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NO Reduction by Carbon Monoxide Over Cobalt on Zeolite Beta

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This study focused on the selective catalytic reduction of nitric oxide (NO) by carbon monoxide (CO) over cobalt supported on zeolite beta (Co/BEA) with and without the presence of oxygen or water. The Co/BEA catalyst with 2.6% metal loading was prepared by solid state ion exchange from freshly synthesized HBEA and $CoCl_2 \cdot 6H_2O$. The adsorption behavior of NO on Co/BEA investigated by temperature programmed desorption (TPD) revealed two peaks for NO at 100 and 260 °C indicating that there were at least two adsorption modes. The desorption of CO completed near 200°C along with a small amount of CO_2.

The activity of Co/BEA catalyst for NO reduction by CO was lower than 20% at 100–300°C but higher than 50% at 400–500°C with the maximum conversion of 60% at 500°C. Products were selectively N_2 and CO_2. However, the activity in the presence of oxygen was low due to the more favorable reaction between CO and O_2 to form CO_2. The catalytic activity in the presence of water was also low but higher than that in the presence of oxygen.

Keywords: NO reduction by CO, cobalt on zeolite beta, *and* solid state ion exchange.

INTRODUCTION

Removal of nitrogen oxides (NO_x), composed of nitric oxide (NO) and nitrous oxide (NO_2), has been one of the major investigations globally in environmental catalysis. Several studies focused on the selective catalytic reduction of NO_x on metal supported catalysts by reacting with hydrocarbons and carbon monoxide (CO). Those gases were selected because they are generally present in the emission of exhaust stream. Reports on metal activity for NO_x reduction by hydrocarbons were found on supported metals such as Co, Cu, Fe, and Pt group metals (Hamada et al. 1996, Frache et al. 2002, Praliaud et al. 1998, Yahiro and Iwamoto 2001, Chen et al. 1998, Burch et al. 2002). In addition, the reaction of NO on CO proceeded well on transition metals such as Pt, Pd, and Rh (Kondarides et al. 2000, Di Monte et al. 2000, Pisanu and Gigola 1999, Kondarides et al. 2000).

Although cobalt based catalysts were reported to be active and selective for NO_x reduction when hydrocarbons such as methane (Campa et al. 1996, Armor 1995, Seyedeyn-Azad and Zhang 2001, Ohtsuka et al. 1998), propene (Ohtsuka et al. 1998), propane (Tabata et al. 1998) were used as reductants, only little research utilizing CO as a reductant was reported. As shown in Eq. (1), the reaction between NO and CO produces nitrogen and carbon dioxide which are non-toxic products. The investigation is worthwhile if both toxic compounds could be removed at the same time.

$$2NO + 2CO \longrightarrow N_2 + 2CO_2 \qquad (1)$$

Tabata et al. (1998) reported the activity of cobalt for NO reduction by propane on various zeolite supports where the activity on zeolite beta (BEA) was higher than others in the absence of SO_2. In addition, the activity of Co/BEA remained stable in the presence of SO_2. Metal cation could be introduced into zeolite by ion exchange with an aqueous solution of metal salts in the conventional method. However, such ion exchange process has to be repeated several times to reach the desired metal loading. The exchange process can be accomplished effectively in a short time with solid state ion exchange which is a simple procedure (Kinger et al. 2000).

This research investigated adsorption behavior of NO and CO on Co/BEA by temperature programmed desorption (TPD) and reduction of NO by CO over Co/BEA catalyst prepared by solid state ion exchange. The tests were also done in the presence of oxygen or water vapor.

EXPERIMENTAL PROCEDURE

Catalyst preparation

NaBEA was synthesized by a method modified from literatures (Camblor and Perez-Pariente 1991, Camblor, Mifsud and Pérez-Pariente 1991). Batch preparation of zeolite beta was prepared by mixing gel of silica and alumina, and crystallization in a rotating autoclave at 135°C for 15 hours. Tetraethylammonium hydroxide (TEAOH) was used as a template reagent to assist BEA framework formation. After the autoclave was quenched in cold water, the product was separated by centrifugation, washed until the pH ~ 9, and dried at 100°C. The TEA template was removed by calcinations at 550°C for 6 hours. The resulting NaBEA was characterized by powder X-ray diffraction (XRD, Phillips PW 1710) comparing with commercial HBEA zeolite from Degussa, Germany. NaBEA was then converted to HBEA by exchange with 20% solution of NH_4NO_3 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) with 4 cm^{-1} resolution. The amount of acid sites determined by thermogravimetric analysis (NETZSCH STA 409 PC) was 0.90 mmol/g.

Cobalt catalyst on zeolite beta (Co/BEA) was prepared by solid state ion exchange in vacuum by grinding HBEA with $CoCl_2{\cdot}6H_2O$ until homogeneous and heating under vacuum at 550°C for 12 hours. The metal loading of 2.6%, corresponding to acid sites was employed. After the exchange, the catalyst was washed with deionized water several times to remove trace of chloride and dried at 100°C.

TPD of NO and CO

The adsorption ability of Co/BEA for NO and CO was tested by TPD technique in vacuum. In pretreatment, the sample powder was degassed by heating in vacuum at 500°C for one hour. After being cooled down, the sample tube was filled with NO (1000 ppm in helium) overnight or CO (99.99%) for 2 hours to allow adsorption to reach saturation. Then the sample was evacuated to remove unadsorbed species for two hours. 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 using mass spectrometer.

The nature of NO adsorption on Co/BEA was also investigated by *in situ* FTIR from 100 to 250°C where the flow of NO (10 vol% NO in helium) was introduced over self-supported sample wafer. The sample was heated at 300°C in helium for two hours as a pretreatment. The spectra of adsorbed NO in helium were recorded after the sample was exposed to the gas for 30 minutes.

Catalytic testing for NO reduction by CO

A quartz tube containing sample pellets (~ 1 mm in diameter) was placed in an oven of a flow reactor connected with temperature controller, chemiluminescence analyzer (Horiba APNA-350E), and gas chromatograph (HP 6890). Pretreatment included heating in helium flow at 40 ml/min to 500°C and held for 3 hours before cooling down. The catalyst was tested for reduction of NO by CO from 100 to 600 °C with and without the presence of oxygen or water. The gas mixture contained NO (850 ppm) and CO (0.5 vol%) in helium balance. When the presence of oxygen was required, a concentration of 3 vol% was employed. Water was pumped into the heated gas line by a syringe pump to obtain 4 vol% vapor. The total flow rate was 100 cm³/min.

RESULTS AND DISCUSSION

Characterization of BEA support by XRD and FTIR

Powder XRD pattern of synthesized NaBEA after calcination (Figure 1) showed strong 2θ peaks at 7.7 and 22.5 degree. All peak positions were similar to those of commercial HBEA indicating that BEA framework was successfully obtained. In addition, the pattern was in a good agreement with simulated pattern in Database of Zeolite Structures (Baerlocher, Ch. and McCusker, L.B). The synthesized NaBEA was exchanged with NH_4NO_3 calcined at 550°C to convert into acidic form (HBEA) and used as catalyst support for cobalt throughout this study. HBEA and Co/BEA were characterized by FTIR to confirm its

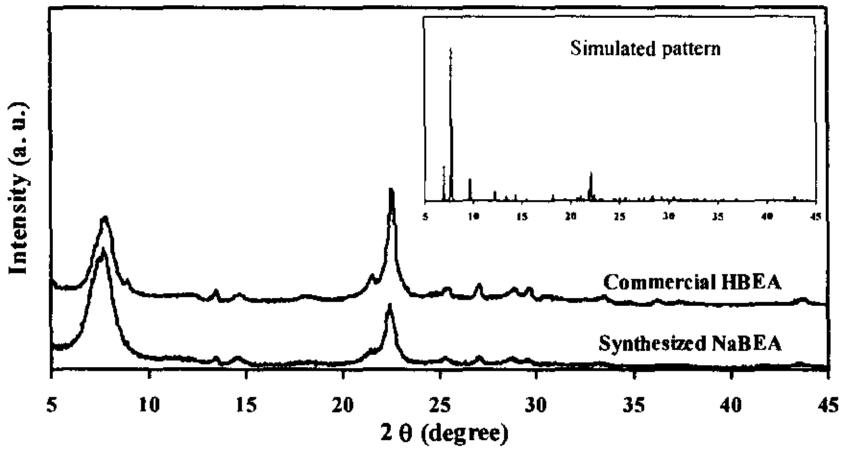

Figure 1. Powder XRD Spectrum of Synthesized NaBEA Compared with Commercial HBEA and Simulated Pattern

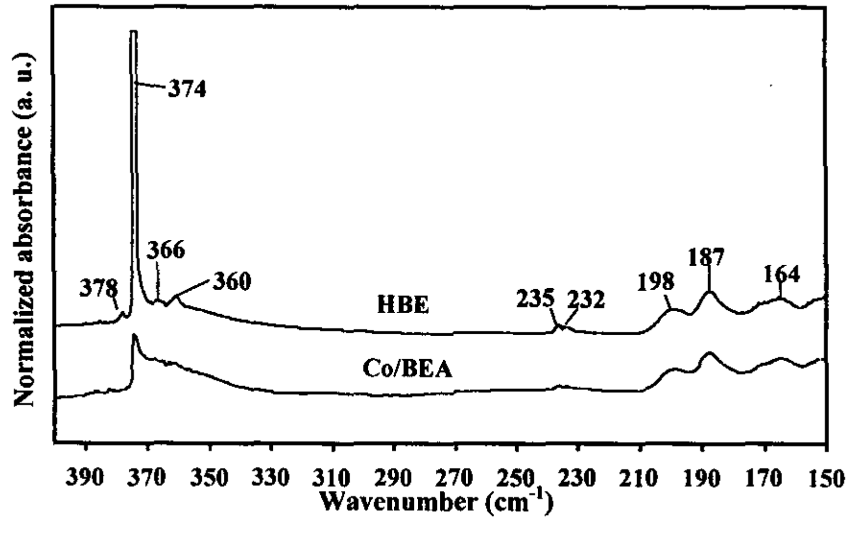

Figure 2. Infrared Spectra of HBEA and Co/BEA

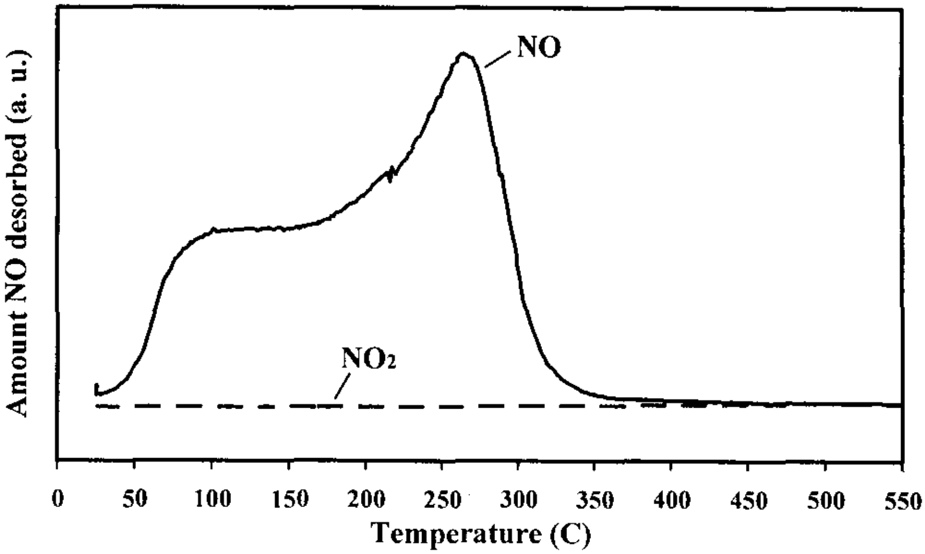

Figure 3. NO TPD Profile of Co/BEA in Vacuum

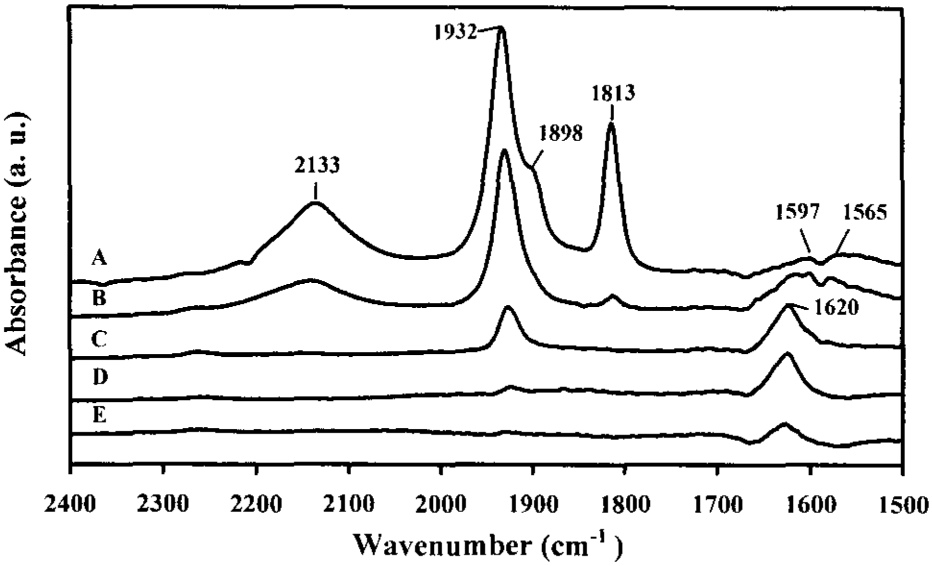

Figure 4. Infrared Spectra of NO Adsorbed on Co/BEA Self-Supported Wafer at (A) 50, (B) 100, (C) 150, (D) 200, and (E) 250°C

functional groups and to observe the change after ion exchange. The normalized spectra in Figure 2 were collected after HBEA and Co/BEA were degassed at 300°C in vacuum for one hour.

For HBEA, the wavenumbers lower than 2,000 cm^{-1} were assigned to the overtone of lattice vibrations including Si-O-Si and Si-O-Al. The small peaks at 2,352 and 2,324 cm^{-1} were readily assigned to trace carbon dioxide. The peak positions of stretching hydroxyl groups on tetrahedral silicon and aluminum center were between 3,600 and 3,800 cm^{-1}. The weak peak at 3,608 cm^{-1} was assigned to hydroxyl groups in the bridging Si-OH-Al while the strong peak at 3,745 cm^{-1} was the IR peak of terminal, non-acidic Si-OH groups. The peak at 3,669 cm^{-1} was caused by OH groups associated with Al framework. In addition the peak at 3781 cm^{-1} was the OH groups from very high frequency (VHF) hydroxyl due to defective structure (Thormählen et al. 1999).

There was little change in the infrared spectrum for Co/BEA compared with HBEA. The intensity of Si-OH group at 3,745 cm^{-1} on Co/BEA from both preparation methods was lower than that of HBEA. The intensity of the peaks at 3,669 and 3,608 cm^{-1} were also decreased. After ion exchange, cobalt cations were expected to reside mainly in the exchange position of BEA.

However, some may replaced protons on hydroxyl groups and cause the decrease of the intensity of the hydroxyl peaks. The peak at 3,781 cm^{-1} from defective structure was not further observed because the sample was heated for several hours during solid state ion exchange. There was no change on lattice vibrations of BEA support which were the wavenumbers lower than 2,000 cm^{-1}.

TPD of NO on Co/BEA

The TPD profile of NO over Co/BEA powder in static apparatus is shown in Figure 3. The desorption began after heating from room temperature and completed at 450°C. The first peak which looked like a shoulder was near 100°C. The second peak appeared near 260°C and was stronger than the first peak. Thus, there were at least two adsorption forms of NO on the catalyst with different strength. In addition, NO_2 was not observed in all TPD temperature range. Thus, the adsorbed NO molecules did not disproportionate to NO_2.

The NO adsorption mode was investigated by *in situ* FTIR at 50, 100, 150, 200, and 250°C. The spectra shown in Figure 4 in the range 2400 and 1500 cm^{-1} are difference spectra in which adsorbed NO spectrum was subtracted by a spectrum in helium. At 50°C there was a broad peak at 2,133 cm^{-1} corresponding to trace of carbon dioxide. A strong peak at 1,932 cm^{-1} was assigned to terminal Co-NO bond. A shoulder at 1,898 cm^{-1} and a peak at 1813 cm^{-1} were assigned to symmetric and asymmetric $Co\text{-}(NO)_2$, respectively (Tabata et al. 1998).

There were also broad peaks at 1,597 and 1,565 cm^{-1} with were caused by formation of surface nitrate. As the temperature increased, the intensity of the peaks at 1932, 1898, and 1813 cm^{-1} decreased and disappeared almost completely at 250°C. The peaks at 1597 and 1565 cm^{-1} slowly converted to 1,620 cm^{-1} which was the only remaining peak at 250°C. Although the infrared measurement was possible only to 250°C, it was expected that all surface species would disappear completely at higher temperature (i.e. at 300–600°C).

TPD of CO on Co/BEA

The desorption profile of CO in vacuum over Co/BEA from room temperature to 550°C is shown in Figure 5 where the CO desorption took place at 40-190°C with a peak at 120°C. In the same scale plot, a small amount of CO_2 was also observed at the same temperature range. At this point, it was not clear that the state of cobalt on Co/BEA was Co^{2+} in the exchange position or oxides. Thormählen et al (1999) reported that the desorption of CO also took place at similar range on oxidized CoO_x/Al_2O_3. It was possible that the Co/BEA catalyst contained cobalt oxides which can reacted with adsorbed CO to formed adsorbed CO_2.

The other possibility for CO_2 formation is the surface CO can disproportionate to form surface carbon and CO_2. The disproportionation of CO has been known on cobalt which was utilized to produce carbon nanotube (Pinheiro et al. 2002). Mohana Rao et al. (1988) reported disproportionation of CO on cobalt particles on MgO at room temperature in vacuum leading to surface carbon and CO_2.

Catalytic Ability of Co/BEA for NO_x reduction by CO

The ability of Co/BEA to catalyze NO_x reduction by CO was investigated in a flow reactor where changes in NO and NO_2 concentration were measured continuously. Note that a small amount of NO_2 was always found in NO, thus, the term NO_x would be a more precise representation of the gas reactant. Figure 6 shows the percent NO_x conversion from 100 to 600°C after reaching each temperature for 1000 seconds. In the first test the gas reactants were only NO and CO in helium while water and oxygen was introduced to the flow of gas mixture in the second and the third test, respectively.

The conversion was less than 10% at 100–300°C. Because NO desorption was observed in this temperature range, it could be suggested that the adsorption of NO was strong enough to prevent surface species to react with CO. The activity at these temperatures was also reported to be low by several authors when hydrocarbons were used instead of CO (Campa et al. 1996, Armor 1995, Seyedeyn-Azad and Zhang 2001, Ohtsuka et al. 1998, Tabata et al. 1998). The conversion increased to 51% at 400°C, and reached 59% at 500°C. The conversion then decreased after the temperature reached 600°C.

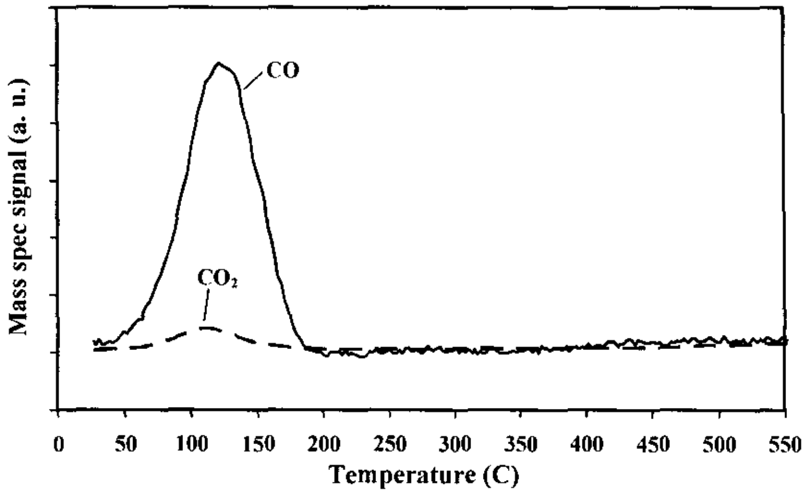

Figure 5. Desorption Profile of CO and CO_2 During CO TPD on Co/BEA

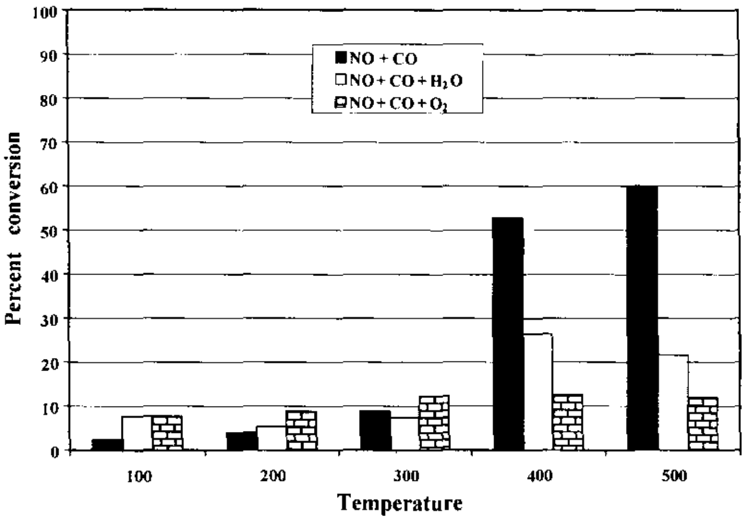

Figure 6. Percent Conversion of NO_x on Co/BEA for the Reaction Between NO and CO During the First 1,000 seconds

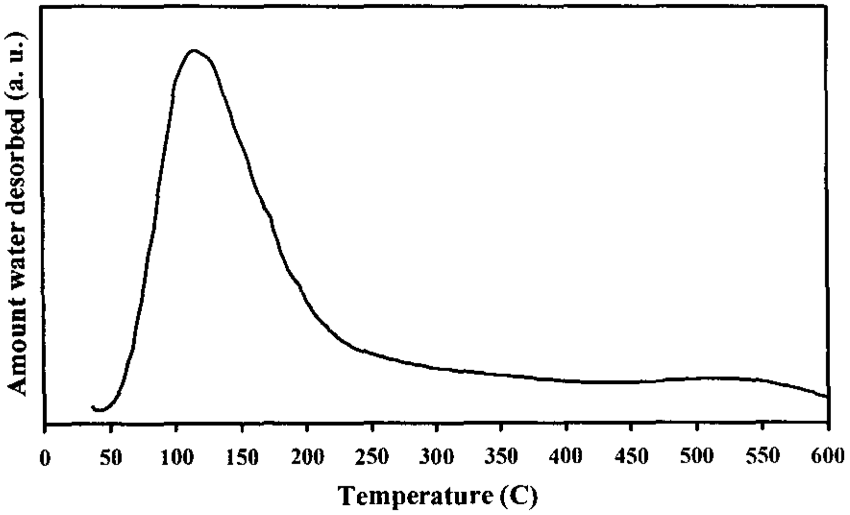

Figure 7. Desorption Profile of Water from Co/BEA

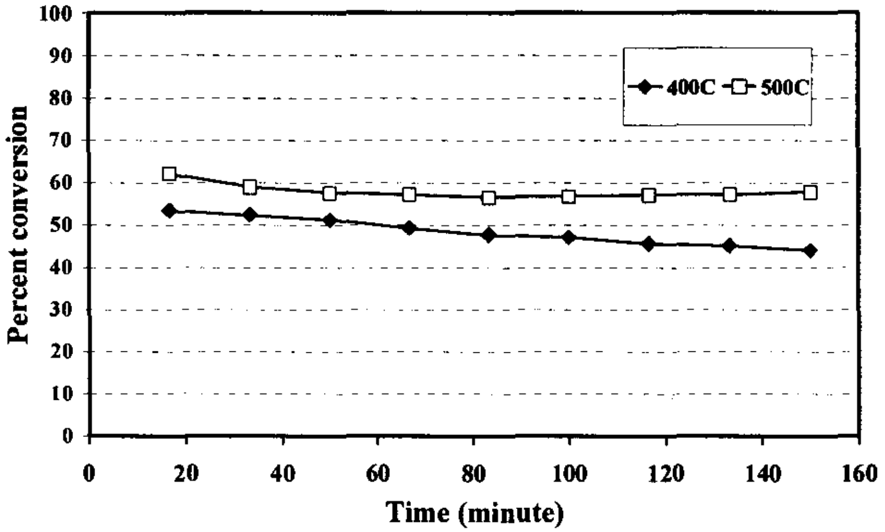

Figure 8. Stability of Co/BEA for the Reaction Between NO and CO in Helium with Time

In the presence of water, there the conversion at 100–300°C was lower than 10% and the conversion was between 20–30% at 400–600°C. It can be concluded that water inhibited the reaction between NO and CO. Water might adsorb on the catalyst and block the active sites for NO and CO. Figure 7 shows desorption of water from Co/BEA in vacuum after heating from room temperature to 600°C. The desorption began after heating and had a peak at 130°C. Although the desorption was much lower at high temperature, water was released in all temperature until 600°C. This indicated that some water molecules adsorbed strongly on the catalyst and such adsorption behavior could be responsible for low catalytic activity in the presence of water.

Only a small amount of NO_2 was found during the first and second test (i.e. less than 5% at 100°C and less than 1% at 200–500°C). Thus, the presence of CO prevented the NO disproportionation on catalyst active sites. In addition, N_2O was not detected by gas chromatography at all temperatures.

When oxygen was present in the flow, the conversion was low at all temperature. Between 400 and 600°C all CO reacted with oxygen to form CO_2. This statement was confirmed by gas chromatograph where CO peak disappeared completely coincident with the growth of CO_2 peak. In all temperature approximately 20% of NO reacted with O_2 to form NO_2. After the flow of oxygen or water vapor was terminated, the catalyst activity was fully regained.

Because the activity was high at 400 and 500°C, the catalyst duration was tested for both temperatures for 150 minutes. The conversion after every 1000 seconds (16.7 mins) were plotted in Figure 8. The conversion at 400°C slightly dropped throughout the study period. In contrast, the conversion at 500°C just dropped slightly at the beginning from 60 to 55% and remained constant after 50 minutes to 150 minutes.

CONCLUSIONS

Co/BEA prepared by solid state ion exchange was effective for adsorption of NO and CO. The desorption of NO took place from room temperature to 450°C with two peaks at 100 and 260°C indicating there were at least two adsorption modes which were confirmed by FTIR The desorption of CO completed near 100°C along with a small amount of CO_2.

The Co/BEA catalyst was active for reduction of NO_x by CO from 400 to 600°C with activity higher than 50% and the maximum conversion reached 60% at 500°C. The activity was lower than 20% at 100–300°C. Products from the reaction at all temperatures were selectively N_2 and CO_2. However, the activity in the presence of oxygen was low due to the more favorable reaction between CO and O_2 to form carbon dioxide. The catalytic activity in the presence of water was lower than 10% at 100–300°C and lower than 30% at 400–600°C. Evidence form water TPD suggested the possibility that water blocked active sites for NO and CO.

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REFERENCES

Armor, J. N. (1995). "Catalytic reduction of nitrogen oxides with methane in the presence of excess oxygen: A review," *Catal. Today*, *26*, 2, 147–158.

Burch, R., Breen, J. P., and Meunier, F. C. (2002). "A review of the selective reduction of NO_x with hydrocarbons under lean-burn conditions with non-zeolitic oxide and platinum group metal catalysts," *Appl. Catal. B-Environ.*, *39*, 4, 283–303.

Camblor, M. A., Mifsud, A., and Pérez-Pariente, J. (1991). "Influence of the synthesis conditions on the crystallization of zeolite Beta," *Zeolites*, *11*, 792–797.

Camblor, M. A., and Pérez-Pariente, J. (1991). "Crystallization of zeolite beta. Effect of Na and K ions," *Zeolites 11*, 202–210.

Campa, M. C., De Rossi, S., Ferraris, G., and Indovina, V. (1996). "Catalytic activity of Co-ZSM-5 for the abatement of NO_x with methane in the presence of oxygen," *Appl. Catal. B-Environ.*, *8*, 3, 315–331.

Chen, H., Voskoboinikov, T., and Sachtler, W. M. H. (1998). "Reduction of NO_x over Fe/ZSM-5 catalysts: Adsorption complexes and their reactivity toward hydrocarbons," *J. Catal.*, *180*, 2, 171–183.

Di Monte, R., Fornasiero, P., Kapar, J., Rumori, P., Gubitosa, G., and Graziani, M. (2000). "$Pd/Ce_{0.6}Zr_{0.4}O_2/Al_2O_3$ as advanced materials for three-way catalysts: Part 1. Catalyst characterisation, thermal stability and catalytic activity in the reduction of NO by CO," *Appl. Catal. B-Environ.*, *24*, 3–4, 157–167.

Frache, A., Palella, B., Cadoni, M., Pirone, R., Ciambelli, P., Pastore, H. O., and Marchese, L. (2002). "Catalytic $DeNO_x$ activity of cobalt and copper ions in microporous MeALPO-34 and MeAPSO-34," *Catal. Today*, *75*, 1–4, 359–365.

Hamada, H., Kintaichi, Y., Inaba, M., Tabata, M., Yoshinari, T., and Tsuchida, H. (1996). "Role of supported metals in the selective reduction of nitrogen monoxide with hydrocarbons over metal/alumina catalysts," *Catal. Today*, *29*, 53–57.

Kinger, G., Lugstein, A., Swagera, R., Ebel, M., Jentys, A., and Vinek, H. (2000). "Comparison of impregnation, liquid- and solid-state ion exchange procedures for the incorporation of nickel in HMFI, HMOR and HBEA: Activity and selectivity in *n*-nonane hydroconversion," *Micropor. Mesopor. Mat.*, *39*, 1–2, 307–317.

Kondarides, D. I., Chafik, T., and Verykios, X. E. (2000). "Catalytic reduction of NO by CO over rhodium catalysts: 2. Effect of oxygen on the nature, population, and reactivity of surface species formed under reaction conditions," *J. Catal.*, *191*, 1, 147–164.

Konsolakis, M., Yentekakis, I. V., Palermo, A., and Lambert, R. M. (2001). Optimal promotion by rubidium of the CO + NO reaction over Pt/γ-Al_2O_3catalysts," *Appl. Catal. B-Environ.*, *33*, 4, 293–302.

Ohtsuka, H., Tabata, T., Okada, O., Sabatino, L. M. F., and Bellussi, G. (1998). "A study on the roles of cobalt species in NO_x reduction by propane on Co-Beta," *Catal. Today*, *42*, 1–2, 45–50.

Pinheiro, J. P., Schouler, M. C., and Dooryhee, E. (2002). "In situ X-ray diffraction study of carbon nanotubes and filaments during their formation over Co/Al_2O_3 catalysts," *Solid State Commun.*, *123*, 3–4, 161–166.

Pisanu, A. M., and Gigola, C. E. (1999). "NO decomposition and NO reduction by CO over Pd/α-Al_2O_3," *Appl. Catal. B-Environ.*, *20*, 3, 179–189.

Praliaud, H., Mikhailenko, S., Chajar, Z., and Primet, M. (1998). "Surface and bulk properties of Cu–ZSM-5 and Cu/Al_2O_3 solids during redox treatments. Correlation with the selective reduction of nitric oxide by hydrocarbons," *Appl. Catal. B-Environ.*, *16*, 4, 359–374.

Rao, K. M., Scarano, D., Spoto, G., and Zecchina, A. (1988). "CO adsorption on cobalt particles supported on MgO: An IR investigation," *Surf. Sci.*, *204*, 3, 319–330.

Seyedeyn-Azad, F. and Zhang, D. (2001). "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," *Catal. Today*, *68*, 1–3, 161–171.

Tabata, T., Ohtsuka, H., Sabatino, L. M. F., and Bellussi, G. (1998). "Selective catalytic reduction of NOx by propane on Co-loaded zeolites," *Micropor. Mesopor. Mat.*, *21*, 4–6, 517–524.

Thormählen, P., Skoglundh, M., Fridell E., and Andersson, B. (1999). "Low-temperature CO oxidation over platinum and cobalt oxide catalysts," *J. Catal.*, *188*, 2, 300–310.

Yahiro, H., and Iwamoto, M. (2001). "Copper ion-exchanged zeolite catalysts in deNO$_x$ reaction," *Appl. Catal. A-Gen.*, 222, 1–2, 163–181.