal axial profile and at various reaction temperatures. The support catalysts are presented by Fe(a)Ni(b)Zr(c), where (a), (b) and (c) represent the weight percentages of Fe, Ni and Zr in the catalysts including the weight of the substrate. The catalyst substrate was weighed to measure the amount of catalyst coated on it. If the quantity of the coated catalysts was not satisfactory, the impregnating process was repeated.

Description of test rig

As shown in Fig 1, urea solution is used to provide gas phase ammonia that is employed by most SCR systems as the reducing agent. The ammonia generated from urea is either anhydrous or aqueous and is vaporised before being supplied to the reactor (SCR).

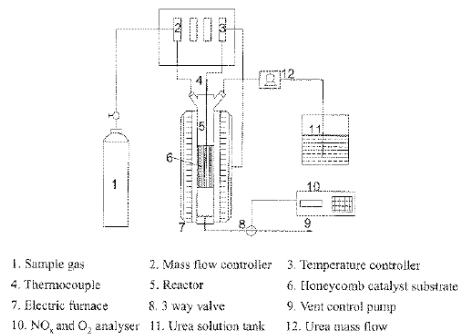
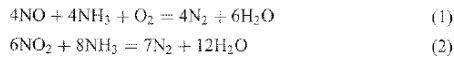


Fig 1: Schematic diagram of testing rig

In the presence of a suitable catalyst, the following processes will take place inside the reactor:



NO_x in diesel exhaust gases is typically over 95% of NO and less than 5% of NO₂. Therefore, the main reaction of an SCR with ammonia is represented by equation (1), which indicates that one mole of NH₃ is required to remove one mole of NO. The presence of a catalyst lowers the required activation energy for the reduction and increases the NO conversion rate.

A laboratory-scale stainless steel fixed-bed reactor (with inner diameter of 10mm and a length of 200mm) was used in the experiment to investigate the activity of each chosen synthetic catalyst in reaction with NH₃ at atmospheric pressure. A catalyst substrate of 8mm diameter and 40mm in length was installed inside the reactor for the catalytic testing, as shown in Fig 1. The reaction temperature was maintained by a programmed temperature controller at 150°C to 350°C with increments of 50°C. Every measurement temperature was maintained for 30min before sampling was taken.

Sample gas was prepared to simulate an engine exhaust gas. This comprised 1200 ppm NO, 2% by vol. of O₂ balanced by N₂, and was fed into the reactor at a flow rate of 180 ml/min controlled by a flowmeter. 10% by mass of urea solution was used to provide the required NH₃. The urea solution was injected into the reactor at a flow rate of 0.015 ml/min. It vaporised inside the reactor due to heating and released NH₃ to perform the chemical reactions presented in equation 1 and 2.

A gas analyser, model-FGA-4100, was used to measure the concentration of NO and O₂ before and after the reactor. The reaction results were evaluated in terms of NO_x conversion rate, ie, the ratio of NO_x converted via the reactor to the total NO_x level before the reactor.

RESULTS AND DISCUSSION

SCR performance with different catalysts

Effect of Fe catalyst

Fig 2 shows the results of NO_x conversion rate with Fe as the catalyst. The reaction temperature was from 150 to 350°C. Other test conditions were GHSV= 12000 h⁻¹, NO_x = NH₃ =1200 ppm, 2.0 vol. % O₂, N₂ balance.

The balance between dispersion and loading of metal catalysts is a vital factor and affects the catalytic activity directly. Increasing the catalyst loading will result in an aggregation of the catalyst and a decrease in the dispersion. Although low loading is beneficial for a good dispersion, it results in a low number of the active sites over the support and consequently the catalytic performance will be reduced. NO_x conversion rates with different Fe loadings are shown in Fig 2.

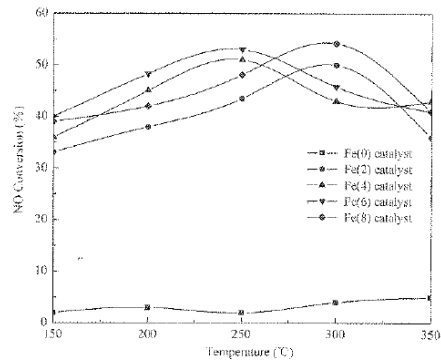


Fig 2: Catalytic performance with Fe catalyst

It was found that at 250°C, the NO_x conversion rate increased as the Fe loading increased and reached its maximum at 53% when loading was 6%wt. When the Fe content was 8%wt, the NO_x conversion rate was reduced to 43%.

A possible reason for the drop of NO_x conversion rate

at a high loading is there might be a clustering of Fe species when its loading is high. This is consistent with the results shown in Table 1, where the BET surface at 8 %wt. of Fe catalyst was significantly small compared with that at 6%wt.

Therefore, the catalysts with 6%wt Fe content were selected for the subsequent experimental work. Fig 2 also shows that the low temperature performance of the catalytic reduction was improved significantly.

Effect of Fe doped with Ni and Zr

Fig 3 represents NO conversion rates with different mixtures of catalysts as a function of reaction temperatures that varied from 150 to 350°C. Other test conditions were GHSV = 12000 per hour, NO_x = NH₃ = 1200 ppm, 2.0vol% O₂, N₂ balance.

Based on the catalytic results of different Fe loading catalysts, different loadings of metal Ni and Zr were doped into the 6%wt Fe catalyst. As shown in Fig 3, the combination of iron-nickel- zirconium (Fe-Ni-Zr) offered the highest reaction activity amongst the catalysts studied at the full temperature measurement range, with the maximum NO_x conversion rate of 95.1% at a temperature of approximately 250°C. The activity of Fe itself was the lowest, reaching its maximum NO_x conversion rate of 52% at 250°C. It was observed that the order of activeness of the catalysts for NO_x conversion was Fe(6)Ni(2)Zr(2) > Fe(6)Ni(2)Zr(1) > Fe(6)Ni(2) > Fe(6)Ni(1) > Fe(6).

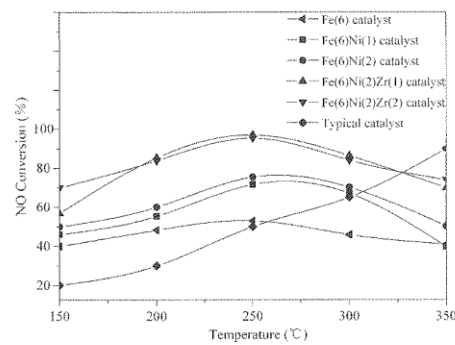


Fig 3: NO_x reduction rate with different mixtures of catalysts

The activity of Fe catalyst was substantially lower than that of other Fe based oxides catalysts. Thus, iron alone was unsuitable due to its low activity. The catalysts iron-nickel (Fe-Ni) have an improved activity compared with Fe and the NO conversion increased more rapidly when the temperature was over 200°C. but it then dropped again when the temperature was over 300°C. However, the activity of Fe-Ni catalyst was lower than 50% when the temperature was higher than 300°C. The Fe-Ni catalyst with 2%wt Ni had an increased catalytic performance compared with the

Fe-Ni catalyst with 1%wt Ni. The effect of increasing Ni on the NO_x conversion was not obvious. Based on this, the metal Zr was introduced to promote the NO_x conversion rate.

After the introduction of Zr, it was found that the Fe-Ni-Zr catalyst had superior activity during the whole temperature window, especially in the lower temperature range. But the NO_x conversion of the catalysts dropped slightly when the temperature was over 300°C.

For the purposes of comparison, a widely commercial catalyst (V₂O₅/WO₃)³⁷ in an SCR system was also presented in Fig 3, where it exhibited a high conversion rate at temperatures above 300°C, However, its low NO_x conversion rate was poor.

According to the catalytic results of Fe(6)Ni(2)Zr(2), the catalyst can enhance the NO conversion dramatically at a low temperature.

Effect of gas hourly space velocity (GHSV) on NO conversion

Fig 4 shows catalytic performance of 6%wt Fe catalyst doped with Ni and Zr as a function of GHSV at a temperature of 250°C. Other test conditions were NO_x = NH₃ = 1200 ppm, 2.0 vol % O₂, N₂ balance.

Space velocity is defined as the volume ratio of gas flow rate relative to the catalyst volume flow rate, expressed 'per-hour'.

At a constant gas flow rate, space velocity is inversely proportional to catalyst volume such that decreasing catalyst volume corresponds to increasing space velocity.

Typically, an increase in the space velocity decreases the NO_x conversion for most catalysts since the net residence time of the gas species over the surface of the catalyst decreases. To some extent, temperature plays a role in determining the degree to which space velocity affects the NO_x conversion.³⁷

According to the above results, the temperature of best catalytic performance of the investigated catalysts was at 250°C. Thus this temperature was selected to investigate the effort of GHSV on NO_x conversion.

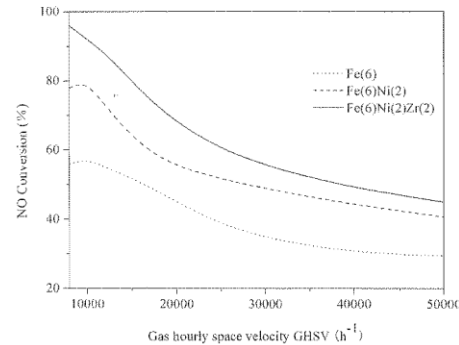


Fig 4: NO reduction rate change with GHSV

Fig 4 shows the effect of space velocity on the conversion rate of NOx. The NOx conversion rate is high when the space velocity is low. This is because a low space velocity property is beneficial for the diffusion, adsorption and reaction of the reactants. It also promotes the desorption and diffusion of reaction products. When the space velocity is high, the contacting time of reactants and catalysts becomes less. This will result in the contacting time of the reactants and the catalyst being insufficient for the catalytic reaction.

Consequently, the NOx conversion rate drops quickly. Therefore it is beneficial to decrease the space velocity for the NOx conversion. However, to achieve a low space velocity for a given engine exhaust system, the size (cross section area and/or length) of the catalyst converter will have to be increased accordingly.

X-ray diffraction

Fig 5 shows the XRD patterns of the pure honeycomb ceramic and that supported with Fe₂O₃, NiO, ZrO or a mixture of different oxides. All the samples exhibited the typical peaks of the ceramic honeycomb, indicating that the structure of the ceramic honeycomb remained intact after the treatment. Compared with the intensity of the XRD peaks of the bare ceramic honeycomb, the intensity of the peaks of the catalysts under investigation decreased. The reason for this is that the addition of metals caused the dispersion of the elements on the ceramic honeycomb.

As shown in Fig 5, typical lines of Fe catalyst were detected at 23.8°, 33.3°, 35.2°, 49.5° and 64.2° (2θ). These lines were due to the strongest lines of Fe₂O₃.

The additional lines appear in the XRD pattern of Fe-Ni catalyst at 43.3, 43.5, and 62.7° (2θ). These lines detected to be NiO. In the catalysts of Fe-Ni catalysts, the diffraction peaks of Fe₂O₃ were observed the same phase as Fe catalyst.

The diffractions at 30.2° and 60° (2θ) due to zirconia

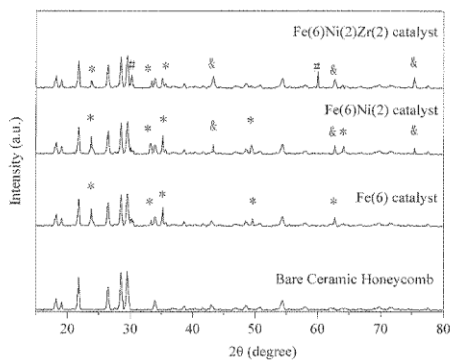


Fig 5: XRD patterns of bare ceramic honeycomb, Fe(6) catalyst, Fe(6)Ni(2) catalyst and Fe(6)Ni(2)Zr(2) catalyst. (*: Fe₂O₃; #: NiO; #: ZrO₂)

phase^{31,32} were clearly observed on the Fe-Ni-Zr catalyst sample. It was found that some of the lines of Fe disappeared and the intensity of some Fe₂O₃ decreased. This suggested that the Zr doping caused the dispersion of Fe and they interacted strongly.

Temperature programme reduction

Temperature programmed reduction (TPR) was used to characterise the ceramic honeycomb supported catalysts as shown in Fig 6. During the TPR process, the reduction sequence of iron oxide is as following Fe₂O₃ → Fe₃O₄ → FeO → Fe.

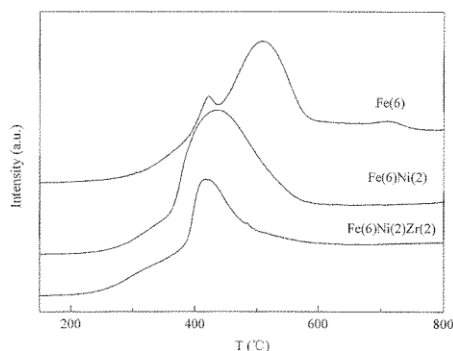


Fig 6: TPR profiles of Fe(6), Fe(6)Ni(2) and Fe(6)Ni(2)Zr(2) catalyst

From various H₂-TPR studies of Fe catalyst³⁸⁻⁴⁰ there is general agreement that the peak for hydrogen consumption – centred at around 410°C – can be attributed to the reduction of the Fe₂O₃ to Fe₃O₄ in Fe species. The second reduction peak was assigned to the reduction of Fe₃O₄ to Fe⁰. But according to³⁰ there have two reduction peaks attributed to the reduction of Fe₂O₃ small nanoclusters to FeO, and then of FeO to Fe⁰. Some theories suggest that the two processes of the reduction from Fe₃O₄ into Fe and from FeO into Fe⁰ are completed by one step. So the two reduction peaks should be one. Therefore there is only one reduction peak of hydrogen consumption.

A high temperature reduction peak and a weak temperature peak were observed in the Fe-Ni and Fe-Ni-Zr catalysts. The high peak should be the reduction peak of the Fe₂O₃ to Fe₃O₄ and the low peak could be the reduction of NiO species centred at about 350°C. It was found that Zr reduction peak was not observed in Fe-Ni-Zr catalyst and Ni reduction peak was weak in the catalysts Fe-Ni and Fe-Ni-Zr catalysts. The reason is that the doping of Ni and Zr changed the structure of pure iron catalyst, and the Ni, Zr interact with Fe and substrate strongly. Meanwhile the high peak moved to the lower temperature, and this lead to the decreasing of reduction reaction energy and made the re-

duction reaction much easier than with the iron catalyst and improved the effectiveness of the catalytic reaction.

X-ray photoelectron spectroscopy

Fig 7 shows the XPS spectrum of Fe 2p_{3/2} on the Fe, Fe-Ni and Fe-Ni-Zr catalyst.

A broad XPS band centred at 711.7 eV was observed on the sample of Fe and Fe-Ni catalyst. This value is close to the binding energy of 2p_{3/2} of iron in Fe₂O₃,³ indicating that iron in Fe and Fe-Ni catalysts was mainly present as a valence of +3. As a general rule, if the formation of an interfacial oxide takes place, some modifications of the X-ray photoemission spectrum are expected to have an energy shift and/or the presence of satellite peaks.¹ This can be seen in Fig 7. With the addition of Zr, the binding energy value was increased from 711.3 eV to 712 eV and the intensity of the peak values for this oxidation state was decreased dramatically.

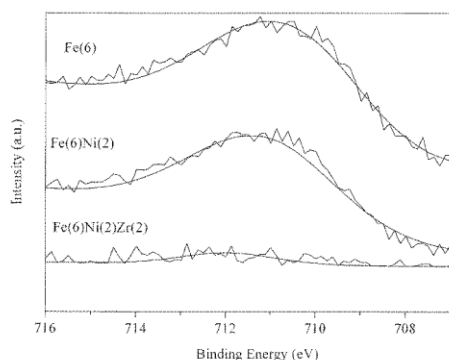


Fig 7: XPS spectra of Fe 2p_{3/2} on Fe(6), Fe(6)Ni(2) and Fe(6)Ni(2)Zr(2) catalyst

Fig 8 illustrates Ni 2p XPS spectrum on both Fe-Ni and Fe-Ni-Zr catalyst. The presence of peak values at 856.0 and 862.5 eV of Fe-Ni catalyst is due to the binding energy of Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, since the nickel is in oxidation state +2. For catalyst of Fe-Ni-Zr, the peaks at 856.8 and 863.8 eV are attributed to the binding energies of Ni²⁺ 2p_{3/2} and Ni²⁺ 2p_{1/2}, respectively. However, with the addition of Zr, the maximum intensity decreased. Furthermore, there were two peaks; each appeared on the higher binding energy side of Ni²⁺ 2p_{3/2} and Ni²⁺ 2p_{1/2}, respectively. Although the exact phase of these peaks was unknown, it is possible to consider that they were the mixture of iron oxides and nickel or zirconium oxides.

Fig 9 shows the binding energy of the Zr 3d photoelectron reach its peaks at 182.3 and 184.5eV for Zr 3d_{5/2} and Zr 3d_{3/2} elements, respectively, due to existence of Zr⁺⁴ in the catalyst. The result agrees with the results of XRD.

According to the results of XRD, TPD and XPS, it was

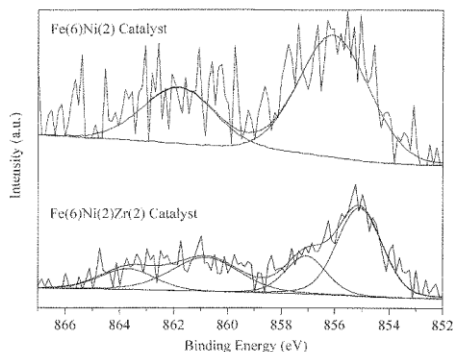


Fig 8: XPS spectra of Ni 2p on Fe(6)Ni(2) and Fe(6)Ni(2)Zr(2) catalyst

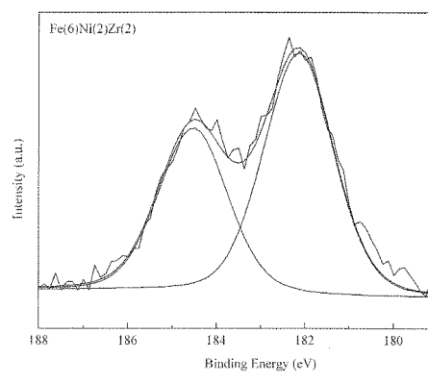


Fig 9: XPS spectrum of Zr 3d on Fe(6)Ni(2)Zr(2) catalyst

reasonable to conclude that the doping Ni can improve the activity of Fe catalyst and NiO played a preponderant role in the SCR reaction. The addition of Zr helped to stabilise and disperse NiO clusters, preventing the known affinity of nickel to form phyllosilicates in silica-based surfaces, and enhance the activity of the Fe-Ni catalyst.

CONCLUSIONS

The paper has presented the results of an investigation into the NO_x conversion rate of Fe-based catalysts at a low temperature range, using ceramic honeycomb as the substrate. The study has revealed properties and their association with the NO_x reduction rate of the catalysts.

Conclusions have been reached that compared with the current commonly used catalysts; Fe-based catalysts have a much higher conversion rate of NO_x in an SCR under the

temperature range of 150°C to 350°C. Results have shown that amongst the catalysts studied, the catalyst of combined Fe-Ni-Zr is the most active one for the SCR of NOx by NH₃. Fe₂O₃ is the main active specie in the catalyst, while the addition of NiO and ZrO₂ is important to improve activities of the catalysts. Tests have found that the catalysts offer the highest NOx reduction rate when the loading ratio of the catalysts is 6% wt. of Fe, 2% wt. of Ni and 2% wt. of Zr.

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