

Activity and characterization of bimetallic ZSM-5 for the selective catalytic reduction of NO_x

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Abstract

Bimetallic catalyst, Pt-Cu-ZSM5 was prepared, tested and characterized for the selective catalytic reduction of NO_x with *i*-C₄H₁₀ in excess of oxygen. The bimetallic catalyst was found to offer wider temperature window than that of monometallic catalysts, Pt-ZSM5 and Cu-ZSM5, respectively, for optimum reduction of NO. More than 50% of NO conversion was obtained in the temperature range of 250–520 °C. Even though the catalyst appeared to be unaffected by the excess oxygen and high space velocity, it was prone to deactivation in water vapor and sulfur dioxide. The formation of nitrous oxide as a major by product was also favorable at low temperatures. Characterization of the bimetallic catalyst suggested that copper and platinum species existed independently in the form of metal particles and metal oxides while successive metal loadings seemed to cause loss of some acid sites.

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1. Introduction

Emission of nitrogen oxides (NO_x) from diesel engine vehicles is a major environmental concern especially in view of the increasingly stringent limits adopted world-wide [1,2]. Selective catalytic reduction using a hydrocarbon as a reducing agent (HC-SCR) has been widely proposed as one of the promising techniques [2–4].



The technique eliminates the use of ammonia and its associated risk of storage commonly used in the selective catalytic reduction (SCR) process at nitric

acid or power plants. Besides, the availability of unburned hydrocarbons in diesel exhaust can be utilized as a reducing agent. Unfortunately, catalysts that suit the reduction process in diesel exhaust environment have not been found. Transition metals supported on ZSM-5 zeolite such as Cu-ZSM5, Co-ZSM5, Ni-ZSM5 and Fe-ZSM5 appear to have received much attention in many reported studies [3,5]. One of the major drawback is that these catalysts operate in a narrow temperature window for optimum reduction of NO_x. Co-ZSM5 and Ni-ZSM5 work actively at high temperature range of 450–500 °C to achieve more than 50% of NO_x reduction [5–8]. The most intensely studied catalyst, Cu-ZSM5, obtained more than 50% of NO_x conversion in 350–500 °C and virtually inert at temperatures below 300 °C [5,9–12]. Fe-ZSM5 that could tolerate the presence of water vapor operates at 300–400 °C to achieve around

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80% of NO_x conversion [5,13–16]. Unlike transition metals, Pt loaded on ZSM5 could achieve high NO_x conversion at a much lower temperature of around 200 °C [17]. Nevertheless, Pt-ZSM5 was not active at temperatures above 300 °C. There appears to be no catalyst possessing temperature window that is wide enough to suit diesel exhaust of around 150–500 °C.

The present study attempts to evaluate activities of ZSM5 zeolite loaded with both Pt and Cu for the reduction of NO especially with respect to the operating temperature window. The most active of sample of bimetallic catalysts was further subjected to catalytic activity measurement under a range of oxygen composition, space velocity and in the presence of water vapor and sulfur dioxide (SO_2). Temperature-programmed desorption (TPD) experiments were carried out to determine the strength of acid sites in comparison with monometallic catalysts. X-ray photoelectron spectroscopy (XPS) was used to characterize oxidation states of metal species in the bimetallic catalyst.

2. Experimental

2.1. Catalyst preparation

Three samples of bimetallic catalysts were prepared by successive loading of metal species into the zeolite support, H-ZSM5 (Si/Al ratio 90) (supplied by Süd-Chemie AG, Munich). The first sample was prepared by wet ion exchange (WIE) of platinum into the support and followed by impregnation (IMP) with copper (WIE–IMP method). The second sample was prepared by reversing the metal loading where copper was first ion exchanged and followed by impregnation with platinum. The third sample was prepared by successive wet ion exchanges (WIE–WIE method) of platinum and copper, respectively. In essence, 10 g of

H-ZSM5 zeolite and 100 ml of respective metal solutions (0.01 M copper nitrate and 0.003 M chloroplatinic acid) were used during WIE process and 10 ml of the same solution was used during IMP process. The WIE process was carried out in three 24 h stages with vacuum filtration in between stages before drying overnight in static air at 110 °C. The IMP process was carried out at 80 °C in the rotavapor set (Buchi model R114) until the slurry became completely dry and free flowing. Samples were calcined in static air by increasing the temperature step-wise at 10 °C/min and held at 500 °C for 1 h. For references, monometallic catalysts, Pt-ZSM5 and Cu-ZSM5 were also prepared using the WIE method. Samples were analyzed in nitrogen adsorption isotherm (Autosorb 1C) and electron dispersive X-ray technique (Editor Camscan) to examine their physical properties and chemical composition, respectively, as presented in Table 1. The powder form of all samples were made into granular forms by pressing under 3–5 tonnes, meshed into 250–355 μm size before catalytic activity measurements.

2.2. Catalytic activity measurement

Catalytic activity measurements were carried out in a micro-catalytic reactor (SS tube and 6 mm diameter), horizontally placed in a mini tubular furnace (Lindberg Blue M). In situ pre-treatment was carried out in flowing H_2 (100 ml/min) at 450 °C for 4 h for reduction of metal oxides to metal form. Type K thermocouple connected to digital scanning thermometer (Cole Palmer model 92000-05) measured the catalyst bed temperature. Mass flow control system (MKS type 1179A controllers connected to MKS type 247 4-channel control box) was used to prepare a feed gas mixture of 1000 ppm NO, 1500 ppm *i*- C_4H_{10} , 3% O_2 , 50 ppm SO_2 (whenever desired) and balanced by N_2 . Water vapor was introduced into the feed stream by passing through a water trap kept in a constant

Table 1
Physical and chemical properties of catalyst samples

Sample	Catalyst	Method	BET area (m^2/g)	Micro volume (cm^3/g)	Metal Pt	(wt.%) Cu
1	Pt-Cu-ZSM5	WIE–IMP	360	0.42	3.5	1.1
2	Cu-Pt-ZSM5	WIE–IMP	369	0.61	4.3	0.9
3	Pt-Cu-ZSM5	WIE–WIE	385	0.47	4.1	0.8
4	Pt-ZSM5	WIE	359	0.55	5.7	–
5	Cu-ZSM5	WIE	370	0.51	–	4.6

temperature water bath. Online gas chromatograph (Shimadzu 8A) equipped with Porapak Q column (80/100 mesh size) and Molecular Sieve 5A was used for analysis of gas (N_2 , O_2 , $i-C_4H_{10}$, N_2O and CO_2) at the inlet and outlet of the reactor. ENERAC 2000E emission gas analyzer was used to measure online concentrations of NO in ppm at the inlet and outlet stream. Percentage of conversion was calculated from the difference in the inlet and outlet concentration of NO (C_{in} and C_{out}) while the formation of CO_2 was assumed mainly from the conversion of $i-C_4H_{10}$.

$$\% \text{ NO conversion} = \frac{C_{in} - C_{out}}{C_{in}} \quad (2)$$

2.3. Catalyst characterization

TPD analysis using Chembet 3000 (Quantachrome) was made to compare acidity profiles of the most active bimetallic sample with monometallic catalysts. Samples for the analysis were pre-treated by heating at $10^\circ\text{C}/\text{min}$ to 500°C in helium flow of 80 ml/min to remove water vapor and other possible impurities. NH_3 adsorption (1% NH_3 in helium) was allowed for an hour at room temperature. Desorption was then performed by linearly increasing the sample temperature at the rate of $10^\circ\text{C min}^{-1}$ to 700°C , during which signals were recorded by the thermal conductivity detector. The bimetallic sample with remarkable activity was further examined under X-ray photoelectron

spectroscopy (Kratos XSAM-HS) equipped with Vision 1 software (Kratos, UK) to study the oxidation states of active metal species. Ultra-vacuum conditions were employed where pre-treatment was carried out overnight at 10^{-7} Torr before analysis at 10^{-9} Torr. The excitation energy was from Mg $K\alpha$ (1253 eV) with scanning performed at 160 eV (wide scan) and 40 eV (narrow scan). Intensity peaks were curved fitted from the Gaussian linear base-line and corrected with respect to graphite carbon, C 1s, at 284.5 eV.

3. Results and discussion

3.1. Catalytic activities

Fig. 1 shows temperature profiles of bimetallic catalysts as compared with monometallic Pt-ZSM5 and Cu-ZSM5 for the reduction of NO. Pt-ZSM5 was clearly active in the low temperature region with maximum NO conversion of 70% at 250°C . Further increase in the temperature caused immediate drop in the NO conversion, which became negligible above 500°C . On the other hand, Cu-ZSM5 had negligible NO conversion below 250°C before a drastic increase to almost 100% conversion at 350°C . The NO conversion remained relatively high even though there was a slight decline as temperatures were further increased. These results on Cu-ZSM5 and Pt-ZSM5 agreed quite well with reported results [9–11,17]. The first

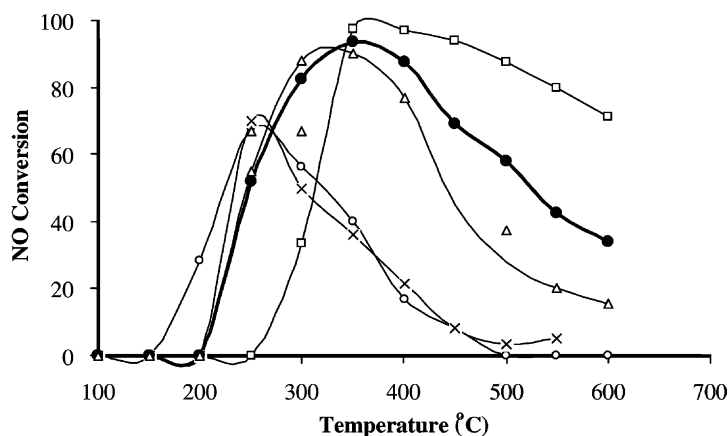


Fig. 1. Temperature profiles of tested catalysts: (x) Pt-Cu-ZSM5 (WIE-IMP), (●) Pt-Cu-ZSM5 (WIE-WIE), (Δ) Cu-Pt-ZSM5 (WIE-IMP), (□) Cu-ZSM5 and (○) Pt-ZSM5. Experimental conditions: 1000 ppm NO, 1500 ppm $i-C_4H_{10}$, 3% O_2 in N_2 at GHSV $20,000 \text{ h}^{-1}$ (0.18 g of catalyst bed at 100 ml min^{-1}).

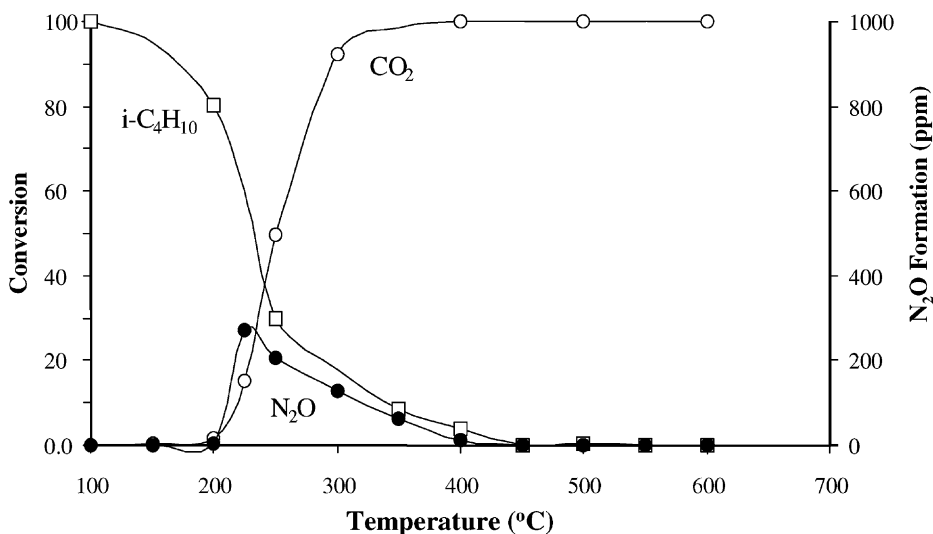


Fig. 2. Conversion of *i*-butane into carbon dioxide and formation of nitrous oxide during HC-SCR of NO_x . Pt-Cu-ZSM5 (WIE–WIE) was used in experimental conditions described in Fig. 1.

bimetallic catalyst, Pt-Cu-ZSM5 (WIE–IMP), showed almost the same temperature profile as Pt-ZSM5 with the maximum NO conversion of 70% at 250 °C. This might suggest that the addition of copper through impregnation did not contribute to the reduction of NO. The significantly low content of copper in the sample might also cause low activity in the high temperature region. Temperature profiles of Cu-Pt-ZSM5 (WIE–IMP) and Pt-Cu-ZSM5 (WIE–WIE) seemed

to show synergistic effects of copper and platinum. In both samples, the range of temperature for optimum NO reduction was expanded. Pt-Cu-ZSM5 (WIE–WIE), offered the largest operating window than any other samples where more than 50% NO could be reduced over 250–500 °C region.

Regardless of the type of catalysts, their temperature profiles illustrated the general trend of catalytic activity for the reduction of NO. The declining NO

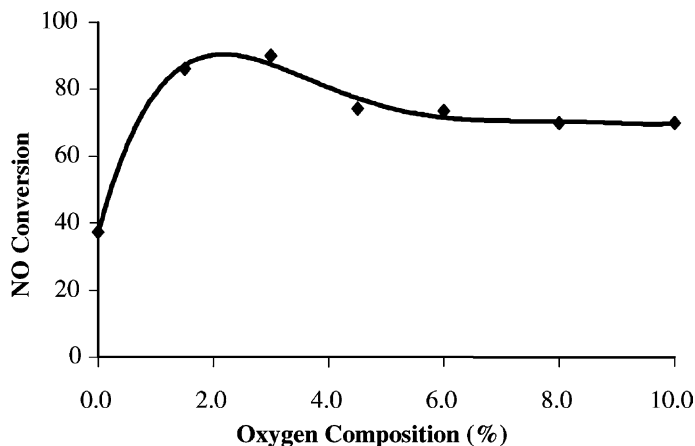


Fig. 3. Effect of oxygen composition on the NO reduction with sample 3.

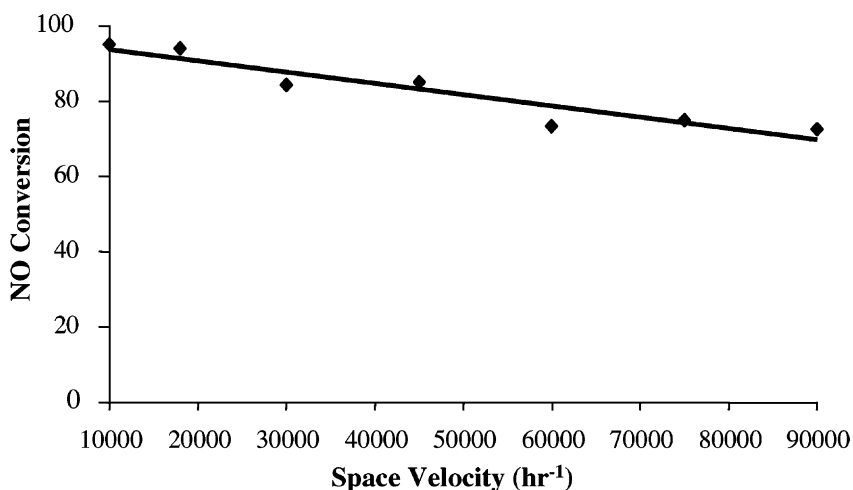


Fig. 4. Effect of space velocity on NO reduction with sample 3.

conversion efficiency at high temperature was primarily attributed to excessive oxidation of hydrocarbon outside zeolite pores as reflected by the increasing formation of CO_2 shown in Fig. 2. Besides, the relatively high temperature environment would possibly inhibit adsorption of intermediate species on the catalyst surface for the SCR process. It was also observed that the high reduction of NO was accompanied by some formation of nitrous oxide, N_2O , a renowned by-product of Pt-based catalyst at low temperatures [18].

Nevertheless, nitrogen gas was assumed to be the major product of NO reduction since other potential products such as NO_2 and CO were found to be negligible.

The most active bimetallic catalyst, Pt-Cu-ZSM5 (WIE–WIE) was further tested to evaluate the effect of oxygen content and space velocity. Figs. 3 and 4 show that the catalyst appeared to be unaffected by increasing composition of oxygen or increasing space velocity. In fact, NO conversion was favored in the presence

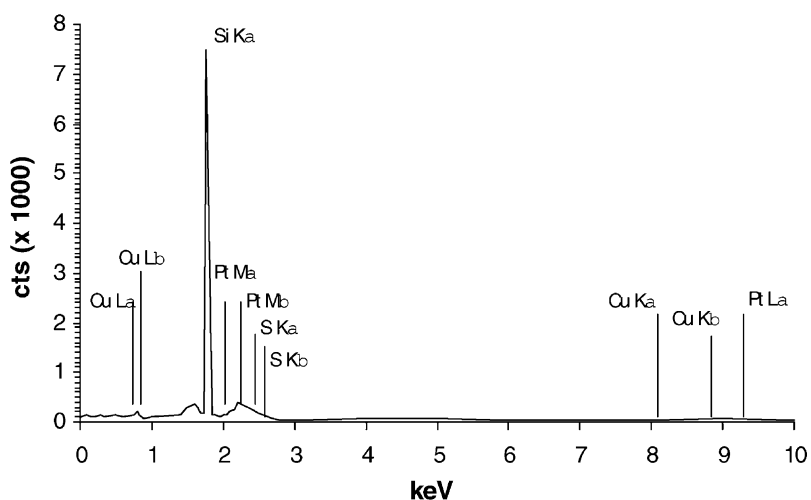


Fig. 5. Effect of the presence of water vapor or SO_2 on the activity of sample 3.

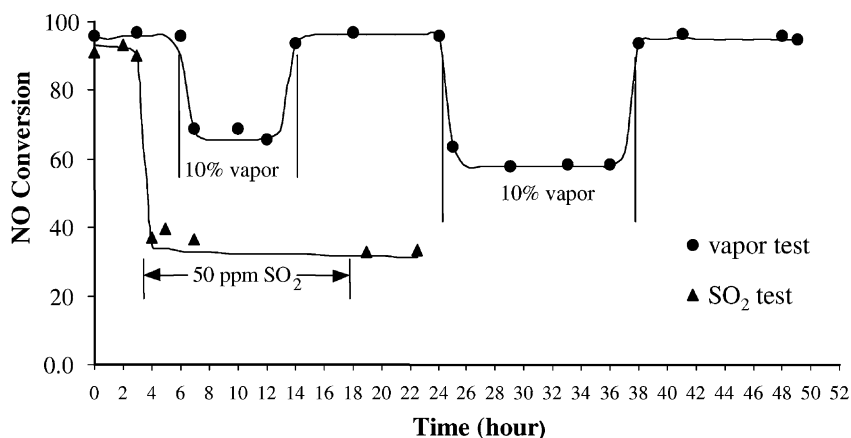


Fig. 6. EDAX spectrum of sample 3 after exposure to SO_2 . Traces of SO_2 adsorption were detected at about 2.65 keV

of oxygen, in which the NO conversion jumped from 40% in the absence of oxygen to 90% in the presence of 2% oxygen. Further increase in the oxygen concentration did not affect the high selectivity towards reduction of NO where the conversion level was maintained around 70%. This was a clear advantage over monometallic catalyst, Cu-ZSM5, which became less selective for the reduction of NO in the presence of a large amount of oxygen [19,20]. The high reduction of NO with the bimetallic catalyst was also maintained over a large range of space velocity, varied by changing the amount of catalyst in the micro-reactor.

There was only 20% drop in the NO conversion level as the space velocity was increased from $10,000 \text{ h}^{-1}$ to $90,000 \text{ h}^{-1}$.

Fig. 5 illustrates the performance of the bimetallic catalyst under separate exposure to water vapor and sulfur dioxide (SO_2). NO reduction was significantly high in the absence of water vapor. Upon introduction of 10% water vapor, the NO conversion immediately dropped to about 60% and it remained low in the presence of water vapor. The NO conversion jumped back to the 90% conversion level when the water vapor supply was terminated. This clearly shows the

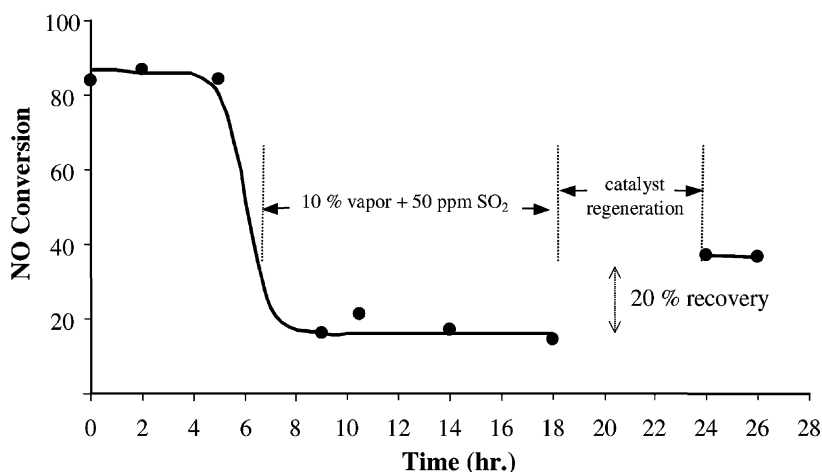


Fig. 7. Effect of simultaneous exposure to water vapor and SO_2 and regenerability on Pt-Cu-ZSM5-WIE-WIE. In situ regeneration process was carried out at 450°C for 4 h in H_2 flow of 100 ml/min.

reversible effect of water vapor on the catalytic activity. It was reported that water vapor had the tendency to attack Bronsted acids and deactivate these sites in the zeolite support [13]. Dealumination, formation of metal-aluminate as well as sintering and agglomeration of metal species in the presence of water vapor were also reported in monometallic catalysts [17,21].

Unlike water vapor that caused reversible effect to the catalytic activity, SO_2 appeared to cause irreversible damage as shown in Fig. 5. Even though SO_2 source was terminated at the 18th hour of the

experiment, the bimetallic catalyst remained inactive for the reduction of NO. Besides, SO_2 caused a larger drop in the NO conversion than the one caused by water vapor. In the presence of only 50 ppm SO_2 , the NO conversion level dropped from 90 to 30%. According to reported studies, SO_2 could poison the catalyst in two ways [13,17]. First, it reduced the reactivity of the reducing agent such as *i*-butane. Second, SO_2 formed intermediate species such as S and H_2S that could easily adsorb on active sites of the catalyst. Evidence of sulfur adsorption on the catalyst surface was

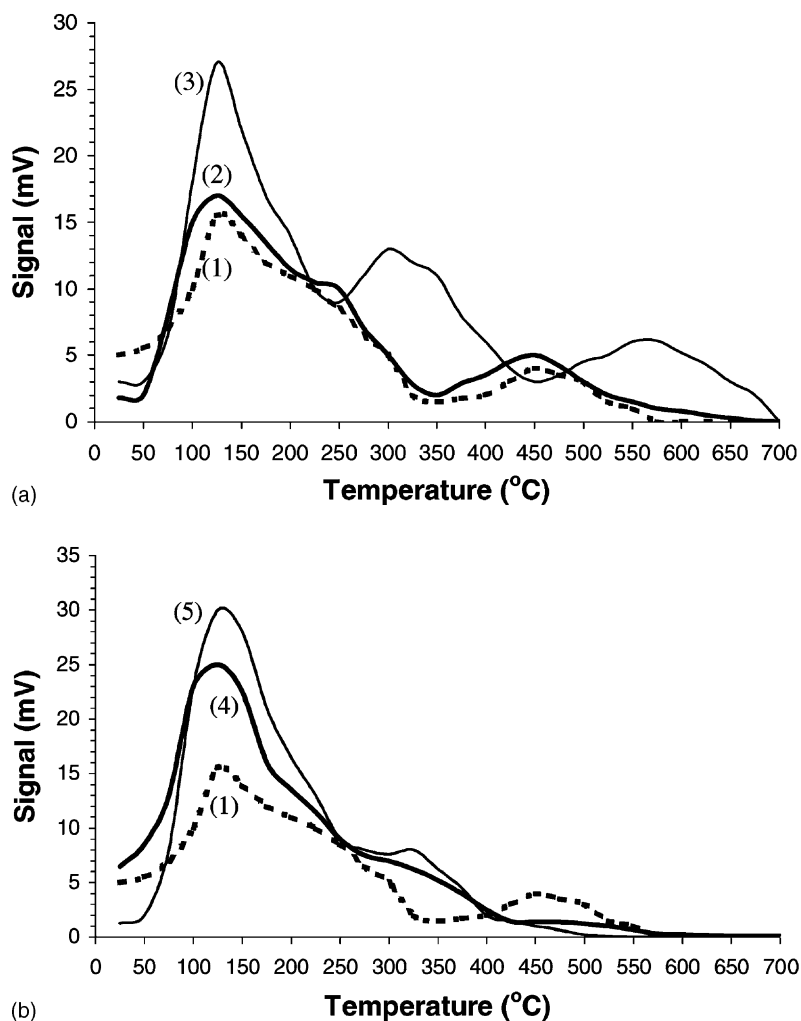


Fig. 8. Profiles of temperature-programmed desorption using ammonia (NH_3 -TPD). (a) Desorption profile of (1) H-ZSM5 as compared with that of monometallic catalysts, (2) Pt-ZSM5 and (3) Cu-ZSM5. (b) Desorption profile of (1) H-ZSM5 as compared with that of bimetallic catalysts, (4) Pt-Cu-ZSM5 and (5) Cu-Pt-ZSM5.

confirmed by the EDAX spectrum in Fig. 6 where sulfur species were detected at 2.65 keV. Simultaneous exposure to 10% water vapor and 50 ppm SO₂ could cause profound deactivation as illustrated in Fig. 7. In the presence of both poisonous components, only 20% of NO could be removed. An attempt was made to regenerate the activity of the catalyst by heating at 450 °C for 4 h in H₂ flow. The catalyst was then re-exposed to dry feed (without poisonous components) where it showed some partial recovery.

3.2. Characterization

It has been reported that surface acidity plays an important role in promoting catalytic reaction [22,23]. It is of interest, therefore, to examine changes in the surface acidity of the zeolite support due to metal loadings. TPD profile of the pure support (H-ZSM5) in Fig. 8A shows two peaks of NH₃ desorption that occurred at around 140 and 450 °C, respectively. Loading of copper alone appeared to introduce additional acid sites at around 300 °C and shifted the second peak to a higher temperature at around 550 °C. On the other hand, the presence of Pt in H-ZSM5 did not seem to change the acidity profile of the zeolite support. When the two monometallic catalysts were further loaded

with a secondary metal, i.e. copper or platinum, strong acid sites (i.e. peak at high temperatures) seemed to diminish from the catalyst surface as shown in Fig. 8B. There was a possibility that some acid sites were lost during successive metal loadings. This might also explain for the relatively faster drop in the activity of the bimetallic catalysts (samples 2 and 3) than that of Cu-ZSM5 at high temperature (i.e. above 500 °C) as shown in Fig. 1.

Pt-Cu-ZSM5 (WIE–WIE) catalyst (sample 3) was further characterized under XPS to examine oxidation state of metal species in the zeolite support. Fig. 9 shows that photoelectron peaks for copper could not be clearly identified. This might be due to extremely low copper content (less than 1 wt.%) in the zeolite support as well as the significant presence of C 1s at 285.4 eV BE as a major impurity. Nevertheless, a narrow scan of Cu 2p peaks showed that most of the copper was present in the form of CuO based on the corrected binding energy (BE) at 934.1 eV. There was some difficulty when the author trying to examine oxidation state of platinum as shown in Fig. 10. Fresh bimetallic sample failed to show any distinct peaks that could be assigned to Pt species. Nevertheless, the regenerated sample did show two distinct peaks corresponding to Pt 4f_{7/2} and Al 2p. The smaller peak of

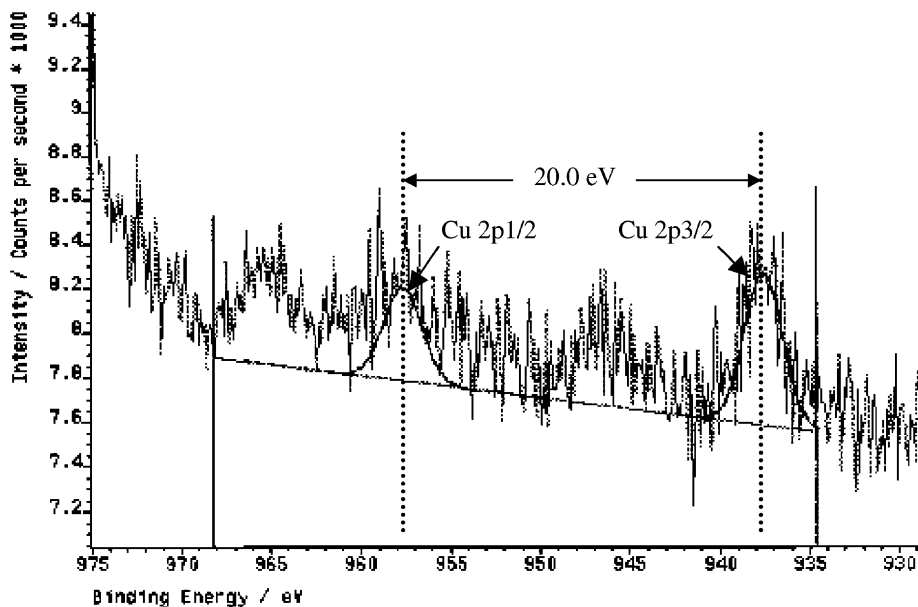


Fig. 9. Photoelectron spectra of Cu 2p_{3/2} before (thin line) and after (bold line) catalytic test.

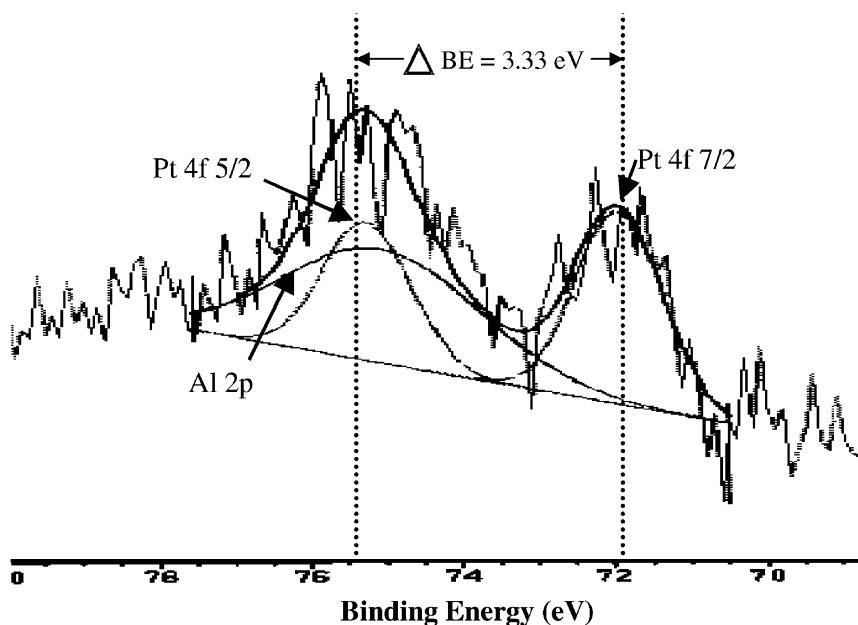


Fig. 10. Photoelectron spectra of Pt 4f showing Pt 4f_{5/2} peak overlapped with Al 2p.

Pt (Pt 4f_{5/2}) was mostly overlapped with Al 2p. This suggested that most Pt species were in the form of Pt metal based on the corrected peak of Pt 4f_{7/2} at 71.2 BE.

4. Conclusions

The bimetallic catalyst, Pt-Cu-ZSM5 prepared by successive wet ion exchanges (WIE–WIE), could widen the temperature window for optimum reduction of NO from diesel exhaust. Experimental results indicated that more than 50% of NO could be removed in the temperature range of 250–500 °C even though formation of nitrous oxide was also favored in the low-temperature region. The activity of the bimetallic catalyst was also not inhibited in the presence of a large presence of oxygen or at high space velocity. These features were clear advantages over monometallic catalysts such as Pt-ZSM5 and Cu-ZSM5, which were active in a narrow range of temperatures. However, the bimetallic catalyst was prone to deactivation in water vapor and SO₂, while formation of N₂O was slightly significant at low temperatures. Besides, it appeared to lose some acid

sites, an important feature for the catalytic reaction, probably due to successive metal loadings.

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