Characterization of the active sites on Pt-loaded ZSM-5 (Pt/ZSM-5) prepared by an ion-exchange method for the oxidation of CO at low temperatures

Yukiko Yamasaki, Masaya Matsuoka, and Masakazu Anpo*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

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Highly dispersed Pt-loaded ZSM-5 (Pt/ZSM-5) catalysts were prepared by a combination of ion-exchange and thermal pretreatment in different temperatures under vacuum. Highly dispersed ion-exchanged Pt^{2+} ions were reduced into Pt^{+} and then Pt^{0}, sustaining their high dispersion state with an increase in the thermal pretreatment temperatures up to 773 K. Thus, prepared Pt^{0} highly dispersed in the cavities of ZSM-5 exhibited high catalytic activity for the oxidation of CO with N_2O at 273 K. However, pretreatment at temperatures higher than 973 K led to the aggregation of highly dispersed Pt^{0} clusters, resulting in a decrease in the catalytic activity for low-temperature oxidation.

KEY WORDS: Pt/ZSM-5; ion-exchange method; CO oxidation.

1. Introduction

Recently, the development of low-temperature oxidation catalysts has been actively pursued not only for their utilization in the complete oxidation of odor or toxic substances such as CO or formaldehyde for the living environment [1,2] but also for various industrial applications [3,4]. It is known that noble metals such as platinum, palladium, and rhodium can act as efficient oxidation catalysts [5–8]. However, the catalytic activities of small noble metal clusters within zeolites for low-temperature oxidation have not yet been fully investigated.

In the present study, Pt^{0} were highly dispersed within ZSM-5 cavities by a combination of an ion-exchange method and thermovacuum treatment, and their catalytic activity for CO oxidation at temperatures as low as 273 K were investigated. Especially, we have focused on the relationship between the local structure of the platinum species, investigated by characterization studies using UV–vis absorption and XAFS measurements, and the catalytic activity.

2. Experimental

Pt/ZSM-5 catalysts were prepared as follows: Ion-exchange of the parent Na/ZSM-5 ($SiO_2/Al_2O_3 = 23.8$) was carried out with an aqueous solution of NH_4OH at 298 K for 24 h and then filtered and washed with distilled water. The resulting solid, NH_4/ZSM-5, was dried at 373 K for 24 h and calcined in O_2 at 773 K for 3 h to form H/ZSM-5. H/ZSM-5 was ion-exchanged with an aqueous solution of $[Pt(NH_3)_4]Cl_2$ in the same manner. The sample was then dried at 373 K for 24 h. The platinum loading on Pt/ZSM-5 was determined to be 2.6 wt% by analysis with an atomic absorption spectrometer. Prior to spectroscopic and reactivity measurements, the samples were calcined in air at various temperatures for 1 h followed by evacuation at the same temperature for 1 h. The oxidation of CO with N_2O was carried out in a closed system at 273 K. The products were analyzed by gas chromatography. The catalysts were then characterized by various spectroscopic methods such as UV–vis absorption, XAFS and FT-IR measurements.

3. Results and discussion

Figure 1 shows the UV–vis absorption spectra of Pt/ZSM-5 pretreated under vacuum at various temperatures. Pt/ZSM-5 pretreated at 273 K (figure 1(a)) exhibited an intense absorption band at around 200 nm, attributed to the $5d^8 \rightarrow 5d^7 6p^1$ transition of Pt^{2+} [9]. After pretreatment at 573 K (figure 1(b)), the absorption band due to Pt^{2+} disappeared, while the band due to the platinum ion clusters appeared. After pretreatment at 773 K (figure 1(c)), an absorption band due to the Pt^{0} metal clusters appeared and this peak shifted to a higher wavelength region at higher temperatures (figure 1(d)). These results suggest that the Pt^{2+} ions exchanged within ZSM-5 are gradually reduced to Pt^{0} clusters with

* To whom correspondence should be addressed.
E-mail: anpo@ok.chem.osakafu-u.ac.jp

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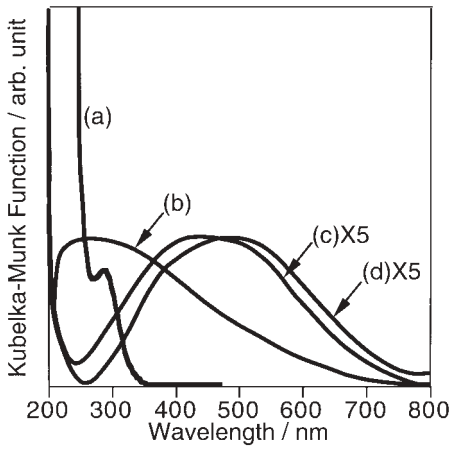

Figure 1. Diffuse reflectance UV–vis absorption spectra of Pt/ZSM-5 pretreated under vacuum at various temperatures. Pretreatment temperature (K): (a) 298, (b) 573, (c) 773, (d) 973.

an increase in the pretreatment temperatures, while above 973 K, the aggregation of the platinum metal occurs.

Figure 2 shows the XANES and Fourier transform of the EXAFS spectra of the catalysts pretreated at various temperatures. Pt/ZSM-5 pretreated below 573 K (figure 2(B)) exhibited a strong white line owing to the Pt^{2+} ions or platinum ion clusters. On the other hand, Pt/ZSM-5 pretreated below 573 K (figure 2(b)) shows a peak due to the Pt–O bond at 1.7 Å, while a strong Pt-Pt peak at 2.7 Å can be observed above 773 K (figure 2(c)) [10]. These results indicate that the Pt^{2+} ions are reduced to Pt^0 metal clusters with an increase in the pretreatment

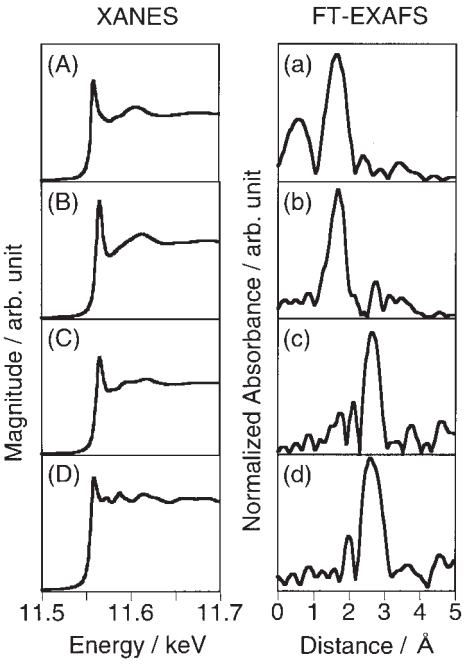

Figure 2. Pt LIII-edge XANES and FT-EXAFS spectra of Pt/ZSM-5 pretreated under vacuum at various temperatures. Pretreatment temperature (K): (A, a) 273, (B, b) 573, (C, c) 773, (D, d) 973.

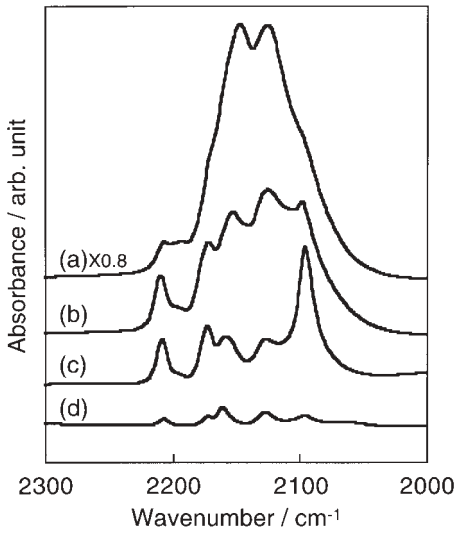

Figure 3. FT-IR spectra of CO adsorbed on Pt/ZSM-5 pretreated under vacuum at various temperatures. Pretreatment temperature (K): (a) 573, (b) 673, (c) 773, (d) 973.

temperatures, being in good agreement with the results obtained by UV–vis spectroscopic analysis.

Figure 3 shows the FT-IR spectra of CO adsorbed on the Pt/ZSM-5 catalysts pretreated at various temperatures. Typical FT-IR peaks due to the CO on the Pt^{2+} and the peak due to CO on Pt^+ at 2150 cm^{-1} and 2125 cm^{-1}, respectively [11], could be observed for the Pt/ZSM-5 pretreated at 573 K (figure 3(a)). However, the intensity of these peaks decreased when the catalyst was pretreated above 673 K (figure 3(b)) and the intensity of the band due to CO on Pt^0 at 2100 cm^{-1} [11] increased, passing through a maximum at 773 K (figure 3(c)) and decreasing at 973 K (figure 3(d)). These results suggest that the Pt^{2+} ions were reduced to highly dispersed platinum metal clusters through the reduction of Pt^+. However, above 973 K, aggregation of the platinum metal cluster occurs and this prevents the adsorption of CO on the Pt^0 clusters.

Figure 4 shows the effect of the pretreatment temperature of Pt/ZSM-5 on the N_2 yields in the oxidation of CO with N_2O as the oxidant. As shown in the bar graph of figure 4, the activity increases with an increase in the pretreatment temperature, passing through a maximum at 773 K and decreasing at 973 K. This figure also shows the effect of the pretreatment temperature on the intensity of the FT-IR peak due to the CO on highly dispersed Pt^0 clusters. It is clear that the intensity of the FT-IR peaks and the N_2 yields in the reaction show a good parallel dependence on the pretreatment temperature, suggesting that highly dispersed Pt^0 clusters play an important role in this reaction. Moreover, this reaction did not proceed on platinum black powders, clearly showing that the highly dispersed platinum metal clusters are the active species for the reaction. This is confirmed by the fact that the aggregated platinum metal clusters formed

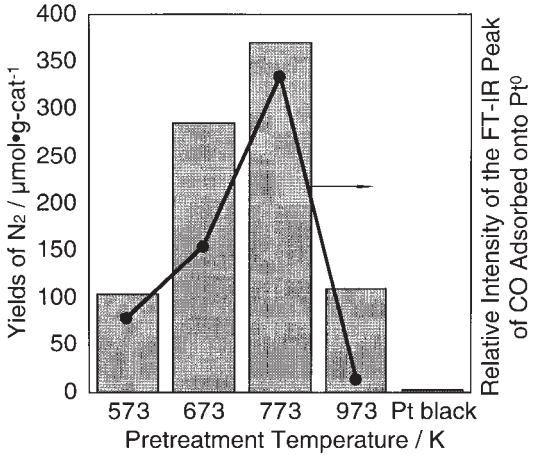

Figure 4. The effect of the pretreatment temperature of Pt/ZSM-5 on the yields of N_2 in the oxidation of CO with N_2O and the relative intensity of the FT-IR peaks due to CO adsorbed onto highly dispersed Pt^0 clusters. (Reaction temperature: 273 K).

within the catalyst pretreated at 973 K did not show a high activity.

4. Conclusions

In conclusion, UV–vis absorption and XAFS and FT-IR investigations of Pt/ZSM-5 catalysts revealed that highly dispersed Pt^{2+} and platinum ion clusters are formed within the catalyst pretreated under vacuum below 573 K, while highly dispersed Pt^0 clusters are formed within the catalyst pretreated at 773 K. Pt/ZSM-5 catalysts showed high catalytic activities for the oxidation of CO with N_2O. Detailed investigations on the effect of the pretreatment temperatures on the catalytic activity showed that highly dispersed Pt^0 clusters play an important role as the active species in the catalytic reactions. The detailed reaction mechanisms as well as their catalytic activities for the oxidation of other organic compounds are now under investigation.

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