

Adsorption Behavior of NO and CO and Their Reaction over Cobalt on Zeolite Beta

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Abstract—Adsorption behavior of NO and CO as well as their reaction was investigated on cobalt supported zeolite beta (Co/BEA) prepared by solid-state ion exchange (SSIE) and by impregnation (IMP). By temperature programmed desorption (TPD), two NO desorption peaks at 100 and 260 °C were observed over both SSIE and IMP catalysts with complete desorption after 450 °C. CO desorbed from SSIE catalyst between 50 and 200 °C. In the same temperature interval negligible CO₂ desorption was observed, most likely due to reaction of CO with trace of cobalt oxides. Over IMP catalysts, desorption of CO₂ was found mainly at 500 °C. By comparing CO TPD profiles from physical mixtures of cobalt oxides and HBEA, SSIE catalysts most likely contained cobalt cations in zeolite exchange position while IMP catalysts had cobalt in oxidic forms. The SSIE catalysts were active for NO reduction at 400 and 500 °C with a maximum conversion at 500 °C. However, the activity in the presence of water and oxygen was low. Water might inhibit the reaction by blocking active sites for NO and CO, while oxygen reacted with CO to form carbon dioxide. The activity of SSIE was better than IMP catalyst.

Key words: NO Reduction by CO, Cobalt Catalysts, Zeolite Beta, CO-SCR, Co/BEA

INTRODUCTION

The removal of nitrogen oxides (NO_x), which mainly contain NO and small amount of NO₂, has been one of the major investigations globally in environmental catalysis. There have been several research publications focusing on the selective catalytic reduction (SCR) of NO_x with various reactants such as ammonia and hydrocarbons (HCs). As HCs are generally present in the emission of exhaust streams along with NO_x, they have been used as reductants to reduce NO_x to nitrogen gas over various catalysts including supported transition metals such as cobalt, copper and palladium group metals [Kim and Nam, 2001; Yahiro, 2001]. Tabata and coworkers reported that the activity of cobalt on zeolite beta (Co/BEA) for NO reduction by propane in the absence of SO₂ was higher than when cobalt was supported on the other zeolites [Tabata et al., 1998]. Moreover, the activity was lower but remained stable in the presence of SO₂.

Another possible reductant for NO_x is carbon monoxide (CO) and the possible reactions are described in Eqs. (1) and (2). The reaction which produces nitrogen and carbon dioxide proceeded well over noble metals such as Pt, Pd, and Rh [Konsolakis et al., 2001; Di Monte et al., 2000; Pisanu and Gigola, 1999; Kondarides et al., 2000].



Although cobalt is an active catalyst for NO_x reduction by HCs, there has been, to our knowledge, no report on its activity by CO

reductant. Thus, we investigated the catalytic activity of cobalt for NO reduction by CO on Co/BEA. The investigation is worthwhile as both the toxic compounds in the exhaust gas can be removed at the same time.

In this study cobalt was loaded on zeolite beta by solid state ion exchange which could be accomplished effectively within a short time under vacuum or inert gas flow [Kinger et al., 2000]. This process has benefits over conventional ion exchange with aqueous solution of metal salts which takes longer time because it has to be repeated several times to reach the desired metal loading. The Co/BEA catalysts were tested for the reduction of NO by CO in a flow reactor in the presence and absence of oxygen and water.

EXPERIMENT

1. Catalyst Preparation

Zeolite beta (BEA) in sodium form (NaBEA) was synthesized by a method modified from literatures [Cambor and Pérez-Pariente, 1991; Cambor et al., 1991]. Tetraethylammonium hydroxide (TEAOH) was used as template reagent to assist BEA framework formation. Gels of silica and alumina were mixed and crystallized in a rotating autoclave at 135 °C for 15 hours. After the autoclave was quenched in cold water, the product was separated by centrifugation, washed until pH~9, and dried at 100 °C for 24 hours. The template was removed by calcination at 550 °C for 6 hours. The resulting NaBEA was characterized by powder X-ray diffraction (XRD, Phillips PW 1710). NaBEA was then converted to HBEA by exchange with 20% solution of NH₄NO₃ at 80 °C overnight, washed several times, calcined at 550 °C for 6 hours, and characterized by Fourier transform infrared spectroscopy (FTIR, Bruker IFS 28 with MCT detector, 4 cm⁻¹ resolution). The amount of acid sites

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determined by thermogravimetric analysis (NETZSCH STA 409 PC) was 0.90 mmol/g.

Co/BEA was prepared by solid-state ion exchange to give the metal loading of 2.6% by weight corresponding to the concentration of acid sites. The preparation involved grinding HBEA with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ until the mixture was homogeneous and heating under vacuum at 550 °C for 12 hours. Evolution of water, hydrochloric acid and hydrogen was recorded by a mass spectrometer (Balzers). A pronounced evolution of HCl was observed from 375 °C with a maximum at 540 °C, indicating the release of HCl due to the exchange between zeolite protons and cobalt cations. After the exchange, the catalyst was washed with deionized water for several times to remove traces of chlorides and dried at 100 °C. The amount of cobalt was confirmed by atomic absorption spectroscopy.

In another method, Co/BEA was prepared by incipient wetness impregnation of HBEA with an aqueous solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ to give a metal loading of 2.6%. The mixture was dried at 100 °C for one hour and calcined at 500 °C for 6 hours. Throughout this article, the notations SSIE and IMP are used for solid-state ion exchange and impregnation, respectively. Physical mixtures of HBEA and CoO or Co_3O_4 with similar cobalt loading to those of Co/BEA from SSIE and IMP were also prepared by mixing the oxides with HBEA and grinding at room temperature.

2. TPD Study of NO and CO

For the TPD experiments 50 mg catalyst was heated in vacuum to 500 °C with a rate of 10 °C/min and held for one hour. After cooling down, the sample tube was filled with NO (1,000 ppm in helium) overnight or with CO (99.99%) for 2 hours to allow saturation. Then the sample was evacuated for two hours to remove physically adsorbed species. The TPD process was started by heating the sample under vacuum from room temperature to 600 °C with rate of 10 °C/min. The gases evolved were detected by the mass spectrometer.

NO adsorption on Co/BEA(SSIE) was also investigated by *in situ* FTIR from 100 to 250 °C. The spectra of adsorbed NO were recorded after a self-supported sample wafer was exposed with NO flow (1,000 ppm in helium) for 30 minutes.

3. Catalytic Testing for NO Reduction by CO

The reaction was carried out in a quartz tube, which was placed in an oven of a flow reactor connected with temperature controller, chemiluminescence analyzer (Horiba APNA-350E), and gas chromatograph (HP 6890). In each test, approximately 80 mg of catalyst was pretreated by heating in a helium flow of 40 ml/min to 500 °C for 3 hours before cooling down. The feed composition was 850 ppm NO and 0.5 vol% CO in helium balance. When the reaction was carried out in the presence of oxygen and water, their concentrations were 3 and 4 vol%, respectively. All gas flows were controlled by mass flow controllers (Brooks 5850E) and the total flow rate was 100 cm³/min.

RESULTS AND DISCUSSION

1. Characterization of BEA by XRD and FTIR

The XRD patterns of NaBEA after calcination and of commercial HBEA are shown in Fig. 1. The peak positions are in agreement with the peak position of a simulated pattern (Baerlocher and McCusker) shown in the insert.

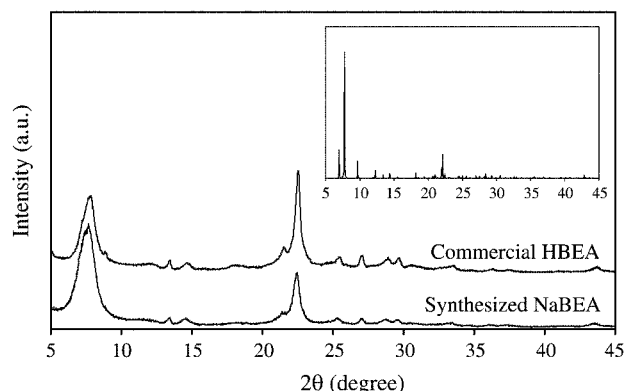


Fig. 1. XRD pattern of synthesized NaBEA after calcination and commercial HBEA compared with simulated pattern.

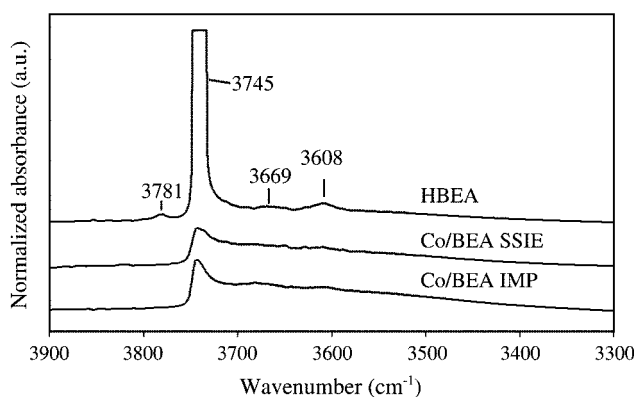


Fig. 2. Normalized infrared spectra of OH region of HBEA and Co/BEA from SSIE and IMP after degassing in vacuum at 300 °C for three hours.

HBEA and Co/BEA catalysts from SSIE and IMP were characterized by FTIR to confirm their functional groups and to observe the change after ion exchange. The OH region of the IR spectra, which are normalized to lattice vibrations are depicted in Fig. 2. The stretching vibrations of hydroxyl groups on tetrahedral silicon and aluminum centers were observed between 3,600 and 3,800 cm⁻¹. The weak band at 3,608 cm⁻¹ was assigned to bridging hydroxyl groups on Si-OH-Al, the strong band at 3,745 cm⁻¹ to terminal Si-OH groups and the band at 3,669 cm⁻¹ to Al-OH. The peak at 3,781 cm⁻¹ was due to high frequency (VHF) hydroxyls of defective structure [Kunkeler et al., 1998].

By comparison of the spectra of Co/BEA catalysts prepared by SSIE and IMP with that of HBEA, one can see that the intensity of all OH bands decreased. The decrease of peak intensity at 3,745 cm⁻¹ on both SSIE and IMP catalysts indicated that cobalt ions might replace the proton of silanol hydroxyl groups in BEA. The peak intensity from Co/BEA(SSIE) catalyst was slightly lower than that of Co/BEA(IMP) catalyst indicating a higher amount of proton was replaced. Disappearance of the peaks at 3,781, 3,669 and 3,608 cm⁻¹ could have resulted from dealumination of BEA framework which was also observed when HBEA was treated by concentrated HCl solution [Oumi et al., 2001]. Oumi and coworkers reported that dealumination was a reversible process which did not cause significant change in BEA framework as XRD patterns of parent, dealu-

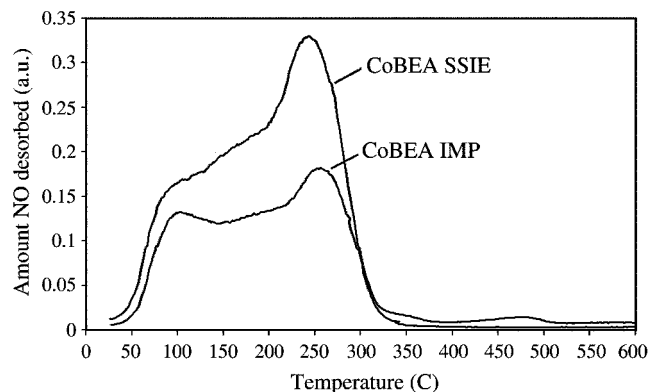


Fig. 3. TPD profile of NO on Co/BEA (SSIE) and Co/BEA (IMP).

minated, and realuminated BEA were similar. Even though dealumination was observed on both Co/BEA(SSIE) and Co/BEA(IMP), the peaks at 3,669 and 3,608 cm^{-1} were still noticeable on IMP suggesting that preparation by IMP caused less dealumination. Although the form of cobalt in SSIE and IMP catalysts could not be distinguished from FTIR results, the difference was observed from adsorption study of carbon monoxide in section 3. By SSIE preparation method, cobalt cations were expected to reside mainly in the BEA exchange positions wherein hydroxyl protons were replaced and hence the infrared intensity decreased. There was no change in the wavenumbers lower than 2,000 cm^{-1} corresponding to lattice vibrations of BEA support.

2. TPD and FTIR Measurement of NO on Co/BEA

The NO TPD profiles in vacuum for Co/BEA catalysts prepared by SSIE and IMP were shown in Fig. 3. The major desorption took place between room temperature and 350 °C. The desorption profiles from both samples were somehow similar except the amount desorbed from SSIE catalyst was higher. The first NO desorption peak was near 100 °C and appeared as a shoulder on the SSIE catalyst. The second peak near 250 °C was stronger than the first peak for both SSIE and IMP catalysts. Thus, there were at least two adsorption forms of NO with different strength on the catalyst. Further, as NO_2 was not observed in the TPD temperature range, it can be presumed that the adsorbed NO molecules did not undergo disproportionation to form NO_2 .

The adsorption modes of NO were investigated by *in situ* FTIR

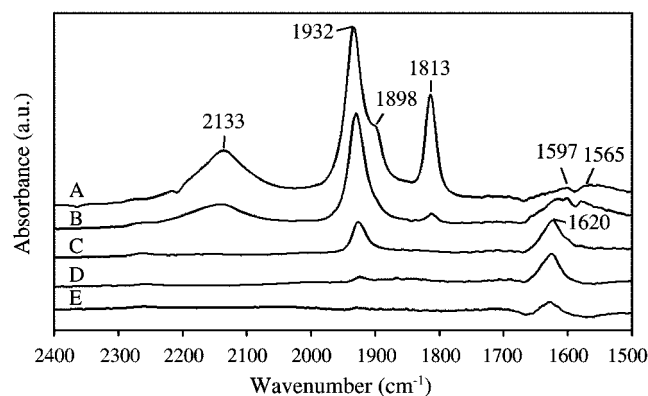


Fig. 4. Infrared spectra of NO adsorbed on Co/BEA (SSIE) at (A) 50, (B) 100, (C) 150, (D) 200, and (E) 250 °C.

at 50, 100, 150, 200, and 250 °C. The sample was degassed in a helium flow at 300 °C for two hours before a flow of NO was introduced. The spectra shown in Fig. 4 are difference spectra in which a spectrum of the activated catalyst was subtracted from the spectrum of the catalyst adsorbed with NO. At 50 °C there was a broad peak at 2,133 cm^{-1} corresponding to weakly adsorbed NO_x species [Hadjiivanov, 2000]. A strong band at 1,932 cm^{-1} was assigned to mononitrosyl Co-NO bond while a shoulder at 1,898 cm^{-1} and a band at 1,813 cm^{-1} were assigned to symmetric and asymmetric dinitrosyl $\text{Co}(\text{NO})_2$, respectively [Tabata et al., 1998; Hadjiivanov, 2000]. As the temperature increased, the intensity of the bands at 1,932, 1,898, and 1,813 cm^{-1} decreased and disappeared almost completely at 250 °C. The bands at 1,650–1,550 cm^{-1} were assigned to surface nitrates [Hadjiivanov, 2000]. The bands at 1,597 and 1,565 cm^{-1} disappeared after 200 °C where the peak at 1,620 cm^{-1} was observed at 150–250 °C. The peak at 1,620 cm^{-1} was assigned to the formation of Co-NO_2 which was formed at high temperature as described in Eq. (3) [Zhu et al., 1996]. Although the infrared measurement was only possible up to 250 °C, it was expected that all surface species would disappear completely at higher temperature (i.e., above 300 °C).



3. TPD of CO on Co/BEA

The desorption profile of CO on Co/BEA(SSIE) from room temperature to 550 °C is shown in Fig. 5. The CO desorption took place between 40 and 190 °C with the maximum at 120 °C. Because CO desorbed completely at lower temperature than NO on the same catalyst, the strength of CO adsorption was weaker than NO adsorption. In the same scale plot, a small amount of CO_2 was also observed. At this point, it was not clear whether cobalt on Co/BEA was in the oxidic form or as Co^{2+} in the exchange position. Thormählen et al. [1999] reported that desorption of CO also took place in a similar temperature range on $\text{CoO}_x/\text{Al}_2\text{O}_3$. Hence, it could be possible that the Co/BEA catalyst contained cobalt oxides which can react with adsorbed CO to form adsorbed CO_2 .

The desorption profile of CO on Co/BEA(IMP) is shown in Fig. 6 where CO desorption took place between 45 and 135 °C with a further broad peak between 250 and 550 °C. The height of the first CO peak was more than double of the second peak, indicating that

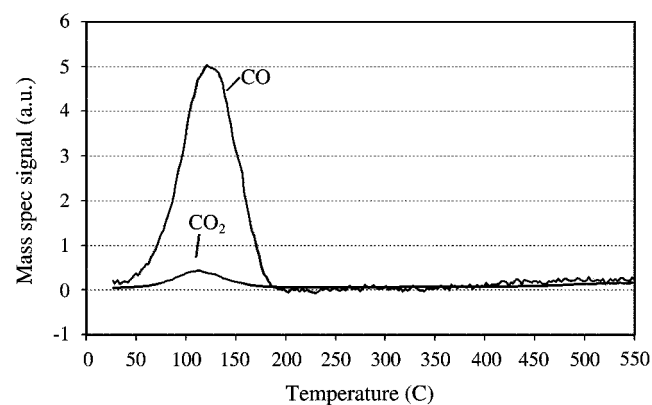


Fig. 5. The mass spectrometer signal of CO and CO_2 during CO TPD on Co/BEA (SSIE).

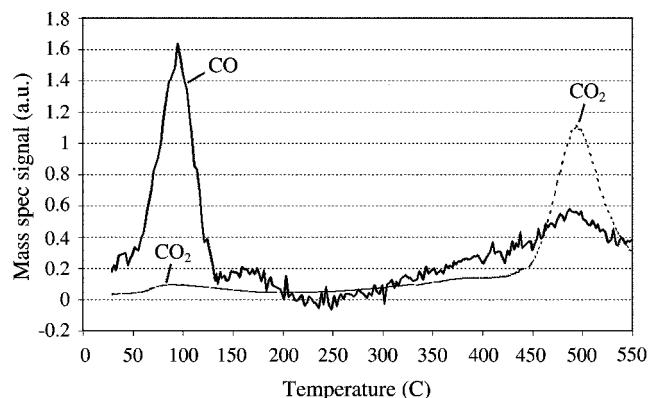


Fig. 6. The mass spectrometer signal of CO and CO₂ during CO TPD on Co/BEA (IMP).

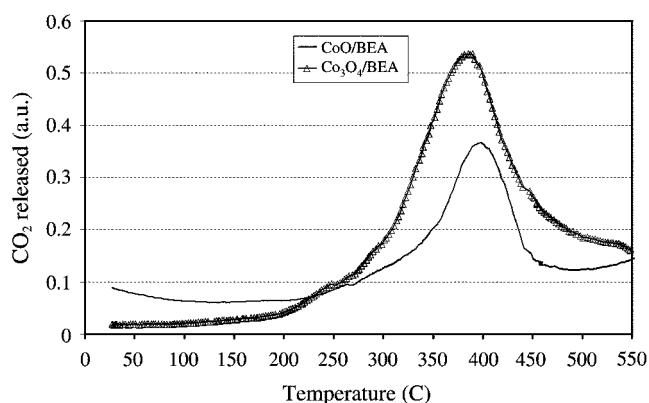


Fig. 7. CO₂ released during CO TPD of physical mixture of CoO and Co₃O₄ with HBEA.

the majority of CO desorbed at lower temperature. The desorption profile of CO₂ was the same as from CO except that the amount of CO₂ released at low temperature was negligible in comparison to the amount released at high temperature. Therefore, one can conclude that a part of cobalt is in the oxidic form on the IMP catalysts. Thus, cobalt oxides could react with CO to form surface CO₂, which desorbed at high temperature.

To confirm that cobalt oxide could react with CO to form CO₂ at high temperature, CO TPD was investigated on physical mixtures of CoO or Co₃O₄ and HBEA under conditions similar to those on Co/BEA catalysts. Note that these samples were not degassed at high temperature in order to prevent any change of the cobalt oxidation state. The release of CO₂ during CO TPD from both oxides is shown in Fig. 7. Desorption of CO₂ from both supported oxides was not detected in the low temperature range but obvious at higher temperatures with a peak maximum at 400 and 385 °C for CoO/HBEA and Co₃O₄/HBEA, respectively. Therefore, it can be concluded that CO adsorbed on cobalt oxides formed surface CO₂ that desorbed at high temperature.

As CO₂ was detected during CO TPD on Co/BEA(SSIE) only in the 40–190 °C range, one can conclude that the major state of cobalt in SSIE catalyst was neither CoO nor Co₃O₄. The active sites responsible for CO adsorption on Co/BEA(SSIE) were thus most likely cobalt cations in exchange position of BEA.

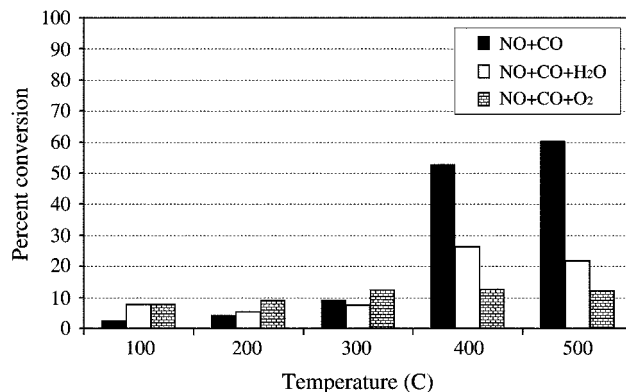


Fig. 8. Conversion of NO_x on Co/BEA (SSIE).

The trend of CO₂ release from Co/BEA(IMP) was different from that of Co/BEA(SSIE). The major amount was detected between 450 and 550 °C and only small amounts were observed between 40 and 190 °C. Thus, the state of cobalt in Co/BEA(IMP) is rather oxidic. However, CO₂ was observed at higher temperature than over both CoO and Co₃O₄, which can be due to a smaller cluster size of Co oxides in the impregnated catalysts.

4. Catalytic Activity of Co/BEA for NO_x Reduction with CO

In Fig. 8 the NO_x conversion over Co/BEA(SSIE) from 100 to 500 °C is shown. The framework of BEA is stable in this temperature range but will slowly collapse at temperature higher than 550 °C. The first test series was done with NO and CO in helium while water and oxygen was introduced to the flow of gas mixture in the second and third test series, respectively. The conversion of NO and CO in the absence of oxygen and water was less than 10% between 100 and 300 °C. The activity of cobalt at these temperatures was low as reported by several authors [Campa et al., 1996; Armor, 1995; Seyedeyn-Azad and Zhang, 2001; Ohtsuka et al., 1998; Tabata et al., 1998]. The cause for low activity might have been the repulsion between NO and CO which prevented the adsorption of one another [Park et al., 1986]. In addition to this, TPD result indicated that NO adsorbed more strongly than CO and could prevent surface reaction from occurring. The conversion increased to 52% at 400 °C and reached a maximum of 60% at 500 °C. It was possible that the repulsion between NO and CO was overcome at high temperature.

In the presence of water, the conversion was lower than 10% at low temperatures (100–300 °C) and increased to 27% at 400 °C. Water seems to inhibit the reaction between NO and CO in the temperature range of 400 to 500 °C. This behavior has also been reported by several authors [Kim and Nam, 2001]. As water was pumped into the reactor continuously, it might have adsorbed and blocked the active sites for NO and CO. This idea was supported by a TPD study of water (Fig. 9) from Co/BEA in vacuum on heating from room temperature to 600 °C. Desorption began after heating with a maximum at 130 °C and a further release until 600 °C. However, the effect of water on catalyst activity was reversible indicating that the state of cobalt was not chemically altered by the presence of water.

When oxygen was present in the gas mixture, the conversion was low at all temperatures. At 400 and 500 °C CO reacted with oxy-

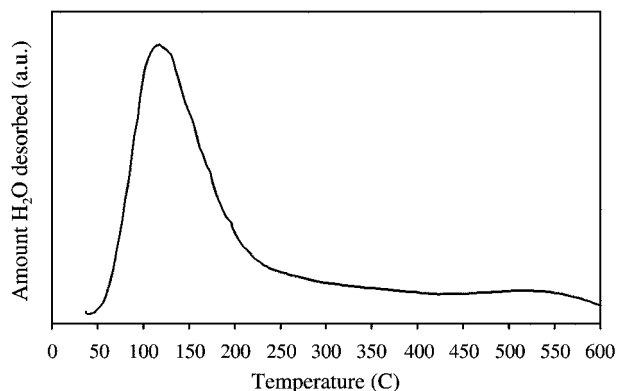


Fig. 9. Desorption profile of water from Co/BEA (SSIE).

gen to form CO_2 . This was confirmed by gas chromatography where CO disappeared completely, which is coincident with the generation of CO_2 . Furthermore, approximately 20% of NO reacted with O_2 to form NO_2 . After the flow of oxygen or water vapor was stopped, the catalytic activity was fully regained. It is because the reaction between CO and O_2 was fast in our reaction conditions that there was no significant effect on the state of cobalt.

The time on stream behavior (TOS) of Co/BEA(SSIE) was tested at 400 and 500 °C because high activity was observed at these temperatures. The conversions after every 1,000 seconds (16.7 minutes)

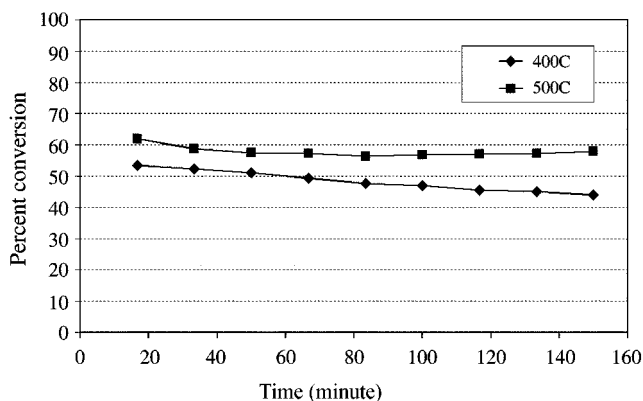


Fig. 10. NO_x conversion on Co/BEA (SSIE) with time.

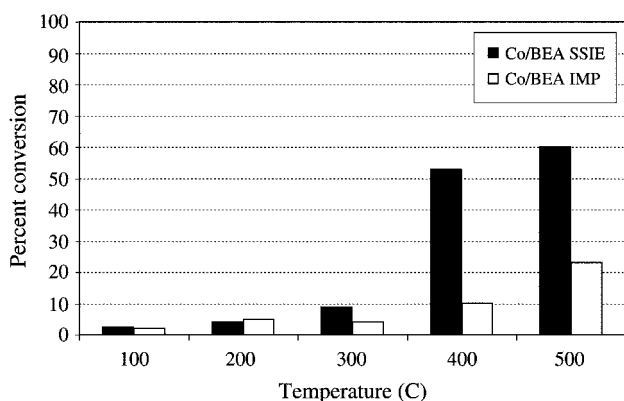


Fig. 11. Conversion of Co/BEA (SSIE) and IMP for NO reduction by CO.

are plotted in Fig. 10. The conversion at 400 °C decreased slightly throughout TOS. Because the NO adsorption from Co/BEA(SSIE) was completed near 500 °C (Fig. 3), it was possible that adsorbed NO species at 400 °C slowly dominated on catalyst and prevented CO to react. Such change was not observed at 500 °C when the conversion just dropped slightly at the beginning from 62 to 58% and then remained constant. This might due to a shorter contact time of NO on the catalyst.

The activity of Co/BEA(SSIE) was compared with that of Co/BEA(IMP). As shown in Fig. 11, the activity from both catalysts was low at 100–300 °C. The activity of IMP catalyst was much lower than that of SSIE catalyst between 400 and 500 °C. This confirmed that cobalt was more active when it was in zeolite exchange position. During the catalytic test N_2O was not detected at each temperature by gas chromatograph.

CONCLUSIONS

1. Desorption of NO from SSIE and IMP catalysts in vacuum was completed near 350 °C and showed two peaks at 100 and 260 °C indicating the presence of at least two adsorption sites on the catalysts.

2. The FTIR spectrum of NO on SSIE catalyst confirmed the adsorbed species to be nitrosyl (Co-NO), dinitrosyl (Co-(NO)₂), Co-NO₂, nitrates, and weakly adsorbed NO_x species.

3. The CO desorption profiles from SSIE and IMP catalysts were different indicating different state of cobalt. Cobalt on BEA from SSIE was possibly in cationic form in zeolite exchange position while that from IMP was in oxidic forms.

4. Both the Co/BEA catalysts obtained by SSIE and IMP were active for the reduction of NO by CO at high temperatures. Catalyst prepared by SSIE was more active than that obtained by IMP at 400 and 500 °C. The SSIE catalyst was active in the absence of water and oxygen from 400 to 600 °C with highest activity at 500 °C.

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