REMOVAL OF VOLATILE ORGANIC COMPOUND (VOC) FROM AIR USING ZEOLITE BASED ADSORPTION-CATALYTIC COMBUSTION SYSTEM

WONG CHENG TENG

UNIVERSITI SAINS MALAYSIA

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REMOVAL OF VOLATILE ORGANIC COMPOUND (VOC) FROM AIR USING ZEOLITE BASED ADSORPTION-CATALYTIC COMBUSTION SYSTEM

by

WONG CHENG TENG

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March 2007
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LIST OF SYMBOLS

A  pre-exponential factor
A_s  cross sectional area of the adsorbent bed (m^2)
b  Langmuir constant
C  the average adsorbed-phase concentration or VOC concentration (mol/m^3)
C*  surface concentration (mol/m^3)
C_e  gas concentration at equilibrium (mol/m^3)
C_n  number of carbon atoms in one molecule of VOC used
C_o  initial concentration (mol/m^3)
D_c  micropore diffusion coefficient (cm^2/s)
D_e  effective diffusion coefficient (cm^2/s)
D_L  dispersion coefficient (m^2/s)
D_m  molecular diffusion coefficient (cm^2/s)
D_s  surface diffusion coefficient (cm^2/s)
E_a  apparent activation energy
F_{CO2}  molar flow rate of carbon dioxide in the product stream (mol/s)
F_{CO2}  molar flow rate of carbon dioxide in the product stream (mol/s)
F_{VOC, in}  molar flow rate of VOC in feed stream (mol/s)
F_{VOC, in}  molar flow rate of VOC in feed stream (mol/s)
F_{VOC, out}  molar flow rate of VOC in product stream (mol/s)
F_{VOC, out}  molar flow rate of VOC in product stream (mol/s)
K  equilibrium constant
k_a  adsorption rate constant
<table>
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<tr>
<td>$k_d$</td>
<td>desorption rate constant</td>
</tr>
<tr>
<td>$k_f$</td>
<td>interphase mass transfer coefficient (m/s)</td>
</tr>
<tr>
<td>$k_{m}$</td>
<td>mass transfer coefficient (s$^{-1}$)</td>
</tr>
<tr>
<td>$k_p$</td>
<td>intrapellet mass transfer coefficient (s$^{-1}$)</td>
</tr>
<tr>
<td>$k_s$</td>
<td>reaction rate constant</td>
</tr>
<tr>
<td>$k_s'$</td>
<td>pseudo first order reaction constant</td>
</tr>
<tr>
<td>$L$</td>
<td>length of adsorbent bed (m)</td>
</tr>
<tr>
<td>$m, n$</td>
<td>reaction order</td>
</tr>
<tr>
<td>$m_e$</td>
<td>mass of VOC adsorbed at equilibrium (mg)</td>
</tr>
<tr>
<td>$MW$</td>
<td>molecular weight (g/mol)</td>
</tr>
<tr>
<td>$N_{\text{final}}$</td>
<td>moles of VOC present after the reaction is completed.</td>
</tr>
<tr>
<td>$N_{\text{initial}}$</td>
<td>moles of VOC present initially</td>
</tr>
<tr>
<td>$P_o$</td>
<td>partial pressure of oxygen (atm)</td>
</tr>
<tr>
<td>$P_v$</td>
<td>partial pressure of considered VOC (atm)</td>
</tr>
<tr>
<td>$Q$</td>
<td>inlet volumetric flow rate (ml/h)</td>
</tr>
<tr>
<td>$q$</td>
<td>mole of adsorbate adsorbed per unit mass of adsorbent (mg/g)</td>
</tr>
<tr>
<td>$q_e$</td>
<td>equilibrium adsorption capacity (mg/g)</td>
</tr>
<tr>
<td>$q_{\text{max}}$</td>
<td>maximum adsorbed phase concentration (mol/kg)</td>
</tr>
<tr>
<td>$R$</td>
<td>ideal gas constant (8.3145 J/mol.K)</td>
</tr>
<tr>
<td>$R_c$</td>
<td>radius of microparticle (m)</td>
</tr>
<tr>
<td>$r_o$</td>
<td>mean pore radius (m)</td>
</tr>
<tr>
<td>$R_p$</td>
<td>equivalent radius of pellet (m)</td>
</tr>
<tr>
<td>$S$</td>
<td>conversion factor between solid and gas phase</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>$t$</td>
<td>time (s)</td>
</tr>
<tr>
<td>$u$</td>
<td>superficial velocity (m/s)</td>
</tr>
<tr>
<td>$V_{\text{cat}}$</td>
<td>the volume occupied by the catalyst bed (ml)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
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<tr>
<td>$V_p$</td>
<td>volume of the pellet (m$^3$)</td>
</tr>
<tr>
<td>$W$</td>
<td>weight of adsorbent (g)</td>
</tr>
<tr>
<td>$W_{cat}$</td>
<td>weight of catalyst used (g)</td>
</tr>
<tr>
<td>$X_{VOC}$</td>
<td>VOC conversion</td>
</tr>
<tr>
<td>$(-r_v)$</td>
<td>rate of reaction (mol/h.g$_{cat}$)</td>
</tr>
<tr>
<td>$\Delta G^o$</td>
<td>Gibbs free energy (kJ/mol)</td>
</tr>
<tr>
<td>$\Delta H^o$</td>
<td>Enthalpy change (kJ/mol)</td>
</tr>
<tr>
<td>$\Delta S^o$</td>
<td>Entropy change (J/mol)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>bed voidage</td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
<td>porosity of particle</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>density of adsorbent (g/m$^3$)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>root mean square error</td>
</tr>
<tr>
<td>$\theta$</td>
<td>surface coverage of VOC</td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>density of bed (g/m$^3$)</td>
</tr>
<tr>
<td>$\tau_{p,s}$</td>
<td>tortuosity, pore, surface</td>
</tr>
</tbody>
</table>
LIST OF ABBREVIATIONS

AgY(IE) Silver-loaded Y zeolite using ion exchange method
AgZSM-5(IE) Silver-loaded ZSM-5(IE) using ion exchange method
AgY(IM) Silver-loaded Y zeolite using impregnation method
AgZSM-5(IM) Silver-loaded ZSM-5(IE) using impregnation method
a.u. Arbitrary unit
ANOVA Analysis of variance
ASTM American Society for Testing and Materials
BA Butyl acetate
BDR Basic dynamical reaction
CCD Central composite design
DOE Design of experiments
EDX Energy dispersive X-ray
EPA U.S. Environmental Protection Agency
FAU Faujasite
FID Flame ignition detector
FTIR Fourier transformed infra red
GC Gas chromatograph
GHSV Gas hourly space velocity
HAP Hazardous air pollutant
ID Inner diameter
IM Incipient wetness impregnation
IE Ion exchange
<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>ICP</td>
<td>Inductive couple plasma</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>LEL</td>
<td>Lower explosive limit</td>
</tr>
<tr>
<td>LDF</td>
<td>Linear driving force</td>
</tr>
<tr>
<td>MEK</td>
<td>Methyl ethyl ketone</td>
</tr>
<tr>
<td>MFI</td>
<td>Mobil Five</td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl isobutyl ketone</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>Oxides of nitrogen</td>
</tr>
<tr>
<td>OD</td>
<td>Outer diameter</td>
</tr>
<tr>
<td>SE2</td>
<td>Secondary electron detector</td>
</tr>
<tr>
<td>QBSD</td>
<td>Quantum back scattered electron detector</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>RSM</td>
<td>Response surface methodology</td>
</tr>
<tr>
<td>scfm</td>
<td>Standard cubic feet per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature Pressure</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Zeolite Socony Mobil Five</td>
</tr>
</tbody>
</table>
PENYINGKIRAN SEBATIAN ORGANIK MERUAP (VOC) DARI UDARA MENGGUNAKAN SISTEM PENJERAPAN-PEMBAKARAN BERMANGKIN BERASASKAN ZEOLIT

ABSTRAK

Pembangunan kaedah termaju dalam proses penyingkirkan sebatian organic meruap (VOC) yang terdiri daripada unit penjerapan diikuti oleh unit pembakaran bermangkin telah dicadangkan dalam kajian ini. Dua zeolit hindar air, bernama HY (SiO₂/Al₂O₃=80) dan ZSM-5 (SiO₂/Al₂O₃=240) dipilih sebagai bahan penjerap. Logam perak telah dimuatkan ke atas bahan penjerap ini untuk digunakan sebagai mangkin bagi pembakaran bermangkin VOC. Zeolit bermuatan perak telah diuji dengan butil asetat (BA) sebagai model sebatian organic meruap bagi system penjerapan dan pembakaran bermangkin.

Kaedah penukaran ion (IE) dan impregnasi (IM) telah digunakan untuk menyediakan zeolit bermuatan perak. Zeolit bermuatan perak yang disediakan dengan kaedah penyediaan impregnasi menunjukkan prestasi yang tidak memuaskan dalam proses penjerapan. Keputusan penjerapan menunjukkan muatan-jerap VOC yang lemah dan masa bulus yang awal. AgY(IE) menunjukkan muatan-jerap VOC yang paling tinggi dan bahan penjerap ini memberikan tempoh khidmat yang paling lama jika dibandingkan dengan AgZSM-5(IE). Kehadiran wap air di dalam suapan merendahkan muatan-jerap VOC pada AgY(IE) disebabkan oleh persaingan penjerapan dengan wap air pada tapak aktif. Namun, muatan-jerap VOC pada AgZSM-5(IE) tidak dipengaruhi oleh kehadiran wap air. Rekabentuk komposit berpusat (CCD) telah digunakan untuk mengkaji kesan tiga parameter pengendalian yang penting (kepekatan VOC suapan, kelembapan nisbi, halaju ruang jaman gas (GHSV)) bagi proses penjerapan. Kaedah
sambutan permukaan (RSM) digunakan untuk mendapatkan keadaan pengendalian yang optimum bagi proses penjerapan.

AgY(IE) dan AgZSM-5(IE) diuji untuk mendapatkan data muatan-jerap pada suhu yang berlainan. Satu model matematik telah digunakan untuk menilai sifat termodinamik bersama dengan garis sesuhi Langmuir untuk penjerapan butil asetat ke atas AgY(IE) dan AgZSM-5(IE). Parameter-parameter yang diperoleh daripada model dinilai dan digunakan untuk meramal penjerapan garis sesuhi dan lengkung bulus di bawah pelbagai keadaan yang berlainan.

Prestasi mangkin zeolit bermuatan perak dalam pembakaran VOC telah dikaji dengan tujuan untuk membangunkan mangkin yang aktif, berkememilihkan terhadap hasil pembakaran lengkap serta stabil. Aktiviti mangkin dikaji dengan menggunakan reaktor yang dikendalikan pada GHSV = 15,000 h⁻¹, suhu tindakbalas 150° hingga 500°C, dengan kepekatan VOC suapan pada 1000ppm. AgY(IE) dan AgZSM-5(IE) menunjukkan prestasi yang tinggi dalam pembakaran butil asetat di mana penukaran menyeluruh butil asetat dicapai pada suhu di bawah 400°C. Rekabentuk komposit berpusat (CCD) telah digunakan untuk mengkaji kesan tiga parameter pengendalian yang penting (kepekatan VOC, suhu tindakbalas, GHSV) bagi proses pembakaran bermangkin. Kaedah sambutan permukaan (RSM) digunakan untuk mendapatkan keadaan pengendalian yang optimum bagi proses ini.

Data yang diperoleh daripada pembakaran butil asetat telah dipadankan dengan satu model mengikut persamaan hukum kuasa. Tertib tindakbalas, \( n \) dan \( m \) telah dinilai dengan mengubah tekanan separa VOC di antara 0.004 hingga 0.018 atm dan tekanan separa oksigen di antara 0.05 hingga 0.20 atm. Tenaga pengaktifan pembakaran ialah 26.30 kJ/mol dan 20.65 kJ/mol bagi AgY(IE) dan AgZSM-5(IE) masing-masing.
REMOVAL OF VOLATILE ORGANIC COMPOUND (VOC) FROM AIR USING ZEOLITE BASED ADSORPTION-CATALYTIC COMBUSTION SYSTEM

ABSTRACT

The development of an advanced VOC destruction process consists of an adsorption unit followed by a catalytic combustion system has been proposed in the current study. The two hydrophobic zeolites, namely HY (SiO$_2$/Al$_2$O$_3$=80) and ZSM-5 (SiO$_2$/Al$_2$O$_3$=240) were chosen as adsorbents. Silver metal was loaded on these adsorbents to use as a catalyst for VOC combustion. The silver-loaded zeolites were tested using butyl acetate (BA) as a model VOC compound for the adsorption and catalytic combustion system.

The ion exchange (IE) and incipient wetness impregnation (IM) methods were used to prepare silver-loaded zeolites. The silver-loaded zeolites by impregnation method did not perform well in the adsorption process. The results showed poor VOC uptake capacity and early breakthrough time. AgY(IE) showed the highest VOC uptake capacity and the adsorbent service time was much longer compared to AgZSM-5(IE). The presence of water vapour in the feed suppressed the VOC adsorption capacity of AgY(IE) due to the competitive adsorption of water vapour on the active sites. However, VOC adsorption capacity of AgZSM-5(IE) was not affected in the presence of water vapour. A central composite design (CCD) was used to study the effect of three important operating parameters (VOC concentration, relative humidity, GHSV) for adsorption process. The response surface methodology (RSM) was used to obtain the optimum operating conditions for the adsorption process.

AgY(IE) and AgZSM-5(IE) were tested for VOC uptake data at different temperatures. A mathematical model was used to evaluate the thermodynamic
behaviour in conjunction with the Langmuir isotherm for the adsorption of butyl acetate over AgY(IE) and AgZSM-5(IE). The model parameters were evaluated and used to predict the adsorption isotherms and breakthrough curves under various process conditions.

The performance of silver loaded zeolite catalysts in combustion of VOC was studied with the objective of developing a catalyst with superior activity, selectivity towards deep oxidation product and stability. The catalyst activity was measured in the reactor operated at GHSV = 15,000 h\(^{-1}\), reaction temperature between 150°C - 500°C and VOC inlet concentration of 1000ppm. AgY(IE) and AgZSM-5(IE) exhibited high activity in the combustion of butyl acetate where total conversion of butyl acetate was achieved at temperature below 400°C. A central composite design was used to study the effect of three important operating parameters (VOC concentration, reaction temperature, GHSV) for combustion process. The response surface methodology was used to obtain the optimum operating conditions for the combustion process.

The combustion data of butyl acetate were fitted to a simple model following power-law rate equation. The reaction orders, \(n\) and \(m\) were evaluated by varying the VOC partial pressure between 0.004 to 0.018 atm and partial pressure of oxygen between 0.05 to 0.20 atm. The activation energies were 26.30 kJ/mol and 20.65 kJ/mol for AgY(IE) and AgZSM-5(IE), respectively.
CHAPTER 1
INTRODUCTION

1.0 ENVIRONMENTAL CATALYSIS

Environmental catalysis has been defined as the development of catalysts to either decompose environmentally unacceptable compounds or provide alternative catalytic synthesis of important compounds without the formation of environmentally unacceptable by-products. It is not enough to simply make an active material but it is also necessary to make it in a form that is thermally and mechanically stable enough to survive in a reactor for the time it is used. Catalyst lifetimes could vary from few seconds to years, depending upon the process. Catalysts are determined by number of factors including reaction rate, selectivity and its usage in the type of process or reactor. The catalyst is normally preferred to have a large surface area in order to maximise the number of sites. All the sites on the surface might not be active – some merely act as an adsorbent site not the centres of reactivity. The reactive sites are known as active sites. The physical shape and size of the catalyst is governed by its application. Powder catalysts are not prepared because of high pressure drop in the reactor. The catalyst shape is selected in order to maximise the catalyst utilization whilst reducing the pressure needed to move the gas through the reactor bed. The catalysts play an important role in environmental pollution control, especially in the removal of organic pollutants from waste water as well as air.

1.1 VOLATILE ORGANIC COMPOUNDS (VOCS)

1.1.1 Definition

One of the most common terms used in the solvent industry is volatile organic compound and is abbreviated as VOC. VOCs are a large group of organic chemicals that readily evaporate at room temperature. The original definition of VOC made reference to the vapour pressure of the any compounds which is greater than 133.3 Pa
at room temperature as a determinant of volatility. However effective as of December 29, 2004, the definition relies solely on any compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participates in atmospheric photochemical reactions (The United State Environmental Protection Agency, U.S. EPA, Definition of VOC: Code of Federal Regulations: Title 40, Part 51 Section 51.100).

Volatile organic chemicals (VOCs) are emitted as gases from certain solids or liquids which contain organic compounds. In many household products, VOCs are one of the common ingredients. Paints, varnishes, and wax all contain organic solvents, as do many cleaning, disinfecting, cosmetic and degreasing products. Fuels are made up of organic chemicals. All of these products can release organic compounds while using them, and, to some degree, when they are stored. When these organic compounds released to atmosphere, they become a key contributor of smog formation.

1.1.2 Health and Environmental Impacts

Emissions of VOCs do not necessarily give rise to health or environmental concern. Ground-level ozone, the primary component of smog is formed when oxides of nitrogen (NOx) and VOCs react in the presence of sunlight. Ozone is not usually emitted directly into the air, but at ground level, it is created by a chemical reaction between NOx and VOC in the presence of sunlight. Motor vehicle exhaust and industrial emissions, gasoline vapours, and chemical solvents as well as natural sources emit NOx and VOC that help to form ozone. Sunlight and hot weather cause ground-level ozone to form in harmful concentrations in the air.

Smog is sometimes called photochemical smog or photochemical air pollution. One of smog's key ingredients is formed when VOCs react with ozone in the presence of sunlight. A simple chemical reaction for this process is represented as:
Ozone + VOC + light $\rightarrow$ oxidized organic compounds \hfill (1.1)

The oxidized organic compounds are then mixed with many other compounds and small particles in the air to create photochemical smog.

Humans feel the effects of smog most often by experiencing respiratory trouble. Although the exact degree of health effects of smog is unknown, lung function and breathing can certainly be affected. Smog is also hazardous because it decreases visibility.

1.1.3 Industrial VOC Emission

Emissions of VOCs have been associated with various atmospheric effects. There are 80\% of the emissions of volatile organic compounds (VOCs) come from natural sources (e.g. biogenic sources, vegetation, biomass, volcanoes eruption), with only 20\% being man-made (for instance, domestic and industrial activities, road, marine and air transport). Before man-made pollution become prevalent, some natural phenomena can lead to air pollution as well. Large natural forest fire and volcanic eruptions are sources of VOC with possible large scale adverse impacts. However, those natural air pollutants phenomena tend to be localized in space and time that is generally uncontrollable (Seigneur, 2005).

Man-made air pollution, on the other hand has become widespread and controllable. Consequently, the study of air pollution has become an important scientific discipline that involves sophisticated experimental techniques and advanced modelling tools. Figure 1.1 shows man-made VOC emissions by four source categories: 1) “fuel combustion” which includes emissions from power plants, industrial, commercial and institutional sources as well as residential heaters and boilers, 2) “industrial and other processes” which includes large point sources such as refineries and smelters as well as smaller sources such as drycleaners and service stations, 3) “on road vehicles”
which includes cars, trucks, buses, and motorcycles and 4) “non-road vehicles and engines” such as farm and construction equipment, lawnmowers, chainsaws, boats/ships, snowmobiles, aircraft.

![Figure 1.1: VOC emissions in USA during 1990 and 1996 to 2002 (The United State National Emissions Inventory (NEI))](image)

### 1.2 VOC CONTROL TECHNOLOGIES

The main selection criteria for VOC abatement technologies are costs, VOC inlet concentration, gas flow rate and the required control level. In addition, pre-treatment of the vent gas may require some control device and could affect project cost. Pre-treatment refers to the methods and practices used to condition a VOC stream prior to its entry into an abatement unit. Table 1.1 summarizes the typical pre-treatment considerations for selected VOC abatement technologies. Particulate removal is an important pre-treatment consideration for thermal and catalytic combustion, adsorption, biofiltration and membrane systems. Particulates can clog catalyst beds or membranes resulting in reduction of VOC removal capacity of the equipment.
Table 1.1: Typical pre-treatment considerations (Moretti, 2001)

<table>
<thead>
<tr>
<th>VOC abatement technology</th>
<th>Typical pre-treatment considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal oxidation</td>
<td>• Dilution</td>
</tr>
<tr>
<td></td>
<td>• Preheating</td>
</tr>
<tr>
<td>Catalytic combustion</td>
<td>• Dilution</td>
</tr>
<tr>
<td></td>
<td>• Particulate removal</td>
</tr>
<tr>
<td></td>
<td>• Preheating</td>
</tr>
<tr>
<td>Adsorption</td>
<td>• Cooling</td>
</tr>
<tr>
<td></td>
<td>• Dehumidification</td>
</tr>
<tr>
<td></td>
<td>• Dilution</td>
</tr>
<tr>
<td></td>
<td>• Particulate removal</td>
</tr>
<tr>
<td>Condensation</td>
<td>• Dehumidification</td>
</tr>
<tr>
<td>Flaring</td>
<td>• Liquid knockout</td>
</tr>
<tr>
<td>Biofiltration</td>
<td>• Humidification</td>
</tr>
<tr>
<td></td>
<td>• Cooling</td>
</tr>
<tr>
<td></td>
<td>• Particulate removal</td>
</tr>
<tr>
<td>Membrane separation</td>
<td>• Particulate removal</td>
</tr>
</tbody>
</table>

The cooling of a VOC gas stream is an important pre-treatment consideration for adsorption and biofiltration systems. For adsorption system, the pre-cooler may be needed to saturate the gas stream or to reduce the inlet air temperature to acceptable levels to avoid solvent evaporation or reduce the adsorption rate. High temperature in biofiltration beds may destroy the micro organisms that convert VOC into carbon dioxide, water and mineral salts.

Dehumidification is an important pre-treatment consideration for adsorption and condensation systems, while humidification is important for biofiltration system. Water vapour competes with VOC for adsorption sites; hence reducing the water vapour in the adsorption inlet stream will subsequently increase the adsorption capacity for VOC. In condenser, water vapour can condense in the condenser tubes, thereby reducing the heat transfer capacity of the system (Dwivedi et al., 2004). On the other hand, biofiltration system requires moisture to prevent the filter bed from drying and cracking, which would permit escape of unreacted VOC to the atmosphere.
Gas flow rate and VOC concentration are the two most important design parameters for VOC control devices and selecting an appropriate VOC control device. Table 1.2 presents an applicability data range among the most popular technology applied in VOC abatement. The table shows the range of flow rate and concentration in which the device operate most efficiently.

Table 1.2: Applicability of VOC abatement systems (Moretti, 2001)

<table>
<thead>
<tr>
<th>VOC abatement technology</th>
<th>Waste gas flow rate (scfm)</th>
<th>VOC concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal oxidation</td>
<td>0 – 10,000 (thermal afterburner)</td>
<td>60% of LEL (thermal afterburner)</td>
</tr>
<tr>
<td></td>
<td>250 – 100,000 (recuperative)</td>
<td>25% of LEL (recuperative)</td>
</tr>
<tr>
<td></td>
<td>2,000 – 500,000 (regenerative)</td>
<td>10% of LEL (regenerative)</td>
</tr>
<tr>
<td>Catalytic combustion</td>
<td>0 – 75,000</td>
<td>25% of LEL</td>
</tr>
<tr>
<td>Adsorption</td>
<td>No practical limit</td>
<td>100 – 5,000</td>
</tr>
<tr>
<td>Condensation</td>
<td>&lt; 3,000</td>
<td>&gt; 1,000</td>
</tr>
<tr>
<td>Flaring</td>
<td>No practical limit</td>
<td>No practical limit</td>
</tr>
<tr>
<td>Biofiltration</td>
<td>&gt; 1,000</td>
<td>&lt; 1,000</td>
</tr>
<tr>
<td>Membrane separation</td>
<td>&lt; 500</td>
<td>&gt; 5,000</td>
</tr>
</tbody>
</table>

Note: LEL: lower explosive limit

As shown in the table, thermal oxidation and catalytic combustion can be used over a fairly wide range of VOC concentrations, provided adequate safety precautions are implemented for VOC loading greater than 25 percent of the lower explosive limit (LEL).

Adsorption systems operate best at medium concentration range and flow rate. VOC concentration as low as 20 ppm are treatable with adsorption but concentration above 10,000 ppm may lead to excessive rising of bed temperature. The flow rate must be high enough to allow time for both diffusion and adsorption. At lower flow rates, the required bed volume is large and its cost becomes prohibitive. Flow rates between 1,000 to 50,000 scfm are ideal for adsorption system.
Condenser can process waste gas stream or high VOC concentration but relatively low flow rate. Flow rate above than 3,000 scfm may require significantly large heat transfer areas. Flaring can be used to control almost any of the VOC stream and can handle fluctuation in VOC concentration, flow rate, heat content and inert gas content. Biofiltration is cost-competitive for flow rates above than 1,000 scfm and VOC concentration below 300 to 500 ppm. Membrane separation systems are suited for low flow rate and high concentration of VOC in the waste gas streams.

1.3 COMBINED ADSORPTION-CATALYTIC COMBUSTION OF VOC

The choice of technique for VOC abatement system depends on the type and concentration of VOC. Adsorption of VOCs is normally carried out on activated carbon or zeolites. Activated carbon is cheaper but zeolites have the advantages of being non-flammable, thermally stable and hydrophobic. Therefore, zeolites are preferred for the treatment of waste gases containing large amount of water and for the processes with repeated adsorbent regeneration by heating (Thomas and Crittenden, 1998).

Catalytic combustion is the method of choice if the concentration of VOC allows performing the process adiabatically. For low VOC concentrations, a two-step adsorption-combustion process is suitable. In this process the VOC are first concentrated by adsorption at low temperature until the breakthrough occurs. The adsorbent is regenerated by desorption by passing a heated inert gas through the catalyst bed. The desorbed concentrated VOC is then passed through a catalytic combustion chamber and converted to harmless compounds in the presence of suitable catalyst.
1.4 PROBLEM STATEMENT

1.4.1 Model VOC

Butyl acetate is produced commercially by esterification of acetic acid with butyl alcohol. It is generally used as a solvent for a variety of coating resins including epoxies, urethanes, cellulosics, acrylics and vinyls. The major applications for these surface coatings are wood furniture and fixtures, containers and closures, automotive refinishing and maintenance, and marine coatings. Figure 1.2 shows the usage of butyl acetate as solvent in various industries. During the 1990s, n-butyl acetate was substituted for solvents such as toluene, xylene, MIBK and MEK, which are classified as hazardous air pollutants (HAPs). Although this substitution has largely completed, consumption of butyl acetate is expected to continue growing modestly in concern with the various coating applications.

![Butyl acetate usage in industry](image_url)

Figure 1.2: Butyl acetate usage in industry (American Chemistry Council: Market Intelligence for the Chemical Process Industry)

In future market, with a modest growth of 1.7 percent annually through year 2007, BA demand is still potential and continued if there is no development of coatings technologies that use little solvent or zero solvent. Table 1.3 tabulates the historical
data of butyl acetate demand from year 1998 to 2003. With the increase in global demand in painting and coating industries, butyl acetate was chosen as the VOC model compound for the present study.

Table 1.3: The historical data of butyl acetate world demand (American Chemistry Council: Market Intelligence for the Chemical Process Industry)

<table>
<thead>
<tr>
<th>Year</th>
<th>Demand (Millions of Pounds)</th>
<th>List Price (US $ per pound)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1998</td>
<td>235</td>
<td>0.45</td>
</tr>
<tr>
<td>1999</td>
<td>230</td>
<td>0.42</td>
</tr>
<tr>
<td>2000</td>
<td>225</td>
<td>0.51</td>
</tr>
<tr>
<td>2001</td>
<td>205</td>
<td>0.51</td>
</tr>
<tr>
<td>2002</td>
<td>195</td>
<td>0.49</td>
</tr>
<tr>
<td>2003</td>
<td>210</td>
<td>0.54</td>
</tr>
</tbody>
</table>

1.4.2 Selection of Adsorbent/catalyst

Selection of an effective and economical catalyst component is as important as the selection of good adsorbent material to embody the best dual functional adsorbent/catalyst media. The adsorbent acts as a separation medium for the process. The primary requirements of an adsorbent are:

⇒ **Selectivity**: The preferential adsorption of one or more component based upon equilibrium and/or kinetic mechanisms.

⇒ **Capacity**: The maximum possible loading of adsorbate on the adsorbent.

⇒ **Stability**: Chemical and physical stability of the adsorbent under the operating conditions.

Activated carbons are generally used in many adsorption processes due to their higher adsorption capacity and lower price. However, their regeneration is very difficult because of their thermal and chemical instabilities that may cause significant safety problem (Baek et al., 2004). Recently, the use of hydrophobic zeolites is attracting more and more attention due to their resistance to humidity and their non-flammability.
The use of hydrophobic zeolite for the dual function adsorbent/catalyst medium is justified in two aspects. One is safety concern for the operation of catalytic oxidation at high temperature and secondly is high adsorption affinity for VOC in humid condition (Baek et al., 2004; Thomas and Crittenden, 1998).

Zeolites can be used as supports or even as catalyst for combustion of VOC. In order to minimize the energy consumption and to cut down the operating cost, it is required that the reaction temperature is as low as possible, and the catalyst can be recycled and regenerated many times. However, at low temperature, water vapor generated from VOC combustion can be easily condensed in the micro/mesopores of metal oxide support, drastically reducing the catalyst activity. Hence, the advantage of using a hydrophobic support is that moisture, both from the atmosphere and formed as a reaction product, will not adsorb on the catalyst. It is therefore, of great interest to use the hydrophobic catalyst having high VOC adsorption capacity and oxidation activity.

There have been a number of reports and patents on catalytic processes for the oxidation of VOC (Everaert and Baeyens, 2004; Wu and Chang, 1998) mostly related to the development of catalysts based on noble metals or transition metal oxides (Law et al., 2003). Noble metal-based catalysts such as supported platinum and palladium are known to be active catalysts for complete combustion of VOC. Though these catalysts are very active, they are not favoured due to very high cost and susceptibility to poisoning (Zuhairi, 2004). As a result, extensive work has been performed to establish the replacement for these metals especially from transition metals. Silver has been well-known for its epoxidation activity and the reaction most often studied on silver was ethylene oxidation. Silver is the only metal that selectively catalyzes the epoxidation to ethylene oxide (Cordi and Falconer, 1997). There are some reports on deep oxidation of NO, CO and methane using supported silver catalyst (Müselehiddinoglu and Vannice, 2003; Müselehiddinoglu and Vannice, 2004). However,
there are very few reports on their application to the adsorption and complete combustion of VOC. Hence, silver catalyst with zeolite as support has gained much interest on dual functional adsorbent/catalyst media for adsorption and complete combustion of VOC.

1.5 OBJECTIVES

1.5.1 Previous Related Work at USM

Catalytic combustion of VOC studies at USM commenced under the supervision of Professor Subhash Bhatia in 2000. Zuhairi and Bhatia jointly coordinated a theoretical and experimental programme for the study of the catalytic combustion of single and binary VOC systems in a packed bed reactor. The performance of zeolite catalysts in the combustion of VOC was studied with the objective of developing a catalyst with superior activity, selectivity towards deep combustion products and catalyst stability. In his studies, the catalyst support is limited to three types of zeolite which were beta (Si/Al=25 and 50), mordenite (Si/Al=40 and 90) and ZSM-5 (Si/Al=90 and 240). The selection of zeolite catalyst was carried out through metal exchange or impregnation from the active metal species among the elements in the first and second row of transition metal series. Chromium was loaded as first metal by ion exchange method over zeolite support and followed by bimetallic impregnation method with different metal solutions such as cadmium, cobalt, copper, iron, lanthanum, molybdenum and zinc as second metal.

Results showed that chromium exchanged ZSM-5 with Si/Al=240 (Cr-ZSM-5(240)) exhibited high activity and stability among the transition metal catalyst studied. Bimetallic catalyst containing 1.0 wt. % chromium and 0.5 wt. % copper impregnated over H-ZSM-5(240) gave higher carbon dioxide yield and also lower coke. The experimental data for combustion of single VOC over Cr-ZSM-5 (240) were fitted with Mars-van Krevelen model. The model was successfully extended to humid feed and
binary mixture of ethyl acetate and benzene by considering competitive adsorption. The results and findings were useful in the extended work for current project.

1.5.2 Present Research

The principle objective of this research work is to carry out kinetics of VOC combustion and transient adsorption studies on the VOC removal process. It involves modelling of the adsorption process using the Matlab 7.0 simulation program and the kinetics of VOC catalytic combustion using the Polymath 5.0 program. The catalysts, which comprised of silver loaded on zeolites HY (SiO$_2$/Al$_2$O$_3$ = 80) and hydrophobic MFI, ZSM-5 (SiO$_2$/Al$_2$O$_3$=280) were used in the experiment. Butyl acetate was chosen as the VOC model compound in present studies. The measurable objectives of this research are:

1) To obtain concentration breakthrough curves of the proposed VOC on a fixed bed of silver-loaded zeolite at different operating conditions.
2) To propose a suitable model for adsorption process and evaluate process parameters from the experimental breakthrough data.
3) To demonstrate the catalytic performance of silver loaded zeolite in decomposition of the proposed VOC.
4) To propose a suitable kinetic model to represent the combustion of the model VOC over silver loaded zeolite.
5) To determine the optimum process conditions for adsorption as well as catalytic combustion of VOC.

1.6 SCOPE OF THE STUDY

In this study, the selection of catalyst support is limited to only two types of zeolite namely faujasite, Y (SiO$_2$/Al$_2$O$_3$ = 80) and MFI, ZSM-5 (SiO$_2$/Al$_2$O$_3$=280). This selection is based on the hydrophobicity and the type of pore system present in the zeolite and their application in many chemical processes.
The overview flow chart of the research activities carried out throughout the present study is presented in Figure 1.3. This project involved interrelated work in the sequence as shown in the figure. The preparation of the zeolite adsorbent and catalyst involved formulation and preparation of the adsorbent/catalyst by two different methods, namely ion exchange and impregnation method. The effect of various preparatory conditions and procedures were studied and carried out during the adsorbent/catalyst preparation. The prepared adsorbent/catalyst was also characterised to examine the surface of the promising adsorbent/catalyst for a better understanding on the changes in structural integrity after metal loading.

The adsorption process study was carried out at a pre-determined set of variables such as VOC concentration, gas hourly space velocity (GHSV) and the presence of water vapour in the feed for determination of the adsorption capacity (mg/g) of the samples. The experimental data are crucial for determination of the adsorption isotherm of the samples and to study the occurrence of breakthrough and the necessity to start desorption process.

In catalytic combustion process studies, the experimental work was carried out with a set of most affecting variables such as reaction temperature, GHSV and VOC concentration. The kinetic parameters obtained from experimental data were studied to evaluate the performance of catalytic combustion system. The viability of overall process was assessed based on reactor performance and practicality of the reactor operation.

After adsorption and catalytic combustion studies, the combined operation (adsorption-catalytic combustion) was carried out to study the overall removal efficiency of VOC.
CHARACTERIZATION OF METAL LOADED ADSORBENT/CATALYST

PREPARATION OF ADSORBENT/CATALYST

METHOD:
- ION EXCHANGE
- IMPREGNATION

ICP
SEM / EDX
TEM
XRD
FTIR

OPTIMUM PARAMETERS FOR ADSORPTION / DESORPTION PROCESS STUDY

MODELLING OF VOC ADSORPTION PROCESS

OPTIMUM PARAMETERS FOR CATALYTIC COMBUSTION PROCESS STUDY

MODELLING & KINETIC PARAMETERS EVALUATION

COMBINED PROCESS

MODEL VOC:
- BUTYL ACETATE

CATALYTIC COMBUSTION

ADSORPTION

Figure 1.3: Research activities flow chart
1.7 ORGANISATION OF THE THESIS

This thesis describes the research work to investigate the application of dual functional adsorbent/catalyst system for the removal of VOC. This work investigates the fundamental aspects of adsorption and catalytic combustion of butyl acetate in a fixed bed adsorption column and fixed bed reactor respectively.

Chapter 1 (Introduction) includes a brief introduction on what is VOCs, their related environmental significance and current VOC control technologies. This chapter also enclose with problem statement that provide some basis and rationale to justify the research direction to be followed in the current studies. The objectives of the present study are elaborated in detail together with the scope of the study.

Chapter 2 (Literature Review) reviews the related theories of zeolite-based catalyst for the two processes, adsorption and catalytic combustion that are relevant to the present study. Criteria for favourable operating conditions are proposed. Some background information about specific problems to be addressed in this research are also presented in this chapter.

Chapter 3 (Materials and Methods) starts by listing all the materials and chemicals used together with their respective supplier name and purity. Then, all the catalyst preparation procedures and the equipment used during the preparation of catalyst are given. The experimental setup and other experimental procedures are then elaborated in the following section of this chapter. The experimental methods used in the study of adsorption process and catalytic combustion processes are given. Lastly, this chapter presents a description on the design of experiment and process parameters optimisation to determine the most important process variables and their optimum values.
Chapter 4 (Modelling) is divided into two main sections: (a) the equilibrium and kinetic model of adsorption process and (b) the kinetic modelling of VOC combustion process. This chapter also presents the theoretical basis, in particular the background of modelling and simulation of the proposed process. Some assumptions to perform the proposed model are discussed.

Chapter 5 (Results and Discussion) is the core of this thesis and is divided into two different parts covering first the adsorption process studies and second covering the catalytic combustion process studies. The experimental data are presented and discussed to address the specific objectives proposed. In the modelling studies, models are presented and simulated results are compared with the experimental data. The adsorption and kinetics parameters obtained from experimental data are also presented and discussed.

Chapter 6 (Conclusions and Recommendations) presents the main conclusions based on the current studies. This chapter ends with recommendations for future studies in the related field. These recommendations are given based on their significance and importance, taking into account the conclusions obtained in the present study.
CHAPTER 2
LITERATURE REVIEW

2.0 INTRODUCTION

Up to now, only about 10% of the industrial abatement units are based on adsorption. This percentage will increase in the near future given the strict control over VOC releases set by the legislation. This explains the current growing interest in development of highly efficient adsorbents for the treatment of VOC-loaded waste gases. As developments in VOC abatement technology to suit the characteristics of the effluent to be treated, the advanced adsorption-catalytic combustion system offers a promising solution. This chapter reviews the development of metal loaded zeolite as dual functional adsorbent/catalyst role on removal of volatile organic component. Using past accounts of VOC catalytic combustion system, criteria for favourable operating conditions for reaction enhancement are proposed.

2.1 ZEOLITES

2.1.1 Introduction and Pore Structure

Zeolites are porous crystalline aluminosilicates with the general formula $M_{2n}O \cdot Al_2O_3 \cdot ySiO_2$ where $n$ is the valence of the cation $M$ and $y$ may vary from 2 to infinite (Guisnet and Gilson, 2000). Structurally, zeolites comprise the assemblies of SiO$_4$ and AlO$_4$ tetrahedra joined together through the sharing of oxygen atoms with an open structure that can accommodate a wide variety of cations, such as Na$^+$, K$^+$, Ca$^{2+}$ and others as shown in Figure 2.1. These cations can readily be exchanged for others in a contact solution.
Zeolites are usually synthesized under hydrothermal conditions, from solutions of sodium aluminate, sodium silicate, or sodium hydroxide (Szostak, 1998). The tetrahedral formula of SiO$_2$ and AlO$_2^-$ with one negative charge resides at each tetrahedron in the framework containing aluminium in its centre. Silicon and aluminium in aluminosilicate zeolites are referred to as the T-atoms (Weitkamp, 2000). The framework of a zeolite contains channels. Inside these voids are water molecules and small cations which compensate the negative framework charge. Water will desorbs upon heating without destruction of the crystalline structure.

Since adsorption and catalytic processes involve diffusion of molecules in the zeolite pores, only those with a minimum of 8 tetrahedral atoms apertures allowing the diffusion are generally considered. Most of the zeolites can be classified into three categories (Guisnet and Gilson, 2000):

- Small pore zeolites with eight membered-ring pore apertures having free diameters of 0.30 – 0.45 nm
- Medium pore zeolites with ten membered-ring apertures, 0.45 – 0.60 nm in free diameter
- Large pore zeolites with 12 membered-ring apertures with 0.6 – 0.8 nm
In general, zeolites pore sizes fall into the microporous size and with ring size between 8 – 20 (Guth and Kessler, 1999). Zeolite has the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture, where the term "8 ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pore openings for all rings of one size are not identical.

Figure 2.2 shows the structures of four selected zeolites along with their respective void systems and pore dimensions. In general, the T-atoms are located at the vertices and lines connecting them stand for T-O-T bonds. Since the accessibility of the unique features of zeolite is controlled by the pore diameter and pore width in the order of molecular dimension as shown in Figure 2.2, International Union of Pure and Applied Chemistry (IUPAC) has classified the molecular sieve materials based on their pore size into three categories (Weitkamp, 2000):

- **Microporous material**  
  pore diameter < 2.0 nm
- **Mesoporous material**  
  2.0 nm ≤ pore diameter ≤ 50.0 nm
- **Macroporous material**  
  pore diameter > 50.0 nm
2.1.1(a) Faujasite (Y)

Zeolite faujasite, Y ($n_{Si}/n_{Al} > 1.5$) is of utmost importance in heterogeneous catalysis and it is recognised as an active component in catalysts for fluid catalytic cracking (Guisnet and Gilson, 2002). Its pore system is relatively spacious and consists of spherical cages, referred as supercages, with a diameter of 1.2 nm connected tetrahedrally with four neighbouring cages through windows with a diameter of 0.74 nm formed by 12 TO$_4$-tetrahedra (Weitkamp, 2000) as shown in Figure 2.2. Zeolite Y is therefore classified to possess a three-dimensional, 12-membered-ring pore system.

The most important use of zeolite Y is as a cracking catalyst. It is used in acidic form in petroleum refinery catalytic cracking units to increase the yield of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffins into gasoline grade napthas (Wang et al., 2005b). Zeolite Y has superseded zeolite X in this use because it is both more active and more stable at high temperatures due to the higher Si/Al ratio.
It is also used in the hydrocracking units as a platinum/palladium support to increase aromatic content of reformulated refinery products (Thomas and Crittenden, 1998).

2.1.1(b) Zeolite Socony Mobil 5 (ZSM-5)

Zeolite Socony Mobil 5, ZSM-5 is a zeolite with unidimensional pores and its all-silica analogue silicalite-1 \((n_{Si}/n_{Al} = \infty)\) built from the pentasil unit. ZSM-5, with its aluminosilicate framework contains considerably less aluminium than a Y-zeolite specimen (Rachapudi et al., 1999). ZSM-5 is a zeolite with high silica to alumina ratio. The substitution of an aluminum ion (charge 3+) for a silicon ion (charge 4+) requires the additional presence of a proton. This additional proton gives the zeolite a high level of acidity. ZSM-5 is a highly porous material and throughout its structure it has an intersecting two-dimensional pore structure. ZSM-5 has two types of pores, both formed by 10-membered oxygen rings. The first of these pores is straight and elliptical in cross section; the second pores intersect the straight pores at right angles, in a zigzag pattern and are circular in cross section (Weitkamp, 2000) as shown in Figure 2.2.

ZSM-5 is another example of a zeolite which has achieved importance in heterogeneous catalysis. It is used industrially in the synthesis of ethyl benzene, the isomerization of xylenes and recently gained attention in environment catalysis such as the adsorption and destruction of pollutants from water and air (Delahay and Coq, 2001).

2.1.2 Zeolite Acidity

Zeolite surface acidity is among the most important properties in the use as catalysts. In natural zeolites, the excess negative charge is balanced by whatever ions that presents in the surrounding environment such as \(K^+, Na^+, Ca^{2+}\) and \(Mg^{2+}\). The type of counter ion used to balance the charge plays an important part because it constitute
to acid site to zeolite, where the majority of which are Brønsted and Lewis acid sites (Canizares et al., 1998). This cannot be on replacement of the cation with a proton by hydrothermal treatment to form a hydroxyl group at the oxygen bridge (Simon-Masseron et al., 2007). Brønsted acid site presents in the form of bridging hydroxyl and function through its ability to release and accept proton as shown in Figure 2.3 (Thomas and Thomas, 1997).

Figure 2.3: Brønsted acid site formation due to Si/Al substitution in a zeolite framework

Several industrial applications of zeolites are based upon technology adapted from the acid silica/alumina catalysts originally developed for the catalytic cracking reaction. This means that the activity requested is based on the formation of Brønsted acid sites arising from the creation of “bridging hydroxyl groups” within the pore structure of the zeolites. These “bridging hydroxyl groups” are usually formed either by ammonium or polyvalent cation exchange followed by a calcinations step. The “bridging hydroxyl groups”, which are protons associated with negatively charged framework oxygen linked into alumina tetrahedra, are the Brønsted acid sites, as demonstrated in Figure 2.3. The protons are quite mobile at higher temperatures, and at 550°C they are lost as water molecules followed by the formation of Lewis acid sites, as shown in Figure 2.4.
Lewis acid site occurs as threefold-coordinated aluminium or silicon ($\equiv$ Al or $\equiv$ Si$^+$), or extra framework aluminium-containing species such as AlO$^+$. Lewis site form upon dehydroxylation and dealumination of zeolites (Karge et al., 1999). For zeolites, it can be stated that the concentration of aluminium in the lattice is directly proportional to the concentration of acid sites. However, for other microporous solids, corresponding correlations are not significant (Weitkamp, 2000).

Catalytic activity in zeolites is essentially governed by electronic transport between reactive components and local sites within the zeolite framework. In acid-based zeolite catalysts, these sites are typically Brønsted acid sites, containing an $\text{H}^+$ ion localized near a bridging Si-O-Al cluster. The highly acidic sites, combined with the high selectivity arising from shape selectivity and large internal surface area makes the zeolite an ideal industrial catalyst (Weitkamp, 2000). The significance of this acidic proton can be shown quite easily by comparisons of experiments in H exchanged zeolites and their equivalent cation form zeolite. The zeolitic proton has been used as an efficient solid acid catalyst in several industrial reactions.
2.1.3 Modification of Zeolites

2.1.3(a) Ion Exchange

With the negative charge of the zeolite porous framework and the small and mobile cations sitting in the pores, zeolites are typical ion exchangers. Since aluminium is trivalent, every AlO₂ unit carries a negative charge, which is compensated by a positive charge associated with a cation. Therefore, the ion exchange capacity of a zeolite depends on the chemical composition. A higher ion-exchange capacity is observed in zeolites of low SiO₂/Al₂O₃ ratio (Weitkamp and Puppe, 1999). In the manufacture of zeolite catalysts, ion exchange plays an outstanding role. For many catalytic applications, a Brønsted acid form of a zeolite is required. Brønsted acid sites in zeolite can be readily generated by introducing ammonium ions followed by a heat treatment or by introducing multivalent metal cations. Ion exchange is always applied to incorporate the frequently studied metals like Cu, Co, Pt or Pd into the zeolites (Canizares et al., 1998; Tsou et al., 2005).

The ion exchange is performed using a simple technique where the zeolite is suspended in an aqueous solution of a soluble salt containing the desired cation at ambient temperature under stirring. The exchange reaction, in which one type of cation is replaced with another, assumes an equilibrium state that is unique for the particular zeolite and the particular cations. Exchange between ion A⁺, initially in solution and ion B⁺, initially in the zeolite may be expressed as:

\[ bA_s^+ + aB_z^+ \rightleftharpoons bA_z^+ + aB_s^+ \]  \hspace{1cm} (2.1)

where a and b are the valencies of the exchanging cations A⁺ and B⁺, s and z designate the solution and zeolite phases.

The rate of ion exchange depends on the concentration of ions of a size capable of penetrating the pores of the zeolite. At ambient temperature, a solution of a large hydrated ion may contain very few partially hydrated ions of a size smaller than