

Copper Ion-Exchanged SAPO-34 as a Thermostable Catalyst for Selective Reduction of NO with C₃H₆

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Selective reduction of NO with C₃H₆ in the presence of oxygen was studied over Cu ion-exchanged SAPO-*n* (*n* = 5, 11, 34), and Cu ion-exchanged Zeolites β, USY, and ZSM-5. All the Cu ion-exchanged catalysts exhibited high activity for NO reduction with C₃H₆ in a large excess of O₂; however, the temperature for maximum NO conversion depended on the kind of molecular sieve. Although the maximum conversion of NO was attained at a slightly higher temperature in comparison with Cu-ZSM-5, Cu-SAPO-34 exhibited the highest activity for NO reduction among the catalysts studied under the conditions examined. Furthermore, high NO conversion was attained over a wide temperature range, from 623 to 873 K. SAPO-34 has high thermal stability. High activity for NO selective reduction on Cu-SAPO-34 was sustained for more than 60 h at 673 K in an atmosphere containing 15 vol% H₂O. After thermal treatment at 1073 K in humidified atmosphere, the decrease in activity for NO reduction was also small. Redox behavior of Cu ions in SAPO-34 between monovalent and divalent states occurs during the selective reduction of NO, and the reaction seems to proceed via formation of adsorbed nitrate species followed by the formation of organic nitro compounds. © 1997 Academic Press

process for the catalytic removal of NO_x in the exhaust gas of diesel or lean-burn engines (3-6). It is reported that Cu ion-exchanged ZSM-5 is highly active for the selective reduction of NO (7); however, the high activity of Cu-ZSM-5 to NO reduction decreases gradually with time-on-stream at temperatures higher than 973 K. One reason for the decrease in activity seems to be the poor thermal stability of ZSM-5 (8-10). In addition, dealumination easily proceeds on ZSM-5 under a humidified atmosphere, resulting in accelerating decreases in the activity for NO_x reduction. We have investigated Cu ion-exchanged SAPO-*n* for the selective reduction of NO and have found that Cu-SAPO-34 exhibits high activity for NO reduction with C₃H₆ (11). The state of ion-exchanged Cu in SAPO-34 and its catalytic properties are also being studied by other groups (12, 13). In this paper, the activities of Cu-SAPO-*n* (*n* = 5, 11, and 34) for NO_x reduction with C₃H₆ in the presence of O₂ are further studied as a thermostable NO_x removal catalyst. Moreover, the oxidation states of the copper ions in SAPO-34 on treatment with C₃H₆, NO, and O₂ in the working state have been studied to explore the mechanism of the selective reduction of NO with C₃H₆.

1. INTRODUCTION

Aluminophosphates (AlPO₄-*n*) are a new family of molecular sieves that possess the characteristics of a molecular-sized pore structure and solid acidity. In particular, AlPO₄-*n* exhibits extremely high thermal stability as compared with synthetic zeolites. It was reported that the crystal structure of AlPO₄-5 is retained up to 1473 K (1). Similarly, the crystal structure of SAPO-34 is sustained up to 1273 K, even in the presence of humidity (2). Silicoaluminophosphates (SAPO-*n*) exhibit cation-exchange properties as a result of the isomorphous substitution of P in AlPO₄ by Si. Therefore, AlPO₄-*n* and SAPO-*n* have great possibilities as thermostable catalysts; however, the advantages in thermal stability of SAPO-*n* or AlPO₄-*n* have not yet been thoroughly exploited in conventional studies.

Selective reduction of NO_x under an oxidizing atmosphere with hydrocarbons has attracted attention as a new

2. EXPERIMENTAL

Catalyst Preparation

SAPO-5, 11, and 34, (Si, Al, and P contents: 1.77, 12.09, and 10.03 mmol g⁻¹, respectively) and zeolite β (SiO₂/Al₂O₃ = 26) were synthesized according to U.S. patents (14, 15). To prepare SAPO-*n*, colloidal SiO₂, Al compound [pseudo-boehmite phase (Cataloid AP, Catalysis & Chemical Ind.) for SAPO-5 and SAPO-11, Al[OCH(CH₃)₂]₃ for SAPO-34], phosphoric acid (85%), and template amine (triethylamine for SAPO-5, di-*n*-propylamine for SAPO-11, and 10% tetraethylammonium hydroxide for SAPO-34) were mixed at room temperature for a few hours. The precursor of SAPO-*n* obtained in this way was heated (453 K, 12 h for SAPO-5 and SAPO-11, 483 K, 24 h for SAPO-34) in autoclaves (Taiatsu Glass TAF-150) in which all parts were coated with Teflon. The synthesized SAPO-*n* and zeolite β, as well

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as the commercial ZSM-5 (Mobil, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) and USY (Catalysis & Chemical Ind., $\text{SiO}_2/\text{Al}_2\text{O}_3 = 17$), were ion-exchanged with Cu^{2+} in a 0.01 M Cu^{2+} acetate aqueous solution. At the final stage of Cu ion exchange, ammonia water was added to adjust the pH to 7.5 to control the amount of Cu ion-exchanged. Exchanged amounts of Cu^{2+} for each type of SAPO-*n*, β , USY, and ZSM-5 were estimated to be about 3 wt% from ICP analysis. In the case of SAPO-*n*, this amount of Cu corresponds to ca. 75% of the formula ion-exchange capacity, which is estimated by assuming that all the Si forms ion-exchange sites. Before measurement of the activity for NO reduction with C_3H_6 , the catalysts were calcined at 773 K for 4 h in a He stream.

NO Reduction with C_3H_6

The catalytic activities for NO reduction were measured with a fixed-bed microflow reactor. A gas mixture consisting of NO (5000 or 1000 ppm), C_3H_6 (1000 ppm), O_2 (5%), and He (remainder) was fed to the catalyst bed at $W/F = 0.3 \text{ g}\cdot\text{cat}\cdot\text{s cm}^{-3}$ (Space velocity = ca. 8500 h^{-1}), where *W* and *F* stand for catalyst weight and flow rate, respectively. Conversion to N_2 was estimated from analysis of the N_2 concentration in the flue gases by gas chromatography. The heat resistances of SAPO-*n* and ZSM-5 were determined by calcining at a prescribed temperature for 2 h in air containing 3 vol% H_2O .

Characterization of Cu Ion-Exchanged SAPO-34

The valence of the Cu ions in SAPO-34 was determined by ESR (JEOL JEX-FE1X) and XPS (Shimadzu ESCA-850). Before the ESR measurement, the catalyst was evacuated at 773 K for 5 h, calcined in O_2 (100 Torr) at 673 K for 4 h, and then evacuated at 573 K for 4 h. The ESR measurement was performed at room temperature and diphenylpicrylhydrazyl (DPPH) was used as an external standard for the calibration of the *g* value. XPS measurement of the ion-exchanged Cu in SAPO-34 was performed after a calcination in oxygen (1 atm) at 623 K for 3 h in the pretreatment chamber. Magnesium $K\alpha$ (1254.6 eV) was used as the X-ray source for measurement of the XPS of Cu $2p_{3/2}$ and the Auger line of Cu LMM. The binding energy of Cu $2p_{3/2}$ and the position of the LMM Auger peak were corrected by taking the binding energy of deposited Au $4f_{7/2}$ level as 84 eV.

Adsorption states of NO or C_3H_6 on Cu-SAPO-34 were investigated by infrared absorption spectroscopy (Hitachi 270 spectrometer). A sample disk (ca. 0.03 g) was heated at 773 K for 5 h *in vacuo* to remove water and other adsorbed gases. After calcination in O_2 (100 Torr) at 673 K for 4 h, the sample disk was exposed to the adsorbed gas (100 Torr) in an IR cell with KBr single-crystal windows. The background spectrum was subtracted from the IR spectra measured after adsorption treatment. A mass spectrometer (Anelva,

AQA-100R) was connected to the IR cell for qualitative analysis of the gas phase during the adsorption treatment.

The crystal structure of Cu ion-exchanged SAPO-34 was analyzed by X-ray diffraction and NMR measurements. X-ray diffraction analysis (Rigaku, 2013CN) was performed with the Cu $K\alpha$ line and NMR spectra for ^{27}Al , ^{31}P , and ^{29}Si were recorded with a Bruker APR-300 spectrometer operating at a field of 7 T using the magic-angle-spinning (MAS) technique. Spinning speeds of 5.5 kHz were used and the chemical shifts of Al, P, and Si were referred to the external standard of 1.5 M $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in $\text{Al}(\text{NO}_3)_3$ aqueous solution, H_3PO_4 (85%), and 4.5 M tetramethylsilane in benzene solution, respectively.

3. RESULTS AND DISCUSSION

Selective Reduction of NO with C_3H_6 on Metal Ion-Exchanged SAPO-*n*

Figure 1 shows the catalytic activity of Cu ion-exchanged SAPO-*n*, β , USY, and ZSM-5 as a function of reaction temperature. Since it is reported that Cu-ZSM-5 is active for direct decomposition of NO ($2\text{NO} = \text{N}_2 + \text{O}_2$), an excess amount of NO in comparison with that of C_3H_6 was fed in this experiment. Note, therefore, that the reaction conditions in Fig. 1 deviate strongly from the actual flue gases from vehicles. As reported, Cu-ZSM-5 exhibits high activity for NO reduction at 573 K and the activity decreases with increasing temperature (7). Since the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the examined ZSM-5 is 30, which is higher than that of ZSM-5 examined by Hosose *et al.* (7), the NO reduction activity of Cu-ZSM-5 examined in this study was slightly lower than that of Cu-ZSM-5 previously reported (7), albeit

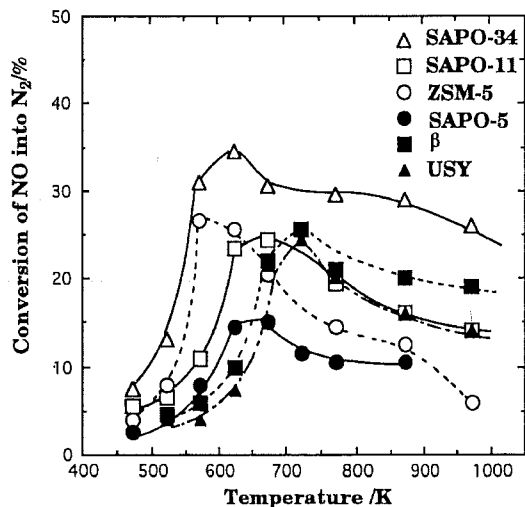


FIG. 1. Temperature dependence of catalytic activity of molecular sieves ion-exchanged with Cu for NO reduction with C_3H_6 ($P_{\text{NO}} = 5000 \text{ ppm}$, $P_{\text{C}_3\text{H}_6} = 1000 \text{ ppm}$, $P_{\text{O}_2} = 5\%$, $W/F = 0.3 \text{ g}\cdot\text{s cm}^{-3}$).

with different reaction conditions. This may result from the different acidity of ZSM-5 resulting from the difference in the SiO₂/Al₂O₃ ratio. Zeolite β and USY ion-exchanged by Cu also exhibit a high activity to NO reduction; however, a temperature higher than 673 K was required to attain the high conversion to N₂. Although the temperature at which each Cu-SAPO-*n* attains maximum conversion to N₂ is higher than that of Cu-ZSM-5 by about 50 K, the activity of Cu-SAPO-*n* for NO reduction is comparable to that of Cu-ZSM-5, except for SAPO-5. In particular, Cu-SAPO-34 exhibits a higher activity to NO reduction than Cu-ZSM-5 over the entire temperature range, although the space velocity of the reactant is low. Furthermore, the high activity was sustained up to 873 K. Therefore, conversion to N₂ is twice higher on Cu-SAPO-34 than on Cu-ZSM-5 at 873 K. Since Cu-SAPO-34 exhibited the highest activity to NO reduction with C₃H₆ among the catalysts examined, catalytic activity for NO reduction and thermal stability were investigated on SAPO-34 in this study.

It has been reported that the activity of ZSM-5 is strongly affected by the ion-exchanged metal cation (16). Figure 2 shows the effects of the metal cation on the NO reduction activity of SAPO-34. Reduction of NO with C₃H₆ proceeded on all metal cation-exchanged SAPO-34 and almost the same maximum conversion of NO to N₂ was exhibited; however, the temperature at maximum NO conversion occurred depended strongly on the metal cations ion-exchanged. Fe-SAPO-34 exhibited high activity in a low temperature range from 473 to 873 K. On the other hand, high activity was attained at temperatures higher than 873 K on Ag-SAPO-34. Among the metal cations examined in this study, copper is the most suitable as an ion-exchanged

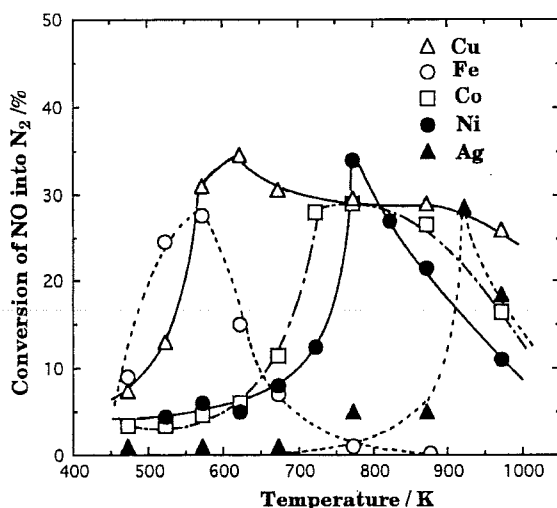


FIG. 2. Effects of different metal cations ion-exchanged in SAPO-34 on the catalytic activity for NO reduction with C₃H₆. The loading of metal is 3.0 wt% ($P_{\text{NO}} = 5000$ ppm, $P_{\text{C}_3\text{H}_6} = 1000$ ppm, $P_{\text{O}_2} = 5\%$, $W/F = 0.3$ g · s cm⁻³).

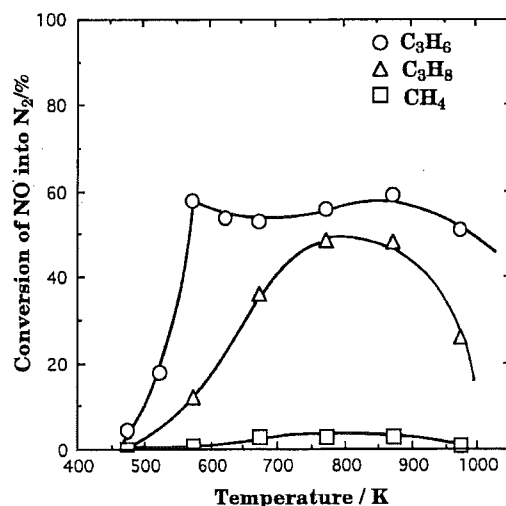


FIG. 3. Effects of different hydrocarbons as reductant on the activity of Cu-SAPO-34 for NO reduction ($P_{\text{NO}} = 1000$ ppm, $P_{\text{hydrocarbon}} = 1000$ ppm, $P_{\text{O}_2} = 5\%$, $W/F = 0.3$ g · s cm⁻³).

cation for SAPO-34, considering the activity and temperature range of high NO conversion.

The activity of Cu-SAPO-34 for NO reduction is strongly dependent on the kind of hydrocarbon used as a reductant (Fig. 3). Although high activity for NO reduction was obtained over a wide temperature range by using C₃H₆ for reductant, the reaction temperature at high NO conversion was shifted to a higher temperature range and became narrow by using C₃H₈. On the other hand, selective reduction of NO to N₂ hardly proceeded when using CH₄ for reductant. The different influences of hydrocarbons as reductants on the activity of Cu-SAPO-34 for NO reduction seem to result from the differences in combustibility, since N₂ began to form on commencement of the oxidation of the hydrocarbons. It is expected that high conversion in NO reduction can be attained on Cu-SAPO-34 by using for reductant various kinds of hydrocarbons, except hydrocarbons with low combustibility such as CH₄.

Figure 4 shows NO conversion to N₂ as a function of the amount of Cu ion-exchanged. Since the number of ion-exchange sites is not completely correlated with the amount of Si in the case of SAPO-*n*, the amount of Cu is expressed on the basis of weight percent. It is also noted that 3.5 wt% Cu corresponds to almost 100% ion-exchange level. Clearly, conversion of NO to N₂ increases with increasing amount of Cu ion-exchanged and attains a maximum around 4 wt%. Although maximum NO conversion was obtained at 4.5 wt%, the activity gradually decreased and the color of the catalyst changed from clear blue to black after reaction. This suggests that some copper ions are reduced and aggregate during reaction. This may result from the fact that the amount of Cu ion is in excess of the ion-exchange sites, because Si in the framework of SAPO-34

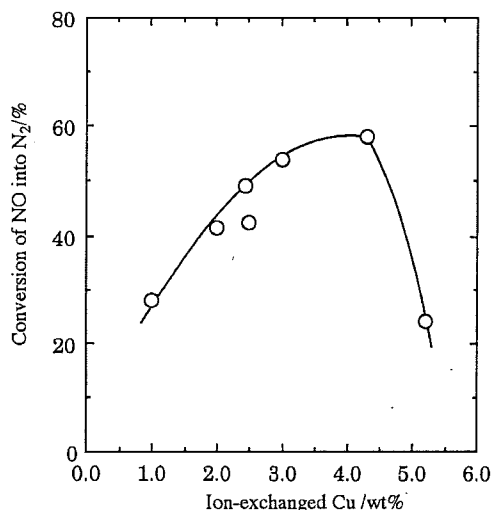


FIG. 4. NO conversion at 623 K as a function of the amount of Cu ion-exchanged ($P_{\text{NO}}=1000$ ppm, $P_{\text{C}_3\text{H}_6}=1000$ ppm, $P_{\text{O}_2}=5\%$, $W/F=0.3$ g \cdot s cm^{-3}).

does not always form ion-exchange sites. This means that isomorphous substitution of Al with Si has also occurred in the case of SAPO- n (17). Consequently, the catalytic performance of Cu-SAPO-34 was studied in more detail with Cu-SAPO-34 at 3.0 wt%.

Thermal Stability of Cu-SAPO-34

Exhaust gases from engines contain humidity at high concentration. The influence of calcination in a humidified atmosphere on NO reduction activity is shown in Fig. 5. Although the activity of Cu-SAPO-34 to NO reduction was unaffected by the calcination up to 1073 K in a dry atmosphere, calcination at 1073 K in a humidified atmosphere decreased the activity for NO reduction. Therefore, the

thermal stability of SAPO-34 is expected to decrease in the presence of H_2O ; however, the extent of the decrease in the activity of Cu-SAPO-34 for NO reduction was relatively small, even after calcination at 1073 K in wet air, as shown in Fig. 5a. In contrast to Cu-SAPO-34, Cu-ZSM-5 became almost inactive by the same heat treatment, as shown in Fig. 5b. The thermal stability of SAPO-34 far exceeds that of the aluminosilicate, ZSM-5, since the crystal structure of synthesized SAPO-34 was sustained up to 1273 K, even in a wet atmosphere (2). Therefore, the thermal stability of Cu-SAPO-34 is satisfactorily high enough that it can be used as catalyst for automotive exhaust gases.

The changes in the crystal structure of SAPO-34 under NO reduction in a wet atmosphere were studied by XRD, as shown in Fig. 6. The XRD pattern in Fig. 6 indicates that the synthesized SAPO-34 is a single phase with good crystallinity (18). It is clearly shown that no changes can be recognized in XRD patterns of Cu-SAPO-34 prior to and after the NO reduction at 973 K for 5 h in an atmosphere containing 15 vol% H_2O . Moreover, degradation of crystals usually decreases the intensity of XRD peaks, and no such decrease was observed after NO reduction in a wet atmosphere. This suggests that the long-range order of SAPO-34 structure is stably sustained under NO reduction at temperatures as high as 973 K, even in an atmosphere containing H_2O .

Since no changes were observed in XRD patterns of SAPO-34 before and after reduction of NO at 973 K in a wet atmosphere, possible changes in the local structure of SAPO-34 ion-exchanged by Cu were investigated by NMR. Figure 7a shows the ^{27}Al -, ^{31}P -, and ^{29}Si -MAS NMR spectra of Cu-SAPO-34 prior to reduction of NO at 973 K for 5 h in an atmosphere containing 15 vol% H_2O . As-synthesized SAPO-34 exhibits MAS NMR spectra for Al, P, and Si similar to those previously reported (2). The resonance at 42 and -13 ppm in the ^{27}Al -NMR spectra seems to be that of a tetrahedral and an octahedral coordinated Al, respectively

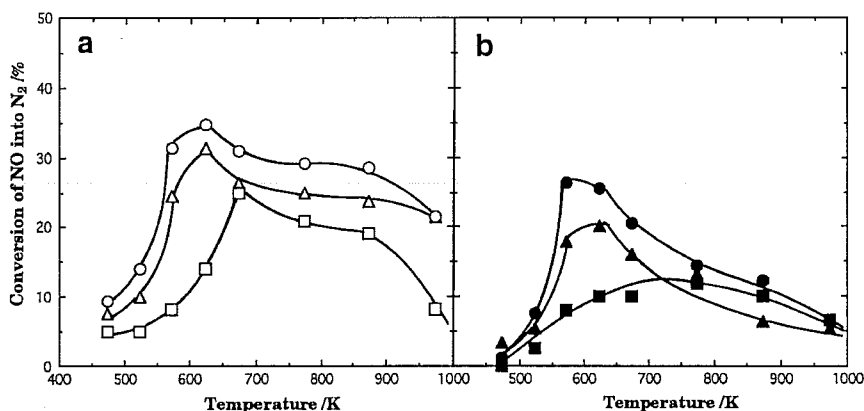


FIG. 5. Effects of heat treatment under an atmosphere containing 3 vol% H_2O on the activity for NO reduction with C_3H_6 ($P_{\text{NO}}=5000$ ppm, $P_{\text{C}_3\text{H}_6}=1000$ ppm, $P_{\text{O}_2}=5\%$, $W/F=0.3$ g \cdot s cm^{-3}). (a) Cu-SAPO-34: (○) 773 K, (△) 973 K, (□) 1073 K. (b) Cu-ZSM-5: (●) 773 K, (▲) 973 K, (■) 1073 K.

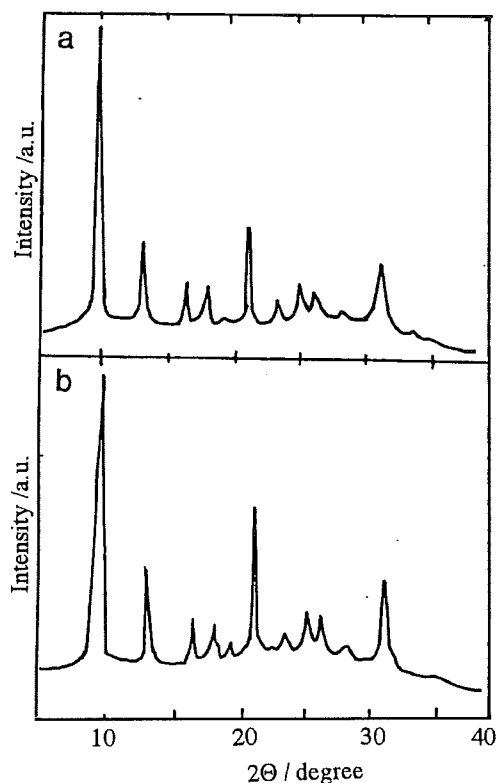


FIG. 6. X-ray diffraction patterns of Cu-SAPO-34 prior to or after NO reduction with C₃H₆ at 973 K for 5 h in an atmosphere containing 15 vol% H₂O. (a) Before reaction, (b) after reaction.

(2, 19). On the other hand, the ³¹P-MAS NMR spectrum consists of a strong resonance line at -26 ppm and a broader line at -19 ppm, which could be assigned to a tetrahedral P without additional coordination or with water coordination, respectively (2, 20). Since the amount of Si is far smaller than that of Al or P, the intensity of the ²⁹Si-MAS NMR spectrum was weaker than those of P or Al; however,

only one resonance due to tetrahedral Si was observed at -89 ppm in ²⁹Si-MAS NMR (2, 21, 22). This peak observed for Si-MAS NMR could be assigned to Si(4Al) according to the reports of Barthomeuf and co-workers (22). At the low concentration of Si in SAPO-*n*, added Si is isomorphously substituted for lattice P atoms; however, it is reported that the substitution of Si in the Al sites in addition to the P sites occurs at high Si content (23). In this study, the Si content in synthesized SAPO-34 was as low as 1.77 mmol g⁻¹. Consequently, all Si atoms added seem to substitute isomorphously at the lattice position of the P sites but not the Al sites. This is because only one kind of Si bonded with 4 Al atoms was recognized in ²⁹Si-MAS NMR spectra.

Figure 7b shows the MAS NMR spectra of ²⁹Si, ²⁷Al, and ³¹P in Cu-SAPO-34 after NO reduction at 973 K, 5 h in a wet atmosphere. Although the relative intensity of peaks in ²⁷Al-NMR spectra was slightly changed, significant changes could not be observed in the MAS NMR spectra of Si, Al, and P. These MAS NMR studies clearly indicate that SAPO-34 ion-exchanged with Cu retained the crystal structure in short-range order as well as long-range order, even after NO reduction at a temperature as high as 973 K in coexistence with water vapor.

Figure 8 shows the temperature dependence of Cu-SAPO-34 for NO selective reduction with C₃H₆ prior to and after treatment at 973 K, 5 h in an atmosphere containing 15 vol% H₂O. It is clearly shown that the activity of Cu-SAPO-34 to NO reduction hardly varied after this heat treatment. These unchanged activities to NO reduction confirm the high thermal stability of the SAPO-34 crystal lattice which is shown by the NMR results.

Conversion of NO to N₂ was studied as a function of time-on-stream in the atmosphere containing 15 vol% H₂O (Fig. 9). Compared with the NO conversion in a dry atmosphere shown in Fig. 1, the presence of water decreased the NO conversion. This may result from the suppression of NO or C₃H₆ adsorption by the coadsorption of water; however,

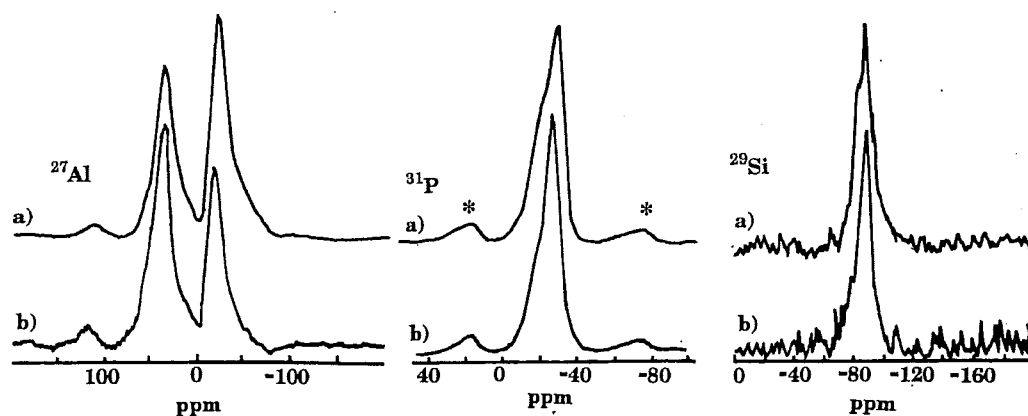


FIG. 7. MAS NMR spectra of Cu-SAPO-34 prior to or after NO reduction with C₃H₆ at 973 K for 5 h in an atmosphere containing 15 vol% H₂O. (a) Before reaction, (b) after reaction. *Spinning side band.

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