

Selective Catalytic Reduction of NO_x by Propene over Copper-Exchanged Pillared Clays

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Abstract—Copper-exchanged pillared clays were examined as an SCR catalyst for NO_x removal by propene. Both micropores and mesopores were simultaneously developed by pillaring a bentonite with TiO₂. Therefore, TiO₂-pillared clay has about 8 to 9 times higher surface area and 3 times higher pore volume than the parent unpillared bentonite. The presence of water in the feed gas stream caused a small and reversible inhibition effect on NO removal activity of Cu/Ti-PILC. The water tolerance of Cu/Ti-PILC was higher than copper-exchanged zeolites such as CuHM and Cu/ZSM-5 due to its high hydrophobicity as confirmed by H₂O-TPD experiment. Copper-exchanged PILC was confirmed to be an active catalyst for NO_x removal by propene. The addition of copper to TiO₂-pillared clay greatly enhanced the catalytic activity for NO removal. Cupric ions on Ti-PILC were active reaction sites for the present reaction system. The state of copper species on the surface of Ti-PILC varied with the content of copper and TiO₂. The catalyst having more easily reducible cupric ions showed maximum NO conversion at relatively lower reaction temperatures. It indicates that the redox behavior of cupric ions is directly related to NO removal mechanism. The redox property of cupric ions depended on the copper content and dehydration temperature of PILC.

Key words: Pillared Clay, Copper Species, SCR, NO_x, Propene, Water Tolerance

INTRODUCTION

Selective Catalytic Reduction (SCR) by NH₃ has been known to be the best available control technology for the removal of NO_x from stationary sources [Boer et al., 1990; Nakajima, 1991; Cho, 1994; Ham et al., 2000; Choi et al., 2001]. However, this technology still has several disadvantages such as NH₃-slip causing secondary pollution and difficulty in the handling of corrosive and toxic NH₃. Therefore, there have been many efforts to replace NH₃ with other reductants such as hydrocarbons and urea. Recently, diesel and lean-burn engines have attracted considerable attention due to their high fuel efficiency. These types of engines present new challenges for NO_x emission control, as they generally operate under oxidizing condition at which typical three-way catalysts show little activity for NO_x removal. Since NH₃ is not suitable for application to motor vehicles, increased effort has been focused on the development of suitable catalysts capable of reducing NO_x with hydrocarbons as reducing agents.

The backbone of SCR by hydrocarbon is also the development of a catalyst that is highly active for NO_x removal and tolerant to water. Many classes of catalysts including metal-exchanged zeolite [Iwamoto et al., 1991; Sato et al., 1992; Teraoka et al., 1992; Li et al., 1993; Kim et al., 1995], supported noble metal [Hamada et al., 1991] and metal oxide catalysts [Kintaichi et al., 1990; Hamada, 1994; Hong et al., 1997] have been examined as SCR catalysts by hydrocarbon. In particular, metal-exchanged ZSM-5 has been widely examined as an SCR catalyst by hydrocarbons due to higher NO removal activity than other catalysts. However, the SCR catalysts

by hydrocarbons still have several problems to be solved such as hydrothermal stability and deactivation by H₂O. One of the most serious problems is the catalyst deactivation by H₂O, since NO removal activity significantly decreases even with a small amount of water in the feed gas stream [Kim et al., 1997, 1999]. Therefore, the water tolerance of the catalyst is the main barrier to be overcome for the development of commercial SCR catalyst using hydrocarbons as reducing agents.

Recently, Li et al. [1997] and Yang et al. [1998] reported that metal-exchanged pillared interlayer clays (PILCs) were more tolerant to H₂O and SO₂ than metal-exchanged zeolites which were widely examined as an SCR catalyst by hydrocarbons. Moreover, PILCs are known to be highly hydrophobic due to the hydrophobic nature of oxide pillar surface [Han et al., 1999]. This is the motivation of the present study examining PILCs as an SCR catalyst. A PILC has a heat-stable porous structure by insertion of robust and large metal oxide between the interlayer of clay. In addition, PILC has peculiar characteristics such as acidity, well-developed 2-dimensional structure and cation exchange capability [Izumi et al., 1992]. Therefore, it has attracted attention as a potential catalyst material in many reaction systems including SCR reactions [Chen et al., 1995; Li et al., 1997; Yang et al., 1992, 1998].

In the present study, copper-exchanged titania pillared clays were examined as a catalyst for the reduction of NO_x by propene. The aim of the present study is to correlate NO removal activity and water tolerance of Cu/Ti-PILC catalysts with their catalytic characteristics. The alteration of pore structure of bentonite by pillaring TiO₂ was identified by N₂ adsorption isotherm and low-angle XRD. The state of copper species was investigated by H₂-TPR and XPS and their role for the present SCR reaction system was elucidated. An H₂O-TPD experiment was conducted to elucidate the water tol-

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erance of the catalyst.

EXPERIMENT

1. Catalyst Preparation

The parent clay for the preparation of Ti-PILC was a bentonite which was a purified montmorillonite supplied from Fisher Chemical Co. The pillaring agent, a solution of partially hydrolyzed Ti-polycations, was prepared by slowly adding TiCl₄ into a 2 M HCl solution and diluted with distilled water to obtain final Ti and HCl concentrations of 0.82 M and 0.4 M in the solution, respectively. The pillaring agent was aged for 12 h at room temperature prior to use. 10 g of clay was dispersed in a 1.5 L distilled water by vigorous stirring for 5 h at room temperature. The pillaring agent was then mixed with a clay suspension in the ratio of 5-15 Ti/clay (mmol Ti/g of clay) and left for contacting with the clay for 12 h at room temperature. The solid product was separated by vacuum filtration and repeatedly washed with deionized water until no formation of white AgCl precipitate by AgNO₃ test. It was air-dried at 110 °C for 12 h and calcined at 300-500 °C for 5 h for dehydration of Ti-polyhydroxy cations and formation of pillar oxides. The TiO₂ content of Ti-PILCs prepared by different Ti/clay ratio is shown in Table 1.

Cu/Ti-PILC catalysts were prepared by ion-exchanging Ti-PILC with a cupric nitrate solution. The copper content of catalysts was adjusted by changing the concentration of cupric nitrate solution and exchanging time. After exchanging with cupric ions, the catalyst was dried at 110 °C for 12 h and followed by calcination at 500 °C for 5 h. The numbers in the name of catalysts indicate the copper contents in wt%.

2. Catalyst Characterization

2-1. N₂ Adsorption

N₂ adsorption-desorption isotherm was measured by a Micromeritics ASAP 2010 sorption analyzer using liquid nitrogen at 77 K. Prior to the adsorption of N₂, the catalysts were degassed at 150 °C for more than 24 h under vacuum. The specific surface area of catalyst was estimated from BET and Langmuir equations.

2-2. H₂-Temperature Programmed Reduction (TPR)

H₂-TPR measurement was made to identify the copper species and their reducibility on the catalyst surface. A catalyst sample of 0.1 g was charged in a U-shaped quartz microreactor with 1/4" O.D. It was then pretreated under an He (40 cc/min) flow at 500 °C for 1 h and cooled to room temperature. The consumption of H₂ up to 800 °C at a heating rate of 10 °C/min was continuously monitored by gas chromatography with a thermal conductivity detector (TCD).

2-3. H₂O-Temperature Programmed Desorption (TPD)

Prior to H₂O-TPD measurement, a catalyst sample was pretreated

in a similar way to that described for the H₂-TPR measurement. The adsorption of water on the catalyst surface was performed by adding water to the feed gas stream using water saturator at room temperature for 30 minutes. After the adsorption of water, the catalyst was fully purged by He to remove loosely bound water molecules on the catalyst surface. The water evolving during the TPD was detected by gas chromatography with a TCD.

2-4. X-ray Powder Diffraction (XRD)

X-ray powder diffraction patterns were observed by an M18XHF X-ray diffractometer (Mac Science Co.) using a high resolution Debye-Scherrer camera. Ni-filtered CuK α radiation ($\lambda=1.5415 \text{ \AA}$) was utilized as an X-ray tube operated at 40kV and 200 mA. To precisely examine the pattern of (001) reflection peak in parent clay and various Ti-PILCs, the XRD patterns in the range of 2θ from 3 to 12 were taken at the steps of 0.02 with a scanning speed of 0.05°/min.

2-5. X-ray Photoelectron Spectroscopy (XPS)

To identify the copper state on Ti-PILCs catalyst surface, X-ray photoelectron spectra were examined by a Perkin-Elmer PHI 5400 XPS using an Mg K α radiation source. Charging effect of XPS spectra was calibrated by carbon (1s) line at 284.6 eV associated with hydrocarbon impurities on the catalyst surface.

3. Reaction Apparatus and Procedures

NO removal activity was investigated in a continuous flow fixed-bed reactor. Typical reactant gases for activity test consisted of 1,000 ppm NO, 1,000 ppm C₃H₆, 4% O₂ and He (balance gas). Water was injected to the feed gas stream by using a glass bubbler. When water was fed to the feed gas stream, its concentration was 10%. Total flow rate of feed gas was 250 cc/min. 0.5 g of catalyst was charged into a reactor made of a 3/8" SUS tube, and heated by an electrical tube furnace. The reactants and products were analyzed by on-line gas chromatography (Shimadzu Model 14A). NO removal activity was evaluated in terms of NO conversion as $2[N_2]_{out}/[NO]_{in}$.

RESULTS AND DISCUSSION

1. Characterization of Pore Structure of PILC

To identify the alteration of pore structure by pillaring TiO₂ into bentonite, the pore structure of PILC was examined by N₂ adsorption method. Fig. 1 shows N₂ adsorption and desorption isotherms of bentonite, PILCs and copper-exchanged PILC. The bentonite reveals a typical adsorption isotherm of microporous material. The hysteresis loop becomes pronounced in all PILCs isotherm, indicating the development of mesoporosity. The adsorption isotherms of PILCs show simultaneous development of micropores and mesopores by pillaring TiO₂ to bentonite. The PILCs prepared in the present study show well-developed bimodal pore size distributions

Table 1. Specific surface area and pore volume of bentonite and TiO₂-pillared clays

Catalysts	BET surface area (m ² /g)	Langmuir surface area (m ² /g)	Pore volume* (cm ³ /g)	TiO ₂ content (wt%)
Bentonite	33	44	0.079	-
Ti-PILC5	289	412	0.255	35.0
Ti-PILC10	264	371	0.283	44.6
Ti-PILC15	283	399	0.293	43.0
Cu5.54/Ti-PILC15	240	336	0.276	43.3

*BJH desorption cumulative pore volume of pores between 8.5 and 1,500 Å radius.

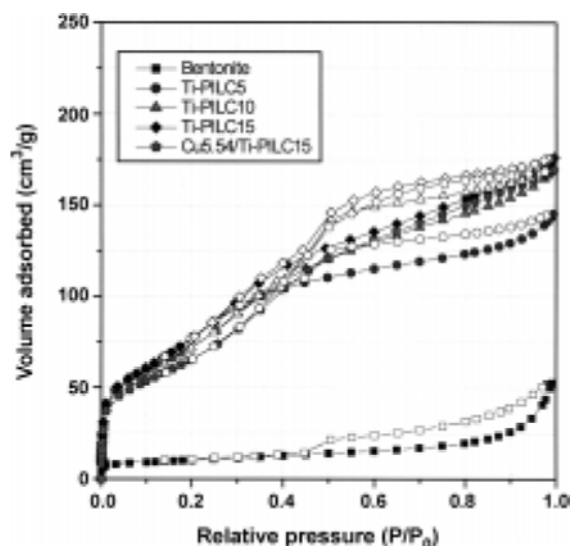


Fig. 1. N_2 adsorption and desorption isotherms of bentonite and Ti-PILCs. Closed symbol: adsorption curve, open symbol: desorption curve.

by pillaring TiO_2 to bentonite, which is a typical pore structure of PILC. The micropore and mesopore structures of the PILC do not seem to be significantly affected by ion exchange of copper ions.

BET and Langmuir surface areas and the pore volumes of all samples are summarized in Table 1. Since almost all the samples contained micropores of only a few molecular dimensions, the BET model based on multilayer adsorption would give an underestimate of the surface area. Therefore, Langmuir surface area is also summarized in Table 1. The BET surface area of parent bentonite was about $30 \text{ m}^2/\text{g}$, while that of Ti-PILCs increased to above $240 \text{ m}^2/\text{g}$, which was 8 to 9 times higher than the parent bentonite. The pore volume also increased up to 3 times higher than that of bentonite.

The alteration of pore structure of PILC was also identified by low-angle XRD patterns. As shown in Fig. 2, bentonite itself exhibits a characteristic peak at 7° of 2θ . It is generally assigned to the basal

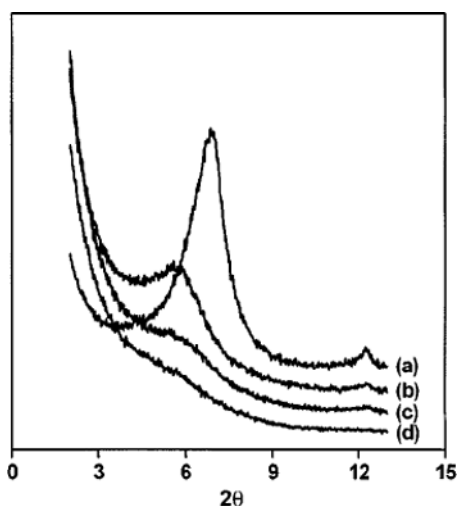


Fig. 2. XRD patterns of bentonite and Ti-PILCs. (a) bentonite, (b) Ti-PILC5, (c) Ti-PILC10, (d) Ti-PILC15.

(001) reflection peak. Compared to the unpillared bentonite, the $d(001)$ peak of the pillared clay was shifted toward lower 2θ angles, indicating an increase in the $d(001)$ basal spacing. As the content of pillared titania increased, the intensity of (001) reflection peak also significantly decreased. It may be due to the characteristic of the large interlayer space and the development of house-of-cards structure that lacked a long range stacking order [Cheng and Yang, 1995; Chae et al., 2001]. The mesopores of PILC might be induced by the increase of the $d(001)$ basal spacing and the formation of house-of-cards structure through the delamination of the long-ranged layer structure as confirmed by XRD patterns.

2. Water Tolerance of Cu/Ti-PILC Catalyst

Water tolerance is most critical for the development of commercially applicable SCR catalyst. The water tolerance of Cu/Ti-PILC was compared with that of CuHM and Cu/ZSM-5 catalysts, which had been widely examined as SCR catalysts by hydrocarbon. As

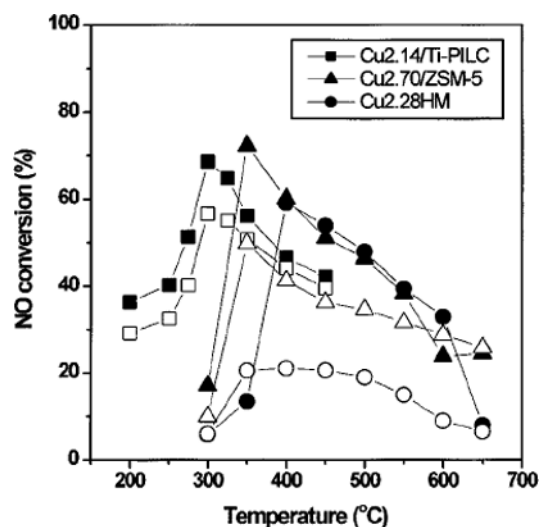


Fig. 3. Comparison of water tolerance of Cu/Ti-PILC with Cu-ZSM-5 and CuHM. Closed symbol: without water; open symbol: with 10% water.

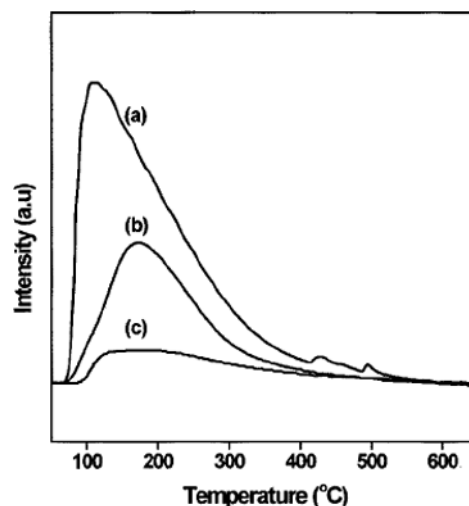


Fig. 4. H_2O -TPD profiles of Cu/Ti-PILC and zeolite catalysts. (a) CuHM, (b) CuZSM-5, (c) Cu2.14/Ti-PILC.

shown in Fig. 3, although NO removal activity of Cu/Ti-PILC decreases to some extent by 10% water in the feed gas stream, the activity loss is not so severe over all the reaction temperatures. In contrast, zeolite catalysts show significant activity loss in the presence of 10% water. To understand the reason why the Cu/Ti-PILC is highly tolerable to water compared to zeolite catalysts, the amount of water adsorbed to the catalyst surface was measured by H₂O-TPD. As shown in Fig. 4, the amount of water adsorbed to Cu/Ti-PILC is much less than that on zeolite catalysts, which indicates that Cu/Ti-PILC is highly hydrophobic, compared to zeolite catalysts. This is the reason why the activity of Cu/Ti-PILC is less inhibited by water than zeolite catalyst as shown in Fig. 3. It is well known that the suppression of water adsorption on pillared clay is due to the hydrophobic nature of oxide pillar surface [Han et al., 1999]. The activity loss of CuHM is much severer than Cu/ZSM-5. The effect of water on NO removal activity of zeolite catalysts seems to largely depend on the hydrophobicity determined by the amount of water adsorbed on their surface. As investigated by H₂O-TPD, the amount of water adsorbed on the surface of CuHM is much higher than that of Cu/ZSM-5. The hydrophobicity of zeolite catalysts is known to primarily depend on their framework Si/Al ratio. It is generally known that the amount of water adsorption on a zeolite catalyst decreases as its Si/Al ratio increases [Flanigen et al., 1978]. The degree of activity loss by water is consistent with the hydrophobic nature of catalysts as confirmed by H₂O-TPD.

The influence of water on NO removal activity of Cu/Ti-PILC was also examined by a cyclic operation in the absence and presence of water alternatively as shown in Fig. 5. NO removal activity was fully reversible with respect to the presence of water. When water was injected to the feed gas stream, the activity quickly decreased, but its original activity was rapidly recovered by stopping the water injection. This result indicates that the activity loss in the presence of water is possibly due to the competitive adsorption between reactants and water on active sites. The alteration of cupric ions on the surface of a zeolite to inactive copper oxide clusters was known to be one of reasons for the deactivation by water [Kharas

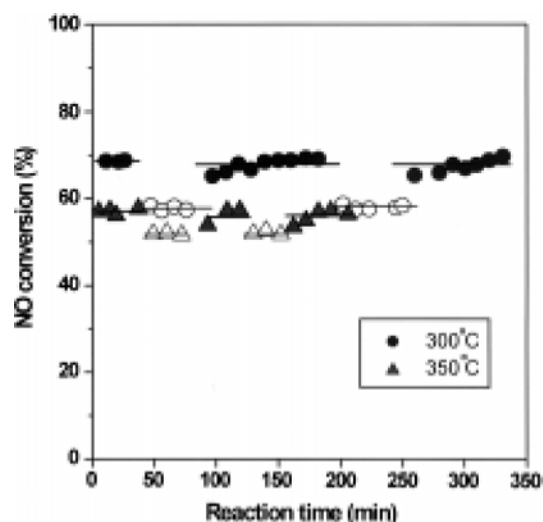


Fig. 5. Reversibility of NO removal activity with respect to the presence of water. Catalyst: Cu_{2.14}/Ti-PILC15, closed symbol: without water, open symbol: with 10% water.

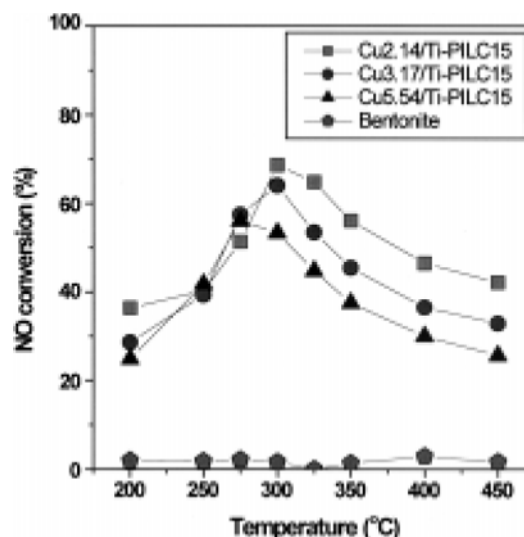


Fig. 6. Effect of copper content on NO removal activity of Cu/Ti-PILC catalysts.

et al., 1993]. However, the reversibility of activity loss with respect to the absence and presence of water may suggest that chemical alteration of copper species on the PILC surface is not expected even in the presence of water.

3. Effect of Copper Content on NO Removal Activity

Fig. 6 shows the effect of copper content of Cu/Ti-PILC catalyst on NO removal activity. The Ti-PILC itself shows negligible NO removal activity over all reaction temperatures. However, NO removal activity significantly increases by the addition of copper and reveals a bell-shaped curve with respect to reaction temperatures. This suggests that the copper species play a role in promoting NO reduction by propene. However, despite the fact that copper species are active reaction sites, it is observed that NO removal activity decreases with the increase of copper content. It may indicate that different copper species exist on the catalyst surface with respect to copper content, and NO removal activity largely depends on the state of copper species. Therefore, an H₂-TPR experiment was made to identify the state of copper species on the catalyst surface. It has been reported that the reduction of isolated Cu²⁺ species occurs by the following two steps [Torre-Abreu et al., 1997a, b].



As shown in Fig. 7, two reduction peaks are observed for all three catalysts with different copper content. It indicates the existence of cupric ions on the catalyst surface. The Cu_{2.14}/Ti-PILC catalyst with the lowest copper content exhibits two distinct peaks at 200 and 325 °C. The peaks appearing at lower and higher temperatures may be due to the reduction of Cu²⁺ to Cu⁺ and Cu⁺ to Cu⁰, respectively. Comparing the area of two reduction peaks, however, it is observed that the peak at higher temperature is slightly larger than that at lower temperature. Moreover, the peak at lower temperature becomes larger with the increase of copper content. This indicates that another type of copper species also exists on the catalyst surface and its ratio to cupric ions becomes larger with the increase of

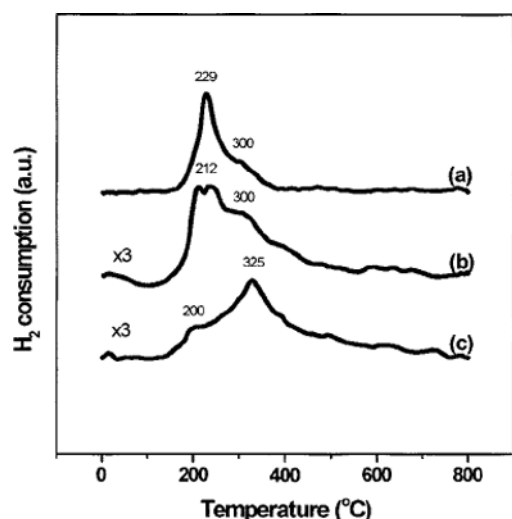


Fig. 7. H_2 -TPR profiles of Cu/Ti-PILC catalysts with different copper content.

(a) $Cu_{5.54}/Ti-PILC15$, (b) $Cu_{3.17}/Ti-PILC15$, (c) $Cu_{2.14}/Ti-PILC15$.

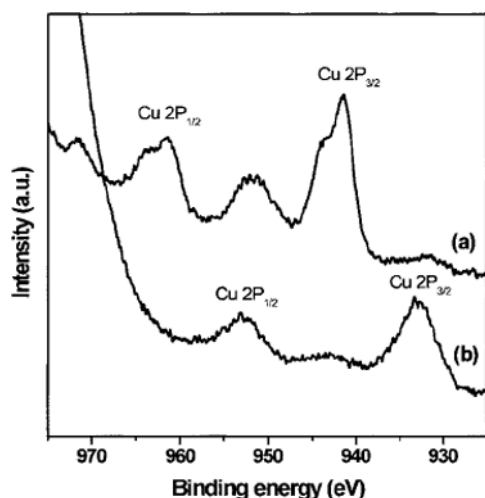


Fig. 8. Cu 2p XPS spectra of Cu/Ti-PILC catalysts.

(a) $Cu_{5.54}/Ti-PILC15$, (b) $Cu_{2.14}/Ti-PILC15$.

copper content.

To identify the other type of copper species predominantly existing on the catalyst with higher copper content, an XPS measurement was conducted for two catalysts with different copper content as shown in Fig. 8. The $Cu_{5.54}/Ti-PILC15$ catalyst reveals shake-up satellite peaks corresponding to two main 2p peaks at higher binding energy. In contrast, the shake-up satellite peaks do not appear for $Cu_{2.14}/Ti-PILC15$ catalyst. The shake-up satellite peak is usually characteristic of CuO species [Wagner et al., 1979]. Therefore, besides cupric ions, the dominant copper species on the catalyst with higher copper content was CuO species, which was suspected to exist from the inequality of two reduction peaks observed by H_2 -TPR of Fig. 7. It is well known that cupric ions are more active reaction sites than CuO for NO_x removal by hydrocarbon [Liese and Grünert, 1997; Yan et al., 1997]. This is the reason why NO removal activity decreases with the increase of copper content, as ob-

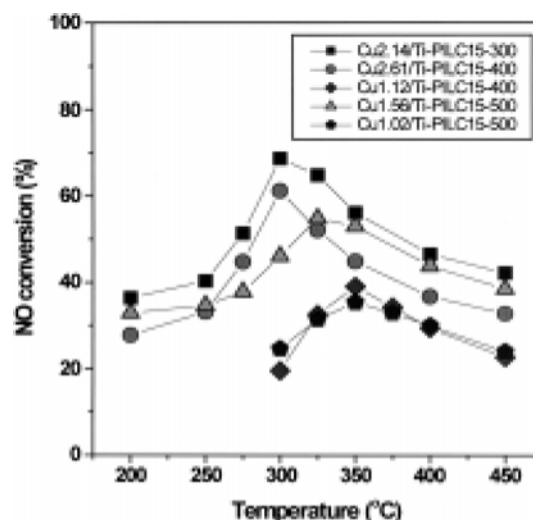


Fig. 9. Effect of dehydration temperature of pillared clay on NO removal activity.

served in Fig. 6. The cupric ions preferentially exist on the catalysts with lower copper content. As the copper content increases, the copper species exceeding the ion-exchange capacity of PILC exist in the form of CuO.

4. Effect of Dehydration Temperature of PILC on NO Removal Activity

As one of the important conditions during the preparation of PILC, the effect of dehydration temperature of PILC was examined, as shown in Fig. 9. NO removal activity increases with the increase of copper content up to 2.14 wt%, regardless of dehydration temperature. This is attributed to the fact that copper species primarily exist in the form of cupric ions, which are active reaction sites, on the catalyst with lower copper content as confirmed by H_2 -TPR of Fig. 10. However, maximum NO conversion shifts to higher tem-

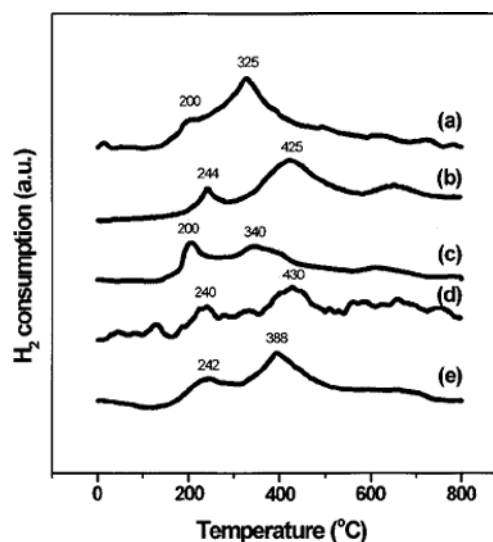


Fig. 10. H_2 -TPR profiles of Cu/Ti-PILC catalysts prepared at different dehydration temperatures.

(a) $Cu_{2.14}/Ti-PILC15-300$, (b) $Cu_{1.12}/Ti-PILC15-400$, (c) $Cu_{2.61}/Ti-PILC15-400$, (d) $Cu_{1.02}/Ti-PILC15-500$, (e) $Cu_{1.56}/Ti-PILC15-500$.

perature for the catalyst dehydrated at higher temperature and that having lower copper content. The cupric ions on catalyst showing maximum conversion at higher temperature are also reduced at higher temperatures as observed in H₂-TPR of Fig. 10. The reducibility of copper species depends on how strongly they interact with the support. The weaker the interaction between copper species and PILC framework, the easier the reduction of copper species. Therefore, the easier reduction of copper species is likely due to a decrease of the electrostatic interaction between copper ions and PILC framework with the decrease of dehydration temperature and the increase of copper content. A similar behavior was observed for CuMOR and CuMFI catalysts [Torre-Abreu et al., 1997a, b].

The reducibility of the copper species affects the operating temperature window of the catalyst. The catalyst containing copper species, which are easily reduced, decreases the temperature of maximum NO conversion and shifts the operating temperature window to lower temperatures. This indicates the redox behavior of cupric ions is directly involved in the reaction mechanism of NO reduction over Cu/Ti-PILC catalyst. The reducibility of cupric ions possibly depends on the dehydration temperature and copper contents of Cu/Ti-PILC catalysts.

5. Effect of TiO₂ Content on NO Removal Activity of PILC

The effect of TiO₂ content on NO removal activity of PILC was examined as shown in Fig. 11. Cu_{4.69}/Ti-PILC catalyst with the lowest TiO₂ content exhibits higher NO removal activity than the other two catalysts. It may indicate that the TiO₂ content of Ti-PILC has an effect on the state of copper species. Note that Ti-PILC5 contains about 35 wt%, while Ti-PILC10 and Ti-PILC15 do more than 40 wt%. As already discussed, NO removal activity of Cu/Ti-PILC catalyst considerably depends on the state of copper species. To identify the state of copper species, an H₂-TPR measurement was made for the three catalysts as shown in Fig. 12. Although not clearly resolved, two reduction peaks are observed for the three catalysts, indicating the presence of cupric ions on the catalyst surface. However, the reduction peak at higher temperature appears as a small shoulder. The large difference of the two peaks area is due to the presence of CuO species, besides cupric ions. The larger reduction

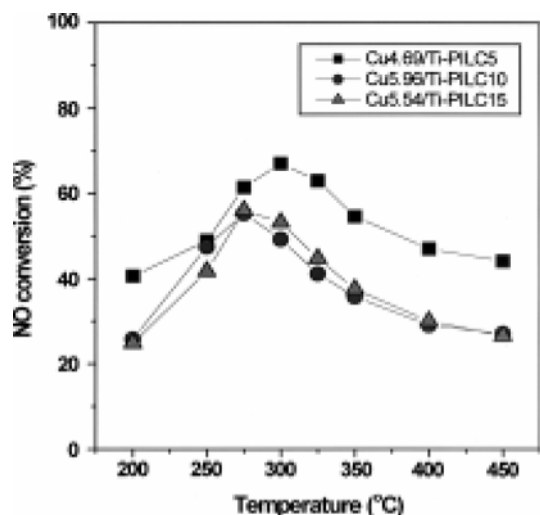


Fig. 11. Effect of TiO₂ content of pillared clay on NO removal activity.

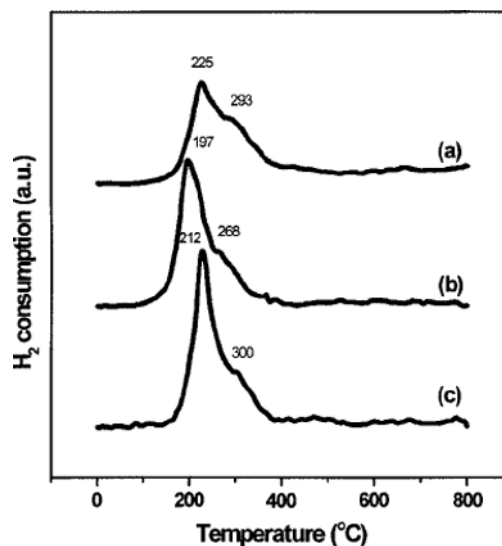


Fig. 12. H₂-TPR profiles of Cu/Ti-PILC catalysts with different TiO₂ content.

(a) Cu_{4.69}/Ti-PILC5, (b) Cu_{5.96}/Ti-PILC15, (c) Cu_{5.54}/Ti-PILC15.

peak at lower temperature is the superposition of reduction of CuO and cupric ions. Comparing the reduction peaks of the three catalysts, it is observed that the shoulder of PILC5 appearing at higher temperature is larger than that of the other two catalysts. It means that the relative amount of cupric ions to CuO species is higher on PILC5 catalyst. As already discussed, cupric ions are more active reaction sites than CuO species for NO_x removal. This is the reason why the Cu_{4.69}/Ti-PILC5 catalyst containing lower TiO₂ content shows higher NO removal activity. Since the pillaring also proceeds by ion exchange of precursor material, the available sites for copper ion exchange of Ti-PILC decrease with the increase of TiO₂ content. This result suggests that TiO₂ content also affects the state of copper species on PILC surface.

CONCLUSIONS

Copper-exchanged pillared clays were examined as an SCR catalyst for NO_x removal by propene. The PILCs prepared in the present study showed well-developed bimodal pore size distribution by pillaring TiO₂ to bentonite, which is a typical pore structure of PILC. The presence of water in the feed gas stream caused a small and reversible inhibition effect on NO removal activity of Cu/Ti-PILC. The water tolerance of Cu/Ti-PILC was much higher than copper-exchanged zeolites such as CuHM and CuZSM-5 due to its high hydrophobicity as confirmed by H₂O-TPD experiment. The reversibility of activity loss with respect to the absence and presence of water might suggest that the activity loss in the presence of water was possibly due to the competitive adsorption between reactants and water on active sites. Cu/Ti-PILC revealed high NO removal activity by propene based upon redox mechanism. Cupric ions on Ti-PILC were active reaction sites for the present reaction system. The state of copper species on the surface of Ti-PILC varied with the content of copper and TiO₂. The reducibility of cupric ions depended on the copper content and dehydration temperature of

PILC. The easier reducibility of the copper species had an effect on the operating temperature of the catalysts by decreasing the temperature of maximum NO conversion, which resulted in the shift of the operating temperature window to lower temperatures. The redox behavior of cupric ions seems to be closely related to NO removal activity of copper-exchanged PILC catalyst.

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