Catalysis Letters Vol. 102, Nos. 3–4, August 2005 (© 2005)
DOI: 10.1007/s10562-005-5847-5

Preparation and Characterization of Pt/Al-ZSM-5 Catalysts and their Reactivities for the Oxidation of CO with N_2O at Low Temperatures

Masaya Matsuoka[a], Kiyoshi Iino[a], Haijun Chen[a], Yukiko Yamasaki[a], Gianmario Marta[b], Salvatore Coluccia[b], and Masakazu Anpo[a,*]

[a]*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture Univerzsity, 1-1 Gakuen-cho, Sakai Osaka, 599-8531 Japan*
[b]*Dipartimento di Chimica IFM, Universita di Torino, Via P. Giuria 7, 10125 Torino, Italy*

Received 12 February 2005; accepted 18 March 2005

Al-ZSM-5 was prepared by treating H-ZSM-5 with an aqueous solution of $Al(NO_3)_3$ and used as a support for Pt catalysts. The Pt-loaded Al-ZSM-5 acts as an efficient catalyst for CO oxidation with N_2O at 273 K. TEM investigations revealed that Pt clusters with an average particle size of around 1–1.5 nm were homogeneously dispersed within Al-ZSM-5. Moreover, FT-IR and XPS analyses indicated that the small Al_2O_3 clusters formed within Al-ZSM-5 plays a significant role in the formation of highly dispersed Pt clusters within the pore structure of the ZSM-5 zeolite, leading to the high catalytic activity of Pt/Al-ZSM-5 as compared to Pt/ZSM-5.

KEY WORDS: CO oxidation; N_2O; Pt/Al-ZSM-5; Ion-exchange method.

1. Introduction

The oxidation of CO on noble metal-supported catalysts have been extensively investigated for applications in various industrial processes such as selective CO oxidation in the presence of H_2 [1–3] as well as for industrial and automotive pollution control [4–7]. Recent studies have shown that noble metals such as Pt, Pd, Au dispersed on easily reducible metal oxides such as TiO_2 or Fe_2O_3 can act as efficient catalysts for CO oxidation even at ambient temperatures [8–11]. Previously, we have reported that Pt-loaded ZSM-5 (Pt/ZSM-5) catalysts prepared by a combination of ion-exchange and thermovacuum treatments exhibit high catalytic activity for the oxidation of CO with N_2O at temperatures as low as 273 K [12]. Detailed characterizations of Pt/ZSM-5 have revealed that the highly dispersed Pt clusters within ZSM-5 plays an important role in the reaction.

In the present study, in order to investigate methods that can enhance the efficiency and reactivity of the catalysts, H-ZSM-5 was treated with an aqueous solution of $Al(NO_3)_3$ and the resulting Al-ZSM-5 was used as a support for the Pt catalysts. Pt-loaded Al-ZSM-5 (Pt/Al-ZSM-5) was prepared by a combination of an ion-exchange method and thermovacuum treatment and its activity for CO oxidation with N_2O was investigated at 273 K. Furthermore, the effect of $Al(NO_3)_3$ aqueous treatment on the chemical states of the framework Al as well as on the particle size of the Pt catalysts have been investigated by FT-IR, XPS and TEM measurements. Significant improvement of the catalytic activity of the Pt-loaded catalysts through $Al(NO_3)_3$ aqueous treatment is reported here.

2. Experimental

The parent H-ZSM-5 ($SiO_2/Al_2O_3 = 23.8$, TOSOR corporation) was treated with an aqueous solution of $Al(NO_3)_3 9H_2O$ (0.6×10^{-2} mol/l) at 298 K for 24 h, then filtered and washed with distilled water, hereafter referred to as the $Al(NO_3)_3$ treatment. The resulting solid was dried at 373 K for 24 h and calcined in O_2 at 773 K for 3 h to form Al-ZSM-5. The SiO_2/Al_2O_3 ratio of Al-ZSM-5 was determined to be 27.0 by analysis with an atomic absorption spectrometer. Pt/Al-ZSM-5 was prepared by ion-exchange with an aqueous solution of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ (1.5×10^{-2} mol/l) at 298 K for 24 h, then filtered and washed with distilled water. After the sample was dried at 373 K for 24 h, the Pt loading of Pt/Al-ZSM-5 was determined to be 0.35 wt% by atomic absorption spectrometry. The Pt loadings for the catalysts are hereafter shown in the parentheses after the catalyst name, e.g., Pt/Al-ZSM-5(0.35). The Pt/ZSM-5 catalysts were prepared by ion-exchange of H-ZSM-5 with a $[Pt(NH_3)_4]Cl_2$ aqueous solution as in the case of Pt/Al-ZSM-5. The Pt loadings on the Pt/ZSM-5 catalysts were determined to be 0.40 and 2.6 wt%, hereafter denoted as Pt/ZSM-5(0.4) and Pt/ZSM-5(2.6), respectively. Prior to spectroscopic and reactivity measurements, the samples were calcined in air at 773 K 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 and the reaction products were

---

[*] To whom correspondence should be addressed.

analyzed by gas chromatography. The catalysts were then characterized by various spectroscopic methods such as XPS, FT-IR and TEM measurements.

3. Results and discussion

The XRD patterns of the Al-ZSM-5 and H-ZSM-5 as a support are shown in figure 1. Both samples exhibit similar XRD patterns typical to the MFI structure of ZSM-5, indicating that the framework structure of ZSM-5 as a support is not strongly affected by the $Al(NO_3)_3$ treatment. Figure 2 shows the N_2 yields in the oxidation reaction of CO with N_2O at 273 K on the Pt/Al-ZSM-5 and Pt/ZSM-5 catalysts with different Pt loadings. These Pt-loaded catalysts exhibited high activity for this reaction, and CO_2 and N_2 were formed as reaction products. The activity of Pt/ZSM-5 was found to increase with a decrease in the Pt loading, i.e., Pt/ZSM-5(0.4) exhibited three times higher activity than Pt/ZSM-5(2.6) when compared by the N_2 yields (mmol·g Pt^{-1}) [12]. Pt/Al-ZSM-5(0.35) exhibited around two times higher activity than Pt/ZSM-5(0.4), as also shown in figure 2.

In order to elucidate the cause of the different activities for the Pt-loaded catalysts, TEM measurements were carried out. Many Pt metal clusters grow in their particle size to around 10 nm on Pt/ZSM-5(2.6), as shown in figure 3. On the other hand, the average particle size of the Pt clusters loaded on Pt/ZSM-5(0.4) is around 2–3 nm, although some large Pt clusters of around 10 nm can also be found. In contrast to these Pt/ZSM-5 catalysts, the particle size of the Pt clusters loaded on Pt/Al-ZSM-5 (0.35) is quite uniform at around 1–1.5 nm. These results clearly show the close relationship between the particle size of the Pt clusters and their catalytic activity, demonstrating that the remarkably high catalytic activity of Pt/Al-ZSM-5 can be attributed to the homogeneous distribution as well as the high dispersion state of the Pt metal clusters within Al-ZSM-5.

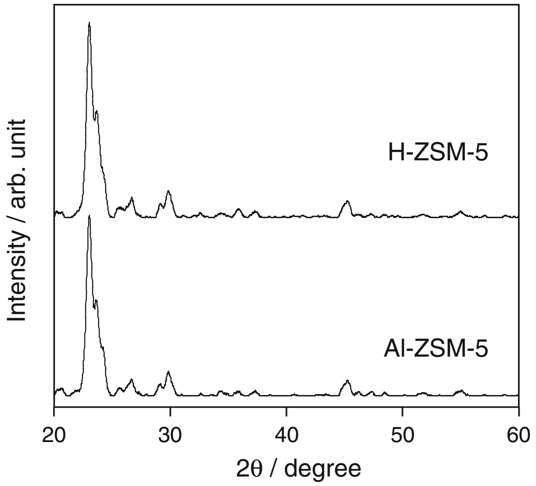

Figure 1. XRD patterns of the H-ZSM-5 and Al-ZSM-5.

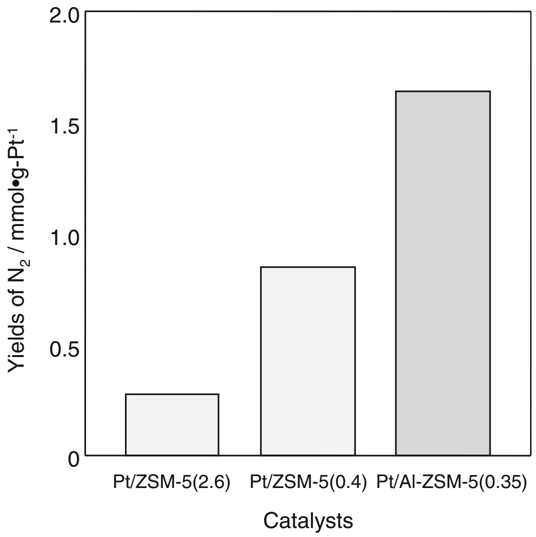

Figure 2. N_2 yield in the oxidation reaction of CO with N_2O on various Pt-loaded catalysts at 273 K. (CO: 5.0 Torr, N_2O: 5.0 Torr, Reaction time: 1 h)

The effect of $Al(NO_3)_3$ treatment on the framework structure of H-ZSM-5 as well as on the chemical states of the framework Al was investigated by FT-IR and XPS measurements. The XRD results indicate that the framework structure of H-ZSM-5 is not strongly affected by the $Al(NO_3)_3$ treatment. However, the SiO_2/Al_2O_3 ratio of H-ZSM-5 increased from 23.8 to 27.0, indicating that the zeolite framework was slightly modified by the $Al(NO_3)_3$ treatment. Figure 4 shows the FT-IR spectra of H-ZSM-5, Al-ZSM-5 and Al_2O_3 . H-ZSM-5 exhibits two well-defined FT-IR bands attributed to the bridging OH groups (3614 cm^{-1}) related to the presence of framework Al [13–16] and the terminal Si-OH groups (3746 cm^{-1}) [13–16]. On the other hand, as can be seen in figure 4, $Al(NO_3)_3$ treatment of H-ZSM-5 led to the appearance of a new band attributed to the extra-framework Al-OH groups at 3667 cm^{-1}[13–16], accompanied by a decrease in the intensity of the band for the bridging OH groups (3614 cm^{-1}). These results suggest that an extra-framework Al species was formed during $Al(NO_3)_3$ treatment, accompanying the dealumination of H-ZSM-5, as indicated by the decrease in the SiO_2/Al_2O_3 ratio after $Al(NO_3)_3$ treatment. In fact, the band due to the extra-framework Al-OH groups (3667 cm^{-1}) located at wavenumber regions similar to where those of the surface Al-OH groups of Al_2O_3 appeared (3676 cm^{-1}).

Figure 5 shows the Al 2p XPS spectra of Pt/ZSM-5(0.4), Pt/Al-ZSM-5(0.35) and Al_2O_3 as reference. Pt/ZSM-5(0.4) exhibits a typical Al 2p peak attributed to the framework Al at 74.5 eV [17]. On the other hand, Pt/Al-ZSM-5(0.35) exhibits an Al 2p peak at 77.7 eV, accompanied by a small shoulder peak attributed to the

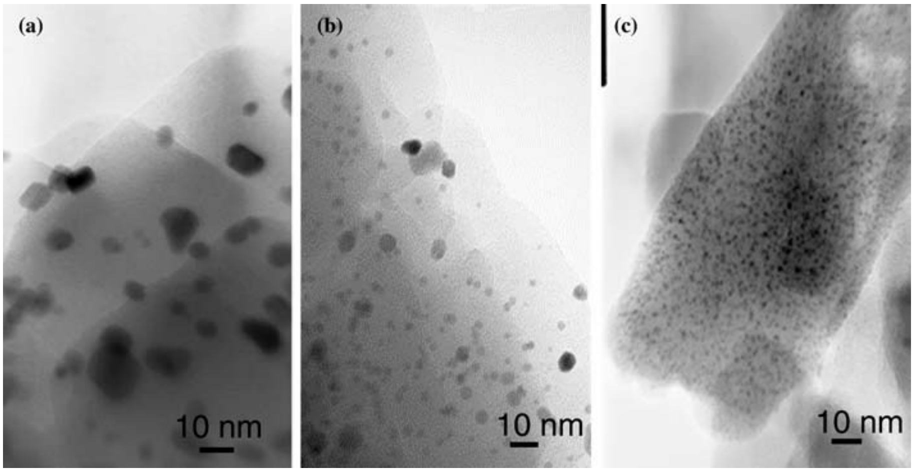

Figure 3. TEM images of the Pt/ZSM-5(2.6) (a) Pt/ZSM-5(0.4) (b) and Pt/Al-ZSM-5 (0.35) (c) catalysts.

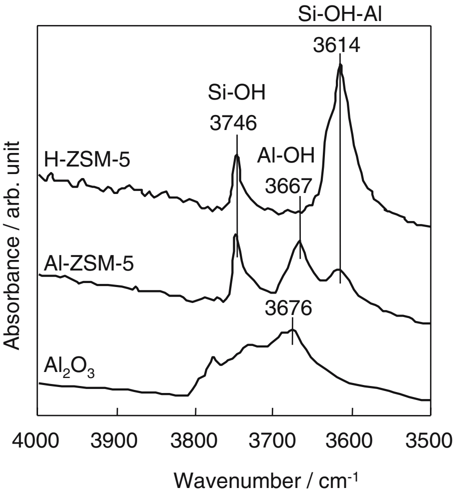

Figure 4. FT-IR spectra in the OH stretching regions of H/ZSM-5, Al-ZSM-5 and Al_2O_3 as reference.

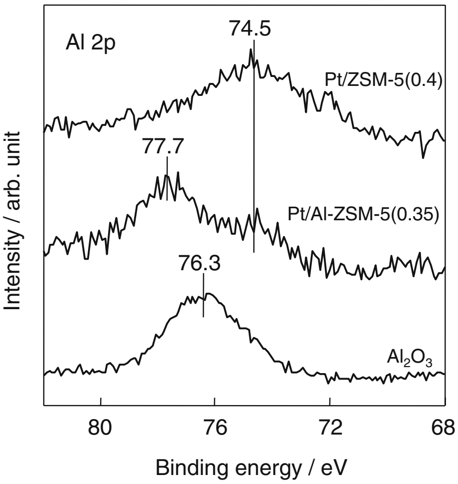

Figure 5. Al 2p XPS spectra of Pt/ZSM-5(0.4), Pt/Al-ZSM-5(0.35) and Al_2O_3 as reference.

framework Al at 74.5 eV. The Al 2p peak at 77.7 eV shifted toward higher binding energy regions as compared to the Al 2p peak observed for Al_2O_3 (76.3 eV). Such a shift in the binding energy of the Al 2p band to higher values can be attributed to the smaller relaxation energy for the highly dispersed aluminium oxide species as compared to the powdered bulk Al_2O_3[18–20]. It was also found that H-ZSM-5 and Al-ZSM-5 exhibit essentially the same Al 2p XPS profiles as observed for Pt/ZSM-5(0.4) and Pt/Al-ZSM-5(0.35), respectively. These results clearly indicate that small Al_2O_3 particles are deposited within Al-ZSM-5 by the $Al(NO_3)_3$ treatment, while parts of the framework Al reaches out from the framework position, as suggested by the FT-IR investigations. Interestingly, although the dealumination of the framework Al occurs during $Al(NO_3)_3$ treatment, ion-exchange capacities can still be maintained sufficiently to introduce 0.35 wt% of the Pt metal.

It could be concluded that $Al(NO_3)_3$ treatment leads to the formation of a highly dispersed Al_2O_3 species within the pore structure of the ZSM-5 zeolite. The small Al_2O_3 species may prevent the aggregation of the Pt clusters during the pretreatment process and stabilizes the Pt clusters in a highly dispersed state. Although the average Pt cluster size (1–1.5 nm) of Pt/Al-ZSM-5 is larger than the pore diameter of ZSM-5 (0.53– 0.56 nm), the uniform distribution of the Pt clusters throughout the Al-ZSM-5 catalyst indicates that the Pt clusters exist at the intersection of the pore channels collapsing some part of the zeolite framework [14]. Since the surface area of Pt/Al-ZSM-5 (322 m^2/g) is comparable to that of Pt/ZSM-5 (257 m^2/g), the pores of Pt/Al-ZSM-5 are not severely blocked by the highly dispersed Pt clusters. In summary, by using Al-ZSM-5 prepared by an $Al(NO_3)_3$ treatment as a support, highly dispersed Pt metal clusters having a uniform particle size (1–1.5 nm) could be incorporated within the zeolite pore structure, leading to the development of an efficient catalyst for a CO oxidation reaction with N_2O at temperatures as low as 273 K.

4. Conclusions

Highly dispersed Pt metal catalysts were prepared by a combination of an ion-exchange method and thermovacuum treatment within Al-ZSM-5 which was prepared by $Al(NO_3)_3$ treatment of H-ZSM-5. It was found that Pt/Al-ZSM-5(0.35) could act as an efficient catalyst for the CO oxidation reaction with N_2O at 273 K, exhibiting around two times higher activity than Pt/ZSM-5(0.4). TEM investigations revealed that the particle size of the Pt clusters uniformly dispersed within Pt/Al-ZSM-5(0.35) is around 1–1.5 nm and small as compared to that of the Pt clusters (2–3nm) loaded on Pt/ZSM-5(0.4). FT-IR and XPS measurements showed that the small Al_2O_3 clusters are formed within Al-ZSM-5 after the $Al(NO_3)_3$ treatment. The small Al_2O_3 clusters formed may prevent the aggregation of the Pt clusters during the pretreatment of the catalysts and stabilizes the Pt clusters in a highly dispersed state, leading to the high catalytic activity of Pt/Al-ZSM-5.

References

[1] S.H. Oh and R.M. Sinkevitch, J. Catal. 142 (1993) 254.
[2] A. Wootsch, C. Descorme and D. Duprez, J. Catal. 255 (2004) 259.
[3] M.M. Schubert, V. Plzak, J. Garche and R.J. Behm, Catal. Lett. 76 (2001) 143.
[4] Y.J. Mergler, A. van Aalst, J. van Delft and B.E. Nieuwenhuys, Appl. Catal. B Environ. 10 (1996) 245.
[5] P. Bera, A. Gayen, M.S. Hegde, N.P. Lalla, L. Spadaro, F. Frusteri and F. Arena, J. Phys. Chem. B 107 (2003) 6122.
[6] T. Bunluesin, R.J. Gorte and G.W. Graham, Appl. Catal. B Environ. 15 (1998) 107.
[7] A. Bielanski and J. Haber in: *Oxygen in Catalysis* (Dekker, New York, 1991) p. 211.
[8] W.S. Epling, G.B. Hoflund, J.F. Weaver, S. Tsubota and M. Haruta, J. Phys. Chem. 100 (1996) 9929.
[9] M. Haruta, Catal. Today 36 (1997) 153.
[10] M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, Catal. Lett. 51 (1998) 53.
[11] M. Manzoli, A. Chiorino and F. Boccuzzi, Appl. Catal. B Environ. 52 (2004) 259.
[12] Y. Yamasaki, M. Matsuoka and M. Anpo, Catal. Lett. 91 (2003) 111.
[13] S. Dzwigaj, P. Massiani, A. Davidson and M. Che, J. Mol. Catal. A Chem. 155 (2000) 169.
[14] C. Bisio, C. Caldeira, V. Dal Santo, G. Martra, P. Massiani, R. Psaro, M.F. Ribeiro, J.M. silva and L. Stievano, Inorg. Chim. Acta 349 (2003) 227.
[15] A. Janin, M. Maache, J.C. Lavalley, J.F. Joly, F. Raatz and N. Szydlowski, Zeolites 11 (1991) 391.
[16] A. Zecchina, L. Marchese, S. Bordiga, C. Paze and E. Gianotti, J. Phys. Chem. B 101 (1997) 10128.
[17] R.B. Borade and A. Clearfield, J. Phys. Chem. 96 (1992) 6729.
[18] J.C. Vedrine, M. Dufaux, C. Naccache and B. Imerik, J. Chem. Soc. Faraday. Trans. 174 (1978) 440.
[19] M. Houalla and B. Delmon, J. Phys. Chem. 84 (1980) 2199.
[20] M. Anpo, T. Kawamura and S. Kodama, J. Phys. Chem. 92 (1988) 438.