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Suppression of Pt sintering on MFI zeolite by modification with tetramethoxysilane

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Platinum sintering on zeolite catalyst is successfully suppressed by modification using tetramethoxysilane. Modification in this manner produces a protective layer of SiO_2 over each Pt particle. High-temperature (1000 °C) aging tests in air confirm the superior durability of the modified catalyst compared to a conventional γ-alumina-supported catalyst.

KEY WORDS: catalyst; durability; MFI zeolite; Pt; sintering.

1. Introduction

The activity of automotive exhaust catalysts deteriorates due to sintering of the noble metal on the catalyst surface at the high temperatures in exhaust systems. Zeolites have good heat resistance and molecular shape selectivity owing to the nanoscale framework of pores and cavities of the zeolite structure [1,2], and are thus highly suitable as supports for automotive catalysts. Zeolite with the MFI structure in particular provides great advantages with respect to the suppression of sintering by physically fixing the catalyst particles (e.g., Pt) within internal mesopores. However, catalyst particles on the external surfaces of the support remain highly susceptible to sintering, forming sinters more than 10 times larger than the original size (ca. 100 nm). In the present study, the Pt/MFI zeolite catalyst surface is modified with tetramethoxysilane as a means of applying a protective layer of SiO_2 to provide a physical constraint on externally exposed catalyst particles and thus inhibit sintering.

2. Experimental

Conventional polycrystalline MFI zeolite ($SiO_2/Al_2O_3 = 1800$) was used as the catalyst support. The catalyst was synthesized using a wet impregnation technique in which MFI zeolite powder was added to distilled water in a beaker, followed by the addition of an aqueous solution of $[Pt(NH_3)_4](OH)_2$ under continuous stirring. The mixture was then heated and stirred until evaporated to dryness. The resulting powder was calcined in air at 500 °C for 2 h, then compacted using a cold isostatic press (CIP), ground, and finally sieved to form a pelletized catalyst with a particle size of 0.5–1.7 mm. The pellet catalyst was impregnated with tetramethoxysilane using a similar method. After air-drying at room temperature, distilled water was added, and the catalyst was again dried at 120 °C for 2 h. Finally, the catalyst was calcined in air at 500 °C for 2 h to afford the sample for testing. It is assumed that a saturated level of tetramethoxysilane adsorption was achieved in the impregnation process. The actual tetramethoxysilane content was judged based on the color of the catalyst. For comparison, a second catalyst was prepared using $[Pt(NH_3)_2(NO_2)_2](NO_3)_2$ and γ-alumina. The γ-alumina support used in this work had a stick-like morphology and a specific surface area of 180 m^2. The Pt loading was 1.6 wt% for both pellet catalysts. For comparison, a portion of the Pt/γ-alumina pellet catalyst was also impregnated with tetramethoxysilane. For aging tests, a portion of these catalysts was heated at 800 or 1000 °C in air for 5 h. Pt on the external surface was observed by transmission electron microscopy (TEM) or scanning electron microscopy (SEM). MFI was made into a thin leaf by ion milling after MFI buries into the resin, and a picture of the edge of MFI was taken by TEM. The catalytic activity, determined by the temperature at 50% HC conversion, was measured using synthetic automotive exhaust at SV = 2,10,000 h^{-1}.

3. Results and discussion

3.1. Suppression of Pt sintering by tetramethoxysilane treatment

SiO_2 was chosen for this modification since it is the primary constituent of MFI zeolite and can therefore

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wet the surface easily. Impregnation of the catalyst powder with tetramethoxysilane caused immediate hydrolysis of the tetramethoxysilane and catalyst heating. This rapid exothermic reaction involving water absorbed on the MFI surface or from ambient air resulted in instantaneous cleavage of the tetramethoxysilane and drying to form a coherent layer of SiO_2 on the Pt surface. This can be confirmed from the TEM image of the Pt particles, as shown in figure 1, where every Pt nanoparticle can be seen to be coated with a layer of SiO_2. The surface part was selected and observed. The Pt particles were seen only on the surface of the outside.

The image in figure 1 is of a sample aged at 800 °C in air for 5 h. Thus, it can also be confirmed that the size of the Pt nanoparticles after aging remained at 3 nm, similar to that in the initial state. Figure 2 shows the Pt on EMI without silica modification. This image shows the reflected electronic image. After 800 °C aging, the 3 nm Pt particle observed before aging disappeared. Comparison with the catalysts prepared without silica modification clearly shows that sintering was effectively suppressed by silica treatment.

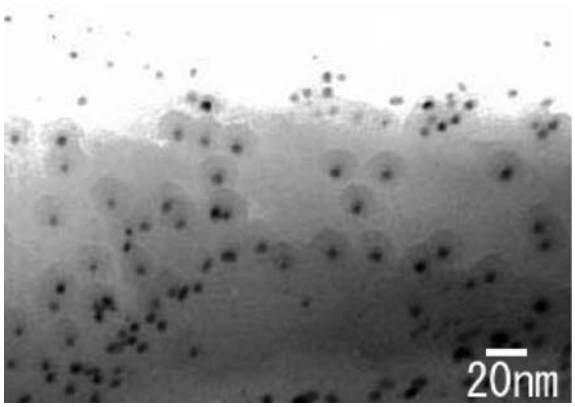

Figure 1. TEM images of Pt on the external surface of MFI zeolite agglomerates after aging at 800°C.

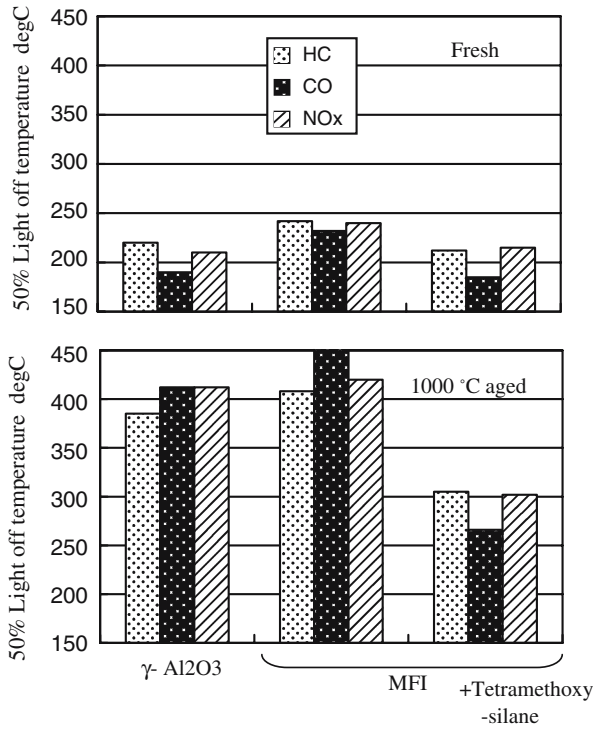

Figure 3. Comparison of three-way catalytic activity of fresh an aged catalysts synthetic exhaust gas composition: C_3H_6, 2400 ppm C; NO, 2400 ppm; CO, 1200 ppm; O_2, 0.3%; CO_2, 14%; H_2O, 3%; N_2, Bal. Pellet catalyst size: 0.5–1.7 mm. SV: 210000 h^{-1}.

3.2. Catalytic performance

The three-way catalyst activity for fresh and aged samples, measured based on the light-off temperature at 50% HC conversion, is shown in figure 3. The SiO_2-modified catalyst was expected to have low activity due to the complete coating of catalyst particles with SiO_2. However, the light-off experiments clearly demonstrate that Pt particle coating did not affect the overall performance, even at the high space velocity used in this experiment. Air aging at 1000 °C caused the same degree of deterioration in the unmodified MFI zeolite-supported catalyst as for the γ-alumina-supported sample. The modified MFI zeolite catalyst, on the other

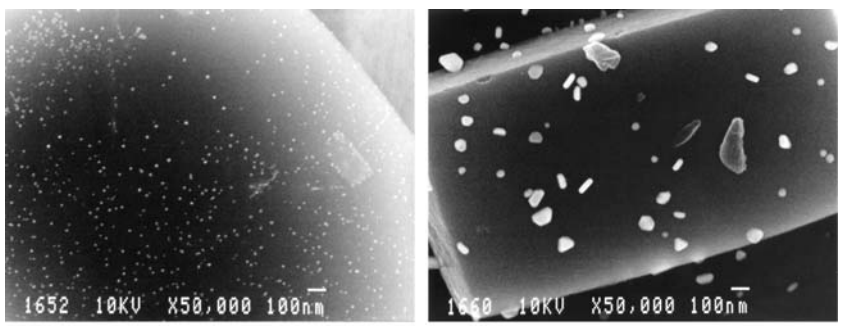

Figure 2. SEM image of outer surface of MFI zeolite: Fresh (left), air-aged at 800 °C (right). This image shows the reflected electronic image.

hand, exhibited a much smaller decrease in activity after similar aging. It is notable that the γ-alumina-supported catalyst modified with tetramethoxysilane underwent severe deterioration in this aging test, so much so that the catalytic activity could not be measured (the purification performance did not reach 50%). Tetramethoxysilane does not enter the MFI super-cage. So tetramethoxysilane can influence only the surface of the outside. Judging from the improvement of catalytic activity and Pt particle size after aging, MFI super-cage is not obviously effective for the control of the Pt sintering.

4. Conclusion

Pt particles on an MFI zeolite support were coated with a coherent layer of SiO_2 by treatment with tetramethoxysilane to inhibit sintering of Pt at high temperatures. The treatment was shown through high-temperature aging tests to suppress sintering and catalyst deterioration significantly compared to a comparable γ-alumina-supported catalyst without affecting the catalytic activity.

References

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