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Selective catalytic reduction of nitric oxide over Cu and Co ion-exchanged ZSM-5 zeolite: the effect of SiO_2/Al_2O_3 ratio and cation loading

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Abstract

The performance of Cu-ZSM-5 and Co-ZSM-5 zeolites for selective catalytic reduction (SCR) of nitric oxide (NO) was examined and compared in a packed-bed tubular reactor using methane and propene as reducing agents. Emphasis was given to the effects of SiO_2/Al_2O_3 ratio and Cu or Co ion loading on the catalyst performance as indicated by the levels of NO conversion into N_2. For Cu ion-exchanged zeolites, the catalysts with the same copper loading but different SiO_2/Al_2O_3 ratios showed different activities. At temperatures greater than 350°C, the NO conversion with increasing SiO_2/Al_2O_3 ratio, whereas the maximum NO conversion decreases with increasing copper loading when the catalysts have the same SiO_2/Al_2O_3 ratio. Catalysts with identical Cu ion-exchange levels, but different SiO_2/Al_2O_3 ratios and different copper loadings, do not show the same activities, indicating the important role of SiO_2/Al_2O_3 ratio. For Co ion-exchanged catalysts with the same Co loadings, however, the activity increases with decreasing SiO_2/Al_2O_3 ratio. For catalysts with the same SiO_2/Al_2O_3 ratios, the catalytic activity decreases with increasing Co loading. Performance of Co ion-exchanged catalysts also appears to be dependent on the preparation method. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; Cobalt; Copper; Nitric oxide; Selective catalytic reduction; ZSM-5 zeolite

1. Introduction

Emissions of nitrogen oxides (NO_x) from anthropological sources have been known to cause serious environmental problems [1]. The most prevalent method for the removal of NO_x from stationary sources is selective catalytic reduction (SCR) using ammonia as a reducing agent [2]. This method which works well under oxidising atmosphere, cannot be practised for transportation applications due to difficulties of storage and maintenance of ammonia on board [3]. Three-way catalysts (TWC) are able to remove 80–90% of NO_x emissions [4] from the mobile sources only when engines operate with a stoichiometric air to fuel ratio, A/F, less than 14.7 [5]. Under this condition, however, the engines incur an energy efficiency penalty. Lean-burn engines can be utilised to overcome the low efficiency [1,5]. However, TWC would be poisoned due to the presence of excessive oxygen remaining in the exhaust.

SCR of nitric oxide (NO) over copper ion-exchanged ZSM-5 zeolite using different hydrocarbons as reducing agents was first introduced as a potential alternative technique by Iwamoto [6]. This was followed

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by a large body of work published in [1,3–5,7,8] on copper (Cu) and cobalt (Co) ion-exchanged ZSM-5 zeolite for SCR of NO. Methane and propene have been known as effective reducing agents for SCR of NO over Co-ZSM-5 [7] and Cu-ZSM-5 [8], respectively. However, comparison of Co-ZSM-5 catalysts with propene and Cu-ZSM-5 catalysts with methane as reducing agents have not been well documented in [9]. In addition, the effects of SiO_2/Al_2O_3 ratio of the parent zeolite and cation loading on the performance of these catalysts require further understanding [9].

The present contribution reports an experimental study of SCR of NO over Cu and Co ion-exchanged ZSM-5 zeolites, which were synthesised in house [9], to obtain desired properties of the parent zeolites. Both methane and propene were employed as the reducing agents. Particular attention is paid to the influence of both SiO_2/Al_2O_3 ratio and cation loading on the performance of the catalysts. Results are reported in the form of NO conversion into molecular N_2. Comparison with literature data is made where possible.

2. Experimental

2.1. Catalyst preparation

A ZSM-5 zeolite sample with a SiO_2/Al_2O_3 ratio of 40 was synthesised via a template-free method [9,10]. Zeolites with SiO_2/Al_2O_3 ratios ranging from 70 to 176 were also synthesised using tetrapropylammonium bromide (TPABr) as a template according to the method described by Sano et al. [9,11]. The zeolites were examined using X-ray diffraction (XRD) technique and, by comparing a reference zeolite made available by Iwamoto and Hamada [12], it was confirmed that these zeolites are Na-form ZSM-5 zeolites and have achieved 100% crystalline. Details of the zeolite synthesis and analyses have been reported elsewhere [9].

Some of the zeolites synthesised were ion-exchanged with 0.1 M ammonium nitrate solution at 50°C and, after washing and drying, calcined in an air oven at 500°C for 3 h to obtain the H-form of zeolites [9]. Both H-form and Na-form zeolites were then ion-exchanged with copper acetate or cobalt acetate to obtain Cu and Co ion-exchanged ZSM-5 zeolite catalysts.

Cu ion-exchange is performed by placing 10 g of zeolite in 500 ml aqueous solution of copper acetate of varying concentration for different durations, depending the desired ion-exchanged level. The slurry is filtered, washed with deionised water and then dried at 110°C overnight.

Cobalt ion-exchanged ZSM-5 catalysts are prepared using two methods, a semi-continuous method and a batch method. In the semi-continuous method, 10 g of zeolite is mixed with 500 ml of deionised water. Cobalt acetate (500 ml) solution (0.01 M) is continuously added drop-wise during the ion-exchange to the zeolite/water slurry while it was continuously stired. A refluxing system is employed to return the evaporated water into the slurry. Therefore, the solution would not be concentrated due to water evaporation. After 24 h, the slurry is filtered and washed with deionised water. This procedure is repeated several times to achieve greater Co loadings. The catalyst, thus, prepared is then dried in an air oven overnight at 110°C [9].

In the batch method, 10 g of zeolite is added to 500 ml aqueous solution of cobalt acetate (0.001–0.02 M). The typical temperature for this ion-exchange is 80°C. The exchange time depends on the desired ion-exchange level. The slurry is filtered, washed with deionised water and then dried at 110°C overnight. The details of the catalyst preparation methods and procedures can also be found in [9].

For convenience, throughout the paper the catalysts are denoted as Cu-ZSM-5 and Co-ZSM-5 for catalysts prepared from Na-form zeolites, and H-Cu-ZSM-5 and H-Co-ZSM-5 for catalysts prepared from H-form zeolite, respectively. The catalysts are also analysed using the whole rock fusion and inductively coupled plasma (ICP) methods to determine silica to alumina ratios and copper or cobalt loadings. The specifications of the catalysts calculated using the results of the analysis, are given in Tables 1 and 2. For example, Cu-ZSM-5-176-199.2 stands for a Cu ion-exchanged ZSM-5 catalyst with an initial SiO_2/Al_2O_3 ratio of 176 and Cu ion-exchange level of 199.2%.

2.2. Experimental apparatus and procedures

A packed bed tubular reactor [13] constructed of stainless steel (i.d. 10 mm) was employed. An appropriate amount (usually 1 g) of a catalyst was loaded into the reactor tube and two thin ceramic fibre disks

Table 1
Specifications of Cu ion-exchanged ZSM-5 catalysts

Catalyst	Initial SiO_2/Al_2O_3ratio	Resulting SiO_2/Al_2O_3ratio	Cu loading (wt.%)	Cu ion-exchange level (%)
Cu-ZSM-5-176-199.2	176	145	1.3	199.2
Cu-ZSM-5-140-160.7	140	144	1.24	160.7
Cu-ZSM-5-100-168.6	100	91.1	1.58	168.6
Cu-ZSM-5-100-127.5	100	97	1.24	127.5
Cu-ZSM-5-100-108.3	100	96.5	1.06	108.3
Cu-ZSM-5-100-99.3	100	96	1.29	99.3
H-Cu-ZSM-5-50-99.3	50	50.7	1.85	99.3
H-Cu-ZSM-5-50-77.3	50	50.8	1.44	77.3

Table 2
Specifications of Co ion-exchanged ZSM-5 catalysts

Catalyst	Initial SiO_2/ Al_2O_3 ratio	Resulting SiO_2/ Al_2O_3 ratio	Co loading (wt.%)	Co ion-exchange level (%)
H-Co-ZSM-5-80-428[a]	80	74.85	4.45	428
H-Co-ZSM-5-80-96.6[a]	80	77	1.04	96.6
H-Co-ZSM-5-80-71[a]	80	80	0.76	71
H-Co-ZSM-5-80-77.9[b]	80	79.98	0.87	77.9
H-Co-ZSM-5-40-45[a]	40	33.75	1.05	45

[a] The catalyst prepared using semi-continuous preparation method.

[b] The catalyst prepared using batch preparation method.

were located on both sides of the catalyst powder to stop movement of the catalyst caused by the flowing gas stream. The reactor was then placed inside an electrically heated, temperature-controlled furnace. Five gas cylinders containing (1) 12% NO in helium, (2) pure helium, (3) 5.24% methane in helium, (4) 5.32% oxygen in helium and, (5) 5.34% propene in helium from BOC gases, respectively, were employed. Five MKS mass flow controllers were utilised to control individual gas flows to achieve the desired initial gas composition. A gas chromatograph (Varian Star 3400CX Series), fitted with a thermal conductivity detector and molecular sieve 5A and Haysep N columns in series, was used to analyse the inlet and outlet gases. All experiments were carried out over 1.0 g of each catalyst using a mixture of 2000 ppm NO, 2000 ppm CH_4 or C_3H_6, 2% O_2, and balance He. The total flow rate of the gas was 100 or 150 ml min^{-1} which are specified in each section below. The temperatures over which the experiments were performed ranged from 250 to 650°C. Details of the experimental system have been reported elsewhere [11,13].

Concentrations of N_2, O_2, CO, CH_4, CO_2, N_2O and C_3H_6 were monitored in both inlet and outlet gas streams. The inlet gas stream was checked particularly for the presence of any nitrogen, which affects the accuracy of NO conversion calculations. Conversion of NO into N_2 was calculated using Eq. (1)

$$\text{NO conversion (\%)} = \frac{2\left([N_{2,\text{out}}] - [N_{2,\text{in}}]\right)}{[NO_{\text{in}}]} \times 100 \quad (1)$$

where $[N_{2,in}]$ is the concentration of N_2 in the inlet gas stream; $[N_{2,out}]$, the concentration of N_2 in the outlet gas stream; and $[NO_{in}]$, the concentration of NO in the inlet gas stream set by the mass flow controllers.

3. Results and discussion

3.1. SCR of NO over H-Cu-ZSM-5 and H-Co-ZSM-5 catalysts

In order to compare Cu and Co ion-exchanged catalysts, experiments were performed on the SCR of NO into N_2 over both Cu and Co ion-exchanged ZSM-5 catalysts by CH_4 and C_3H_6. The inlet gas flow rate was 100 ml min^{-1}, which gave a contact

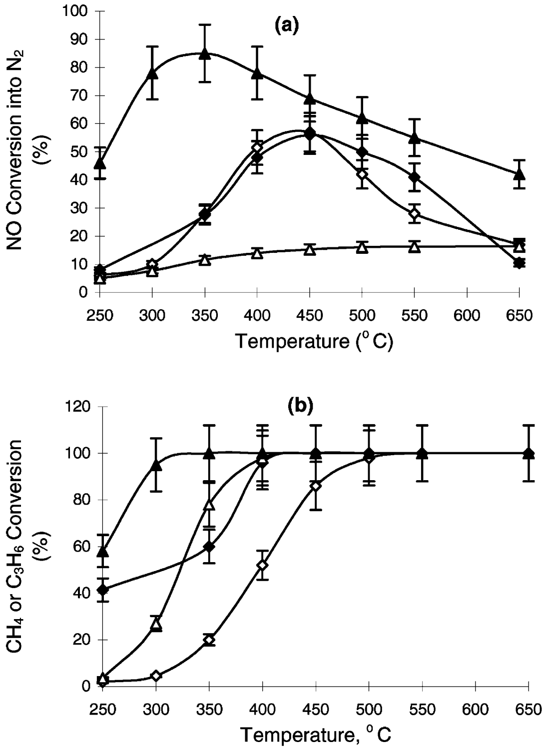

Fig. 1. Dependence of (a) NO conversion and (b) CH_4 or C_3H_6 conversion, on temperature for SCR of NO over various catalysts: (▲), H-Cu-ZSM-5-40–101.7 using C_3H_6; (△), H-Cu-ZSM-5-40-101.7 using CH_4; (◆), H-Co-ZSM-5-40-45 using C_3H_6; (◇), H-Co-ZSM-5-40-45 using CH_4. Reaction conditions: 2000 ppm NO; 2000 ppm CH_4 or C_3H_6; 2% O_2, balanced by He; 1.0 g catalyst; and 100 ml min^{-1} total flow rate.

time of 0.6 g s ml^{-1}. Typical results of NO conversion and CH_4 or C_3H_6 oxidation as a function of temperature are shown in Fig. 1(a) and (b), respectively. The highest NO conversion into N_2 was achieved over Cu-ZSM-5 when C_3H_6 was used. This catalyst showed very low activity for SCR of NO by CH_4 as shown in Fig. 1(a). Similar NO conversions were achieved over Co-ZSM-5 using either CH_4 or C_3H_6 at temperatures between 250 and 450°C, while this catalyst showed slightly higher activity at temperatures between 450 and 625°C when C_3H_6 was the reducing agent.

NO conversion increased with increasing temperature, reached a maximum, and then decreased again. The most effective temperature, defined as the temperature of the maximum NO conversion, was around 450°C over Co-ZSM-5 using either CH_4 or C_3H_6 as the reducing agent, and 350°C over Cu-ZSM-5 using C_3H_6. The decrease in the catalytic activity at temperatures greater than the most effective temperature could not be related to the deactivation of the catalyst or collapse of the zeolite structure, since the results were repeatable and consistent when the experiments were repeated in an inverse order of temperature. The decrease in catalytic activity at high temperatures is thought to be due to a change in reaction mechanism or an increase in the oxidation rate of C_3H_6 at higher temperatures.

Fig. 1(b) reveals that the maximum C_3H_6 conversion and the maximum NO conversion occurred simultaneously when either Cu-ZSM-5 or Co-ZSM-5 catalyst was used. NO conversions of 85 and 56% were achieved over Cu-ZSM-5 and Co-ZSM-5, respectively, although the catalysts appeared to be more active for C_3H_6 oxidation than NO reduction over the entire range of temperature. Both catalysts were very active for C_3H_6 oxidation even at temperatures as low as 250°C, achieving 55 and 40% C_3H_6 conversions, respectively. The C_3H_6 oxidation then increased rapidly with increasing temperature. However, CH_4 oxidation over both catalysts was less than 10% at this temperature. In addition, Cu-ZSM-5, which was less active for NO reduction by CH_4, was a more effective catalyst for CH_4 oxidation than Co-ZSM-5 at temperatures between 250 and 500°C. This indicates that the CH_4 oxidation is not a precursor for reduction of NO over Cu-ZSM-5 or the copper active sites may be competing for oxidation of CH_4 rather than for reduction of NO.

It was found that activities of Co-ZSM-5 zeolite for NO reduction using either CH_4 or C_3H_6 were about the same, of 54%, at the most effective temperature. Witzel et al. [14] also investigated the activity of Co-ZSM-5 by either CH_4 or i-C_4H_{10} and reported that the maximum NO conversions achieved were 62 and 88%, respectively. Fig. 2 compares NO conversions obtained in the present work using CH_4 or C_3H_6 with the data reported by Witzel et al. [14]. Although contact times were shorter, Witzel et al. achieved much higher NO conversions. Higher NO conversions were achieved with i-C_4H_{10} as compared to CH_4 or C_3H_6.

Cu-ZSM-5 was reported to be very different in its response to different hydrocarbons, achieving maximum 40% NO conversion if ethene was present [15],

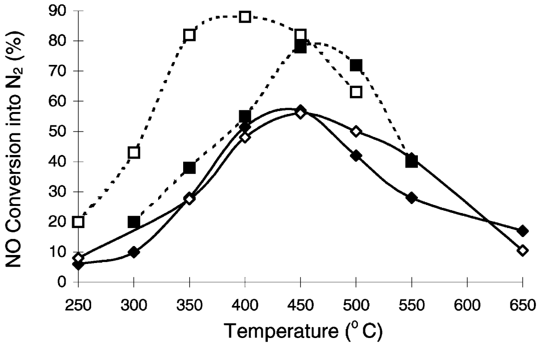

Fig. 2. Dependence of NO conversion on temperature for SCR of NO over Co-ZSM-5 using CH_4 or C_3H_6 in the present work (solid-lines) and using CH_4 or i-C_4H_{10} reported by Witzel et al. [14] (dashed-lines): (■), Co-ZSM-5-22–35 using CH_4; (□), Co-ZSM-5-22-35 using i-C_4H_{10}; (◇), H-Co-ZSM-5-40-45 using C_3H_6; (◆), H-Co-ZSM-5-40-45 using CH_4. Reaction conditions of in the present work: 2000 ppm NO; 2000 ppm CH_4 or C_3H_6; 2% O_2, balanced by He; 1.0 g catalyst; 100 ml min^{-1} total flow rate. Reaction conditions of Witzel et al. work: 2000 ppm NO; 8000 ppm CH_4 or 2000 ppm i-C_4H_{10}; 10% O_2, balanced by He; 0.25 g catalyst; and 75 ml min^{-1} total flow rate.

70% when C_3H_6 was used [8] and was a non-selective catalyst when methane was used in the reaction system [12]. d'Itri and Sachtler [16] confirmed that CH_4 has a non-selective nature for NO reduction over H-Cu-ZSM-5 catalyst prepared via the impregnation method.

Adelman et al. [17] reported that different types of adsorbed nitrogen oxide complexes could be formed over Co-ZSM-5 and Cu-ZSM-5 catalysts when these catalysts were exposed to a mixture of NO and O_2. These complexes were collectively called NO_y. It was believed that due to the different chemistry induced by these catalysts, the types of the complexes formed were different. They employed Fourier transform infrared (FTIR) spectroscopy technique to identify the type of NO_y complexes formed on the surfaces of these catalysts [17]. It was shown that both nitro or nitrito complexes can form over both catalysts, but prominent complexes formed over Co-ZSM-5 were O bound nitrito complexes ($Co^{2+}\cdot ONO$) whereas predominant complexes on Cu-ZSM-5 were N bound nitro complexes ($Cu^{2+}\cdot NO_2$). This produced a variety of Cu species in ZSM-5 including Cu^{2+} ions, oxo-complexes and oxide clusters. CH_4 can react with nitrito groups ($Co^{2+}\cdot ONO$) but not with the complexes formed over Cu-ZSM-5. This could be the reason why CH_4 is an effective reducing agent for SCR of NO over Co-ZSM-5 but not over Cu-ZSM-5. On the other hand, higher alkanes can react with different NO_y complexes. Therefore, these reducing agents are suitable for SCR of NO over both Cu-ZSM-5 and Co-ZSM-5 catalysts.

3.2. SCR of NO by C_3H_6 over Cu-ZSM-5 zeolites

SiO_2/Al_2O_3 ratio is reported to determine the number of Brönsted acid sites and ion-exchange capacity of ZSM-5 zeolite [18]. Therefore, the performance of an ion-exchanged ZSM-5 zeolite can be a function of the SiO_2/Al_2O_3 ratio and cation loading (or ion-exchange level).

The effect of ion-exchange level on the activity of Cu-ZSM-5 for SCR of NO in the presence of ethene and propene was reported by Sato et al. [15] and Kharas [19]. Sato et al. [15] showed that the activity of Cu-ZSM-5 catalysts increased with increasing Cu ion-exchange level up to 80–100% when ethene was used as the reducing agent, but levelled off when the ion-exchange level increased beyond 100%. Kharas [19] also reported that the most effective catalysts for reduction of NO using propene had ion-exchange levels between 150 and 200. The effect of SiO_2/Al_2O_3 ratio on the activity of Cu-ZSM-5 prepared from the H-form of zeolite by propene was also investigated by Torre-Abreu et al. [18], who suggested that the catalytic activity increased with decreasing SiO_2/Al_2O_3 ratio. In order to ascertain the effects of SiO_2/Al_2O_3 ratio and cation loading, performance of a range of catalysts prepared from the Na-form of Cu-ZSM-5 for SCR of NO using C_3H_6 were investigated in this work. The reactor inlet gas flow rate was 150 ml min^{-1}, giving a contact time of 0.4 g s ml^{-1}.

3.2.1. The effect of SiO_2/Al_2O_3 ratio

Three over-exchanged samples of Cu-ZSM-5 zeolite (Na form) catalysts with different SiO_2/Al_2O_3 ratios of 176, 140 and 100 but the same copper loading (i.e. about 1.3 wt.%) were prepared and tested. Accordingly, their Cu ion-exchange levels were 199.2, 160.7 and 127.5%, respectively. The dependence of catalytic performance on SiO_2/Al_2O_3 ratio of these catalysts is shown in Fig. 3. The results reveal that increasing the SiO_2/Al_2O_3 ratio led to a slight increase in NO conversion. This was in contrast to the results

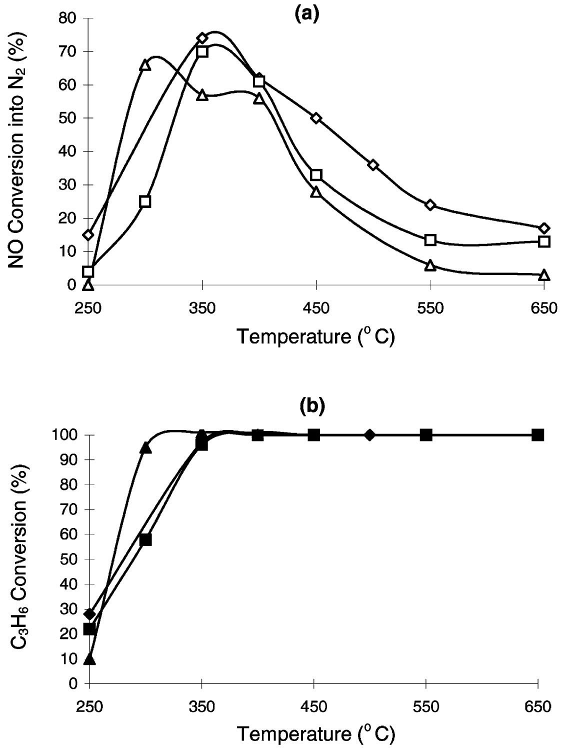

Fig. 3. Dependence of (a) NO conversion and (b) C_3H_6 conversion, on temperature and SiO_2/Al_2O_3 ratio for SCR of NO various catalysts with the same copper loading (1.3%): (▲, △), Cu-ZSM-5-100-127.5; (■, □), Cu-ZSM-5-140-160.7; (◆,◇), Cu-ZSM-5-176-199.2. Reaction conditions: 2000 ppm NO; 2000 ppm C_3H_6; 2% O_2, balanced by He; 1.0 g catalyst weight; and 150 ml min^{-1} total flow rate.

obtained over H-form by Torre-Abreu et al. [18] who reported that a catalyst with SiO_2/Al_2O_3 ratio of 54 was the most active catalyst among catalysts with the same copper loading and SiO_2/Al_2O_3 ratios of 22, 54, 90 and 200. However, they examined only one catalyst with SiO_2/Al_2O_3 ratio greater than 100.

The most effective temperature for SCR of NO slightly decreased with decreasing SiO_2/Al_2O_3 ratio. This temperature was 350°C for both catalysts with higher SiO_2/Al_2O_3 ratios, i.e. 176 and 140, and was 300°C for the catalyst with a SiO_2/Al_2O_3 ratio of 100. The maximum NO conversion and the complete C_3H_6 oxidation occurred at the same temperature. Torre-Abreu et al. [18] reported that the most effective temperature decreased when the SiO_2/Al_2O_3 ratio increased. Their data reveals that for under-exchanged catalysts, this temperature decreased from 500 to 350°C and was 350°C for Cu-ZSM-5-90–140 and Cu-ZSM-5-200-280 catalysts.

Propene conversion showed the same trend as that of NO conversion into N_2 at temperatures lower than the most effective temperature, as shown in Fig. 3(b). For example, the total propene oxidation was low at low temperatures where NO conversion was low, and increased sharply to 100% where the maximum conversion of NO of 70–78% occurred. The conversion of NO decreased with further increasing temperature, while the conversion of propene remained 100% due to competition of propene oxidation reaction with NO reduction.

3.2.2. The effect of copper loading

Fig. 4 indicates the variation of NO conversions with Cu/Al ratio at 350, 450 and 550°C over four Cu-ZSM-5 catalysts with a SiO_2/Al_2O_3 ratio of 100 but different copper ion-exchange levels. It is shown that the NO conversion for over-exchanged Cu-ZSM-5 catalysts decreased with an increase in copper ion-exchange level at the same temperature. The effect of the copper ion-exchange level is more pronounced at lower temperatures, as observed in [17].

NO conversion as a function of temperature is shown in Fig. 5 for over-exchanged samples. It is seen that increasing copper loading results in a decrease in catalytic activity. It is clear that among Cu-ZSM-5 catalysts prepared from Na-form of ZSM-5 zeolites

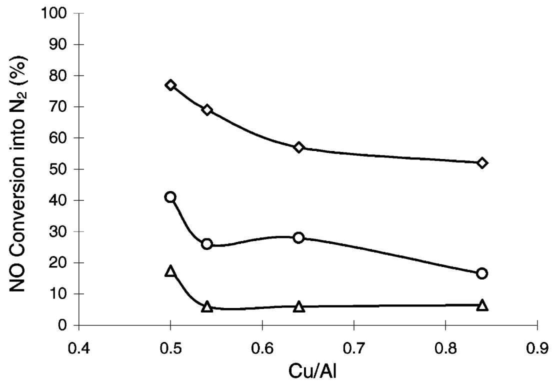

Fig. 4. NO conversion over Cu-ZSM-5-100 catalysts with varying Cu/Al ratio at different temperatures: (◇), 350°C; (○), 450°C; and (◇) 550°C. Reaction conditions: 2000 ppm NO; 2000 ppm C_3H_6; 2% O_2, balanced by He; 1.0 g catalyst weight; and 150 ml min^{-1} total flow rate.

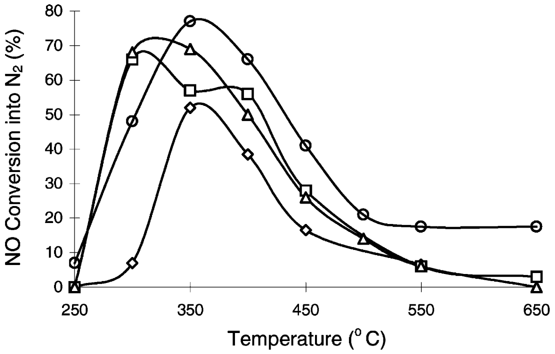

Fig. 5. Dependence of NO conversion on temperature over catalysts of the same SiO_2/Al_2O_3 ratio (100) but varying copper loading for SCR of NO using C_3H_6: (○), Cu-ZSM-5-100-99; (△), Cu-ZSM-5-100-108.3; (□), Cu-ZSM-5-100-127.7; (◇), Cu-ZSM-5-100-168.6. Reaction conditions: 2000 ppm NO; 2000 ppm C_3H_6; 2% O_2, balanced by He; 1.0 g catalyst weight; and 150 ml min^{-1} total flow rate.

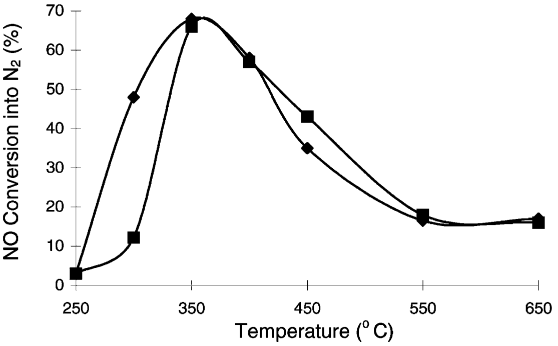

Fig. 6. Dependence of NO conversion on temperature and copper loading over catalysts prepared from H-ZSM-5 zeolites with a SiO_2/Al_2O_3 ratio of 50 for SCR of NO using C_3H_6: (■), H-Cu-ZSM-5-50-77; (◆), H-Cu-ZSM-5-50-99.3. Reaction conditions: 2000 ppm NO, 2000 ppm C_3H_6; 2% O_2, balanced by He; 1.0 g catalyst weight; and 150 ml min^{-1} total flow rate.

with the same SiO_2/Al_2O_3 ratio, the highest activity is shown by a catalyst with 100% copper ion-exchange.

Dedecek et al. [20] believed that the activity of the copper ions relates to the Al atoms which form localised Bronsted acid sites in the zeolite. They reported that Cu sites in ZSM-5 zeolites were associated with two environments, depending on the number of aluminium atoms in the vicinity of the copper site. When a copper ion was adjacent to one Al atom a square planer coordination was assumed to form from a $(Cu^{2+}–OH)^+$ precursor. The other form of coordination was a square pyramidal coordination which was exhibited by a copper site balanced by two framework Al atoms. The Cu site distribution changes in different samples depending on Cu loading and SiO_2/Al_2O_3 ratio. Dedecek et al. [20] assigned those sites adjacent to single framework Al atoms to Cu sites responsible for the Cu over-exchange. These sites are also well occupied below 100% copper exchange level. They concluded that these sites are responsible for the high activity of Cu-ZSM-5 in the direct decomposition of NO, as NO decomposition increases by increasing catalyst copper loading. It is postulated that these sites may not attribute to the activity of the catalyst for SCR, as it is shown that the performance of Cu-ZSM-5 catalysts decreases by increasing copper loading.

Torre-Abreu et al. [18] employed electron spin resonance (ESR) technique to determine the oxidation state of copper ions in zeolite. They reported that copper mainly existed as isolated Cu^{2+} in the catalysts with ion-exchange levels less than 100%, while in over-exchanged catalysts, Cu^+ ions and CuO were also detected.

In order to investigate the effect of copper loading on the performance of the catalysts prepared from the H-form of ZSM-5 zeolite for SCR of NO using propene, two catalysts with copper ion-exchange levels of 77 an 99.3 were prepared from H-ZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 50. As shown in Fig. 6, the maximum NO conversion achieved over both catalysts was 68%, indicating that increasing ion-exchange level from 77 to 99.3% did not improve the maximum NO conversion. However, the catalyst with a higher copper ion-exchange level was more active at temperatures between 250 and 350°C, and slightly less active at temperatures between 400 and 550°C. The most effective temperature over both catalysts was 350°C, the same as that obtained for the catalyst prepared from the Na-form. Achieving the same maximum conversion over the catalysts with copper ion-exchange level of almost 80–100% reveals that SCR of NO over copper ion-exchanged zeolites prepared from H-form by propene is similar to SCR of NO using ethene as reported by Sato et al. [15].

Fig. 7 shows NO conversion as a function of temperature for two catalysts, Cu-ZSM-5-140-160.8 and Cu-ZSM-5-100-168.6, with almost the same copper ion-exchange level but different SiO_2/Al_2O_3 ratios

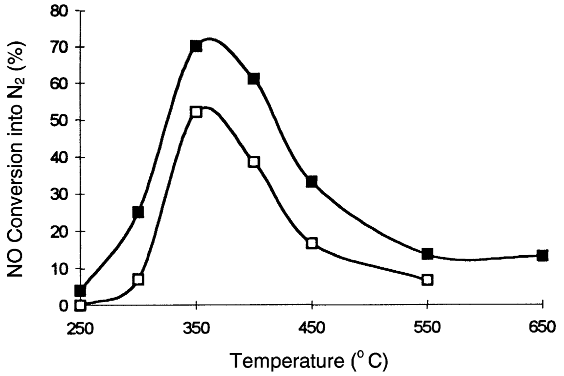

Fig. 7. Dependence of NO conversion on temperature for two samples of Cu-ZSM-5 with the same copper ion-exchange level but different SiO_2/Al_2O_3 ratios using C_3H_6: (■), Cu-ZSM-5-140-160.7 and (□) Cu-ZSM-5-100-168. Reaction conditions: 2000 ppm NO, 2000 ppm C_3H_6; 2% O_2, balanced by He; 1.0 g catalyst weight; and 150 ml min^{-1} total flow rate.

were also tested. Note that they also had different copper loadings, i.e. 1.58 and 1.24 wt.%, respectively. The results obtained over the two catalysts revealed that the catalyst with the higher SiO_2/Al_2O_3 ratio and lower copper loading showed better performance as indicated in Fig. 7. This is in agreement with the results obtained in previous sections that a higher SiO_2/Al_2O_3 ratio combined with a lower Cu loading causes a higher activity for a catalyst.

It can be concluded that for over-exchanged catalysts, the effect of Cu ion-exchange level or cation loading depends on the SiO_2/Al_2O_3 ratio of the catalyst. For catalysts with the same Cu loading (Fig. 3), the activity of the catalysts increased with increasing SiO_2/Al_2O_3 ratio. However, for catalysts with the same SiO_2/Al_2O_3 ratios (Fig. 4), increasing Cu ion-exchange level resulted in a decrease in the activity of the catalysts. It is suggested that both SiO_2/Al_2O_3 ratio and Cu loading should be considered together when evaluating a Cu ion-exchanged ZSM-5 zeolite catalyst.

Torre-Abreu et al. [18] concluded that the catalysts with the same Cu ion-exchange level but different Cu loadings and different SiO_2/Al_2O_3 ratios show the same activity for SCR of NO using propene. They came to this conclusion by testing two groups of samples; each group included two samples with ion-exchange levels of 40 and 80%. From the results presented in this section, it is seen that the behaviour of the over-exchanged catalysts prepared from Na-form was different to the catalysts prepared from H-form. For the former with the same Cu ion-exchange level, the higher the SiO_2/Al_2O_3 ratio the higher the activity.

For each experiment, material balance was conducted. However, 100% carbon balance was not achieved for SCR of NO using C_3H_6 at each reaction temperature. There was less carbon in the outlet stream than in the inlet gas at lower temperatures where C_3H_6 was oxidised only partially. For example, as shown in Fig. 7, in an experiment over H-Cu-ZSM-5-140-109.5, 8–10% less carbon was detected in the outlet gas at 250 and 300°C (considering all carbon available in forms of CO_2, C_3H_6 and very small amounts in forms of CO and CH_4). However, at 350°C and at temperatures greater than 350°C, 6–7% more carbon atoms were detected in the output gas than in the input gas. It seems that carbon atoms available on catalyst surface in any form converted to CO_2 where 100% oxidation of C_3H_6 occurred. It is worth noting that at temperatures $\geq$ 350°C, all carbon atoms were converted to CO_2, and neither CO nor other carbon-containing species were detected.

3.3. *SCR of NO by methane over Co-ZSM-5 zeolites*

It is well documented that CH_4 is a non-selective reducing agent for SCR of NO_x over Cu-ZSM-5. Li and Armor [7] found that NO_x could be selectively reduced by CH_4 in the presence of oxygen over a class of metal exchanged zeolites including cobalt. According to Li and Armor [21], two parallel catalytic reactions occur over the catalyst, i.e. NO reduction (reaction 1) and CH_4 combustion (reaction 2). The presence of O_2 was essential for NO reduction.

$$2NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2H_2O \qquad \text{(reaction1)}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{(reaction2)}$$

Li and Armor [21] also pointed out that Co^{2+} ions were responsible for reduction of NO, and catalytic activity of the catalyst was proportional to the Co^{2+} ion-exchange level. They believed that the importance of the Co-ZSM-5 catalyst lies in its ability to reduce NO in the presence of excess O_2, and simultaneously maximising CH_4 combustion rate.

Systematic studies were undertaken with an aim to understand the dependency of Co-ZSM-5 performance on the catalyst preparation method, SiO_2/Al_2O_3 ratio, and Co loading (or ion-exchange level). The experiments were carried out over four groups of Co-ZSM-5 catalysts by passing a gas stream with a total flow rate of 150 ml min^{-1}. Therefore, the contact time was 0.4 g s ml^{-1}.

3.3.1. The Effect of catalyst preparation method

Two samples of Co ion-exchanged ZSM-5 zeolites were prepared using the semi-continuous system and the batch system, respectively. Although these samples were not very different in Co loading, they showed very different abilities to reduce NO using CH_4 as shown in Fig. 8. The NO conversion over the sample prepared using the semi-continuous system was considerably higher than over the sample prepared using the batch system over the entire range of temperatures. The maximum NO conversion of the former was about twice that of the latter sample. The low activity of the catalyst prepared via the batch system could be due to precipitation of cobalt acetate or cobalt hydroxide in zeolite pores or on the external surface of the zeolite. Evaporation of acetic acid and water at the ion-exchange temperature, i.e. 80°C, may have led to saturation of the cobalt acetate solution. Precipitation of cobalt hydroxide from all Co^{2+} salts may also occur. Therefore, even the sample with 10% more Co loading but the same SiO_2/Al_2O_3 ratios showed less catalytic activity.

3.3.2. The effect of SiO_2/Al_2O_3 ratio

Two samples with SiO_2/Al_2O_3 ratios of 80 and 40, and with 1% Co loading were prepared using the semi-continuous system. Fig. 9 compares the catalytic performance of the two H-Co-ZSM-5 catalysts over a wide range of temperatures. The maximum NO conversion occurred at 450°C for both catalysts, indicating that the most effective temperature was independent of the SiO_2/Al_2O_3 ratio of the catalysts. The results revealed that the NO conversion over the catalyst increased with decreasing SiO_2/Al_2O_3 ratio.

Increasing the activity of Co-ZSM-5 zeolite by decreasing the SiO_2/Al_2O_3 ratio was also reported by Li and Armor [22]. They came to this conclusion

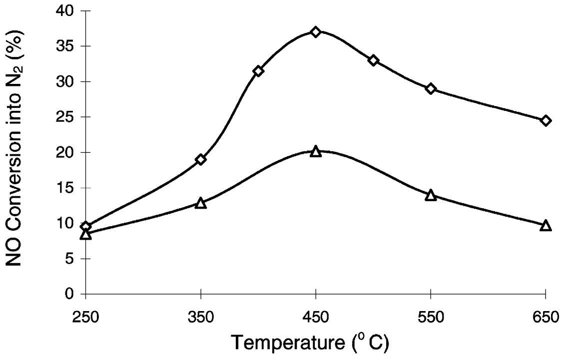

Fig. 8. Effect of catalyst preparation on SCR of NO using CH_4 over Co-ZSM-5 catalysts of the same SiO_2/Al_2O_3 ratio: (△), catalyst prepared using the batch method and (◇) catalyst prepared using the semi-continuous method. Reaction conditions: 2000 ppm NO; 2000 ppm CH_4; 2% O_2, balanced by He; 1.0 g catalyst weight; 150 ml min^{-1} total flow rate.

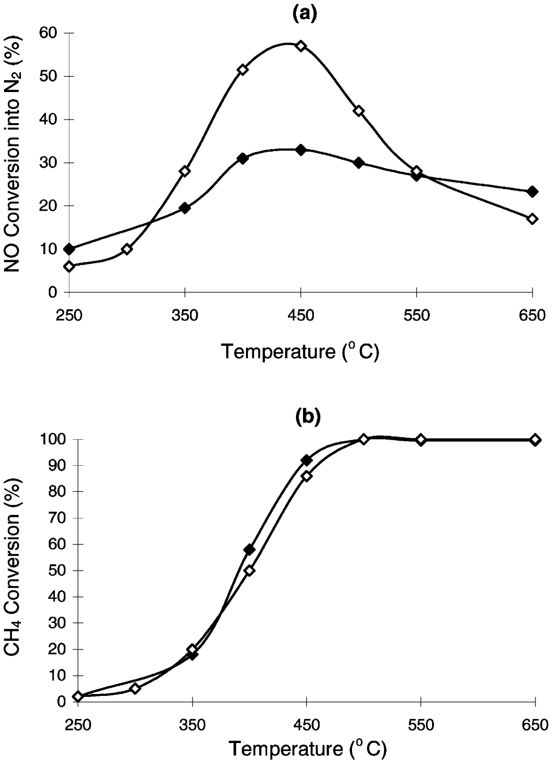

Fig. 9. Dependence of (a) NO conversion and (b) CH_4 conversion, on temperature for SCR of NO over catalysts of the same Co loading (1%) but different SiO_2/Al_2O_3 ratios: (◇), Co-ZSM-5-40-45 and (◆) Co-ZSM-5-80-96.6. Reaction conditions: 2000 ppm NO; 2000 ppm CH_4; 2% O_2, balanced by He; 1.0 g catalyst weight; and 150 ml min^{-1} total flow rate.

by conducting the experiment over three over-exchanged Co-ZSM-5 catalysts and considering that excess amounts of Co ions did not contribute to the NO reduction. In other words, they assumed that the NO conversion obtained over the over-exchanged catalysts served the activity of the fully exchanged catalysts. The suggested trend was correct, however, they did not consider that increasing Co loading may result in decreasing the activity of the catalysts.

Methane conversion was very low at temperatures as low as 250°C, increased slightly up to 350°C, and then increased sharply. Complete conversion of CH_4 was observed at 500°C. The highest NO conversions over the catalysts were achieved where the CH_4 combustion was not completed, indicating that the selectivity of the catalyst for NO conversion into N_2 is higher than that of CH_4 oxidation reaction.

3.3.3. *The effect of Co loading*

Three catalysts with different Co loadings were prepared from an H-form of ZSM-5 with a SiO_2/Al_2O_3 ratio of 80. The Co ion-exchange level of the catalysts varied from 71 to 428%. Fig. 10 compares NO conversions versus temperature for SCR of NO over the three catalysts using CH_4. Although similar conversion profiles were obtained, the NO conversion did not appear to decrease with increasing Co loading. Despite of the vastly different Co loadings, the most effective temperature was the same in all three cases, i.e. 450°C.

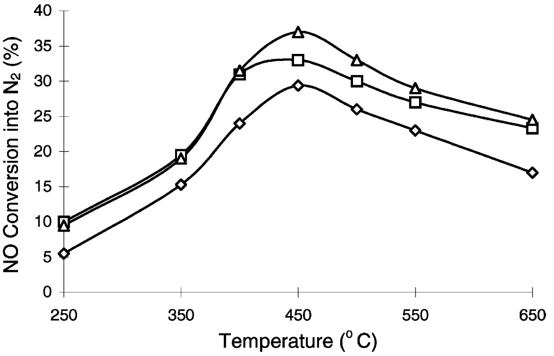

Fig. 10. Dependence of NO conversion on temperature for SCR of NO using CH_4 over catalysts of the same SiO_2/Al_2O_3 ratio but different Co loading: (△), H-Co-ZSM-5-80-71; (□), H-Co-ZSM-5-80-96.6; and (◇), H-Co-ZSM-5-80-428. Reaction conditions: 2000 ppm NO; 2000 ppm CH_4; 2% O_2, balanced by He; 1.0 g catalyst weight; and 150 ml min^{-1} total flow rate.

The performance of the catalysts for the two under-exchanged catalysts was similar at temperatures below 400°C but slightly different at higher temperatures. The catalyst with very high Co loading showed less activity over the whole range of temperatures.The effect of Co loading on the performance of Co-ZSM-5 catalysts with CH_4 was different from that of Cu-ZSM-5 when C_3H_6 was used as shown in Figs. 3 and 10, respectively. For Co-ZSM-5, the catalysts became less active with increasing Co loading for over-exchanged samples while the results obtained over Cu-ZSM-5 showed an opposite trend. This could be due to different reaction mechanisms. Li and Armor [22] reported that a redox process could not involve the reduction of NO over Co-ZSM-5. They also believed that the active site was a single Co^{2+} cation. This is different from the reaction mechanism over Cu-ZSM-5 because it is believed that a redox mechanism is involved for the reduction over Cu-ZSM-5 catalysts.

The most effective temperatures for SCR of NO by CH_4 over H-Co-ZSM-5 catalysts are much higher than the most effective temperatures of Cu-ZSM-5 using C_3H_6 as the reducing agent. This could be due to the high stability of CH_4, which is related to the strong C–H bond (422 kJ mol^{-1}). Therefore, high temperatures are required to activate CH_4.

4. Conclusions

The effects of SiO_2/Al_2O_3 ratio and cation loading (or ion exchange level) on the performance of Cu-ZSM-5 and Co-ZSM-5 zeolites for SCR of nitric oxide (NO) have been studied. For Cu-ZSM-5 catalysts, propene is the effective reducing agent for NO deposition, while for Co-ZSM-5 catalysts, methane is preferred. The activity, as indicated by NO conversion to N_2, of Cu-ZSM-5 increases with increasing SiO_2/Al_2O_3 ratio when the catalysts have similar Cu ion loading. The maximum NO conversion decreases with increasing Cu ion-exchange level when the catalysts have the same SiO_2/Al_2O_3 ratio. For Co-ZSM-5 catalysts with the same Co loadings, however, the NO conversion increases with decreasing SiO_2/Al_2O_3 ratio. With the same SiO_2/Al_2O_3 ratios, the NO conversion decreases with increasing Co loading. The performance of Co ion-exchanged catalysts also depends on the preparation method: catalysts prepared in the semi-continuous system show a high activity than those from the batch system, although they have the same SiO_2/Al_2O_3 ratios and cobalt ion-exchange levels. The oxidation of the reducing agents is enhanced by NO in the presence of the catalysts. They become completely oxidised before maximum NO decomposition occurs.

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