Preparation and three-way catalytic performance of Ir@Pt/SiO_2 nanocatalysts with core-shell structure

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Abstract: The Ir@Pt core–shell nanoparticles (NPs) were synthesized for the first time using successive reduction method based on epitaxial growth. The Ir@Pt/SiO_2 catalysts with core-shell structure were used as three-way catalysts, which exhibited high catalytic activity of NO_x reduction in three-way catalytic reaction.
Keywords: Ir@Pt NPs, Core-shell structure, Three-way catalytic performance.

1. Introduction (11-point boldface)

A recent serious problem with precious metals is concerned with their rapidly increasing use as catalysts in automobile exhaust after-treatment. To lessen the amount of precious metals in automotive catalysts, a concept of bimetallic catalysts has been recently proposed[1], which noble metal were replaced with cheaper metals, such as AuRh catalysts. Furthermore, using core-shell bimetallic catalyst is another effective way to reduce the usage of precious metals with unchanged or enhanced three-way catalytic activity[2]. According the references[3-4], Ir may be a good alternative material as the core with the less cost than Pt. Till now, there are only a few reports focused on the sphere Ir@Pt core–shell NPs used in the three-way catalytic reaction.

2. Experimental

A series of Ir@Pt NPs with different Ir/Pt molar ratio have been fabricated through epitaxial growth of the Pt over the pre synthesized seed Ir NPs. Ir@Pt NPs were deposited on SiO_2 support, and then were calcined in a tube furnace at 500 ℃ for 6 h under air flow, giving the Ir@Pt/SiO_2 catalysts. The theoretic total metal loading was 1.0 wt%. The physicochemical properties of fresh catalysts and aged samples pretreated in a steam of 10 % H_2O-90 % Air (v/v) at 1050 ℃ for 6 h were characterized by various techniques. Three-way catalytic activities were evaluated in a continuous flow fixed-bed quartz reactor (i.d.= 8 mm) with a gas mixture of 1.6% CO, 0.05% HC (propane/propene = 1:3), 0.1% NO, 1.0% O_2, 0.23% H_2, and balanced with N_2. The space velocity was120,000 mL/(g·h).

3. Results and discussion

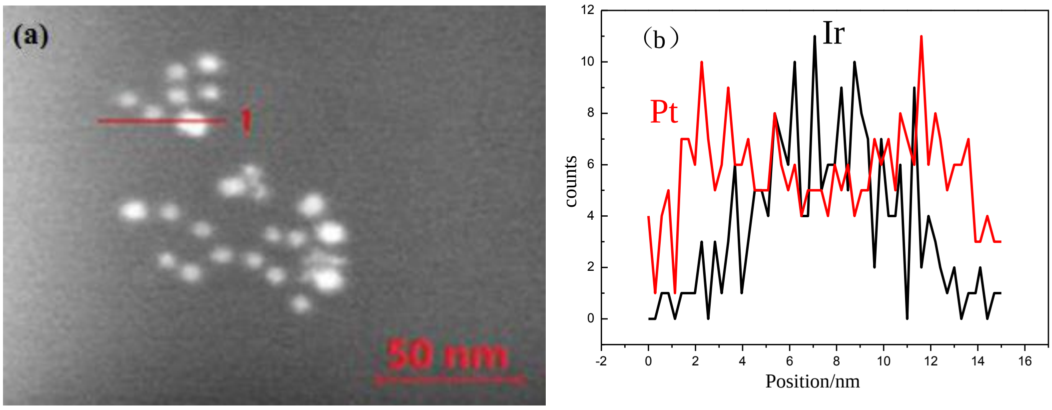

Figure 1. HAADF-STEM image of Ir@Pt NPs with Ir/Pt molar ratio of 1/4 (a) and line-scanning analysis of the NPs(b).

From the TEM images (not display here), one can see that the size distribution of Ir core and Ir@Pt NPs were monodisperse and uniformity. The average sizes of Ir core particles and Ir@Pt particles with the

Ir/Pt ratio of 2/1 were ca. 1 and 2.2 nm, respectively. The size of Ir@Pt NPs could be regulated by the Pt/Ir molar ratio. Figure 1 is the the EDS line-scanning results of Ir@Pt NPs with Ir/Pt molar ratio of 1/4. The Pt element existed with a bimodal Pt distribution, the two maximum peaks appeared at the edge of the nanoparticle. Whereas, the Ir element existed in the center of the nanoparticle with the maximum peak of Ir in the center of the EDS line. The results clarified that Ir NPs were covered by Pt components, which were consistent with the results of CO DRIFT(not display here).

From the results of catalytic test we know that CO and HC conversions on the activities of CO and HC oxidation over the Ir@Pt/SiO_2 catalyst were higher than those over the Ir/SiO_2 catalyst. However, the Ir@Pt/SiO_2 catalyst had better activities of CO oxidation and NO reduction than those of Pt/SiO_2. Furthermore, the Ir@Pt/SiO_2 catalyst widened the air-to-fuel working window and exhibited better three-way catalytic activity and higher thermal stability in the NO reduction than the Pt/SiO_2 catalyst.

Table 1. Three-way catalytic activities of the fresh and aged catalysts.

samples	CO (°C)		HC(°C)		NO (°C)	
	T_{50}	T_{90}	T_{50}	T_{90}	T_{50}	T_{90}
Pt/SiO_2	172	212	367	>420	256	>420
Ir/SiO_2	230	242	>420	>420	265	277
Ir@Pt/SiO_2(2:1)	194	253	340	>420	171	192
Ir@Pt/SiO_2(1:1)	172	230	282	>420	172	192
Ir@Pt/SiO_2(1:2)	173	207	280	>420	172	240
Ir@Pt/SiO_2(1:4)	171	188	298	>420	153	226
Pt/SiO_2-aged	362	400	420	>420	358	>420
Ir/SiO_2-aged	>420	>420	>420	>420	>420	>420
Ir@Pt/SiO_2(1:1) -aged	362	398	371	>420	360	405

It is interesting that the CO and HC conversions on the Ir@Pt/SiO_2 catalyst with Ir/Pt ratio of 1/1 were similar to the Pt/SiO_2 monometallic catalyst and the NO conversion on the catalyst was significantly higher than over the Pt/SiO_2 catalyst. The usage of Pt amount in the Ir@Pt/SiO_2 catalyst was less ca. 50 wt% than that of the Pt/SiO_2, implying the Pt usage can be reduced as the Ir@Pt NPs is employed as the active component in three-way catalysts.

4. Conclusions

In summary, the Ir@Pt NPs with Pt deposition on the Ir NPs were fabricated with epitaxial growth using successive reduction method. The three-way catalytic performance of the Ir@Pt/SiO_2 catalysts with core–shell structure was evaluated. The Ir@Pt(1/1)/SiO_2 catalyst showed similar catalytic activities in CO and HC oxidation to the Pt/SiO_2 catalyst, but it showed higher catalytic activity in NO reduction than the Ir/SiO_2 and Pt/SiO_2 catalysts. From the analysis above, one conclusion could be obtained that the Ir@Pt/SiO_2 catalysts possessed of higher catalytic activity in NO reduction than the Ir/SiO_2 and Pt/SiO_2 catalysts, which have potential to be used as three-way catalysts. Furthermore, the usage of Pt metal in the Ir@Pt/SiO_2 catalyst can be reduced as compared to the Pt/SiO_2 catalyst.

5. Acknowledgements

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References

1. H. He, H.X. Dai, X. H. Zi. US Patent, 8382877 B (2013)
2. Y.W. Ma, H.M. Zhang, H.X. Zhong, T. Xu, H. Jin, X.Y. Geng, Catal Commun 11 (2010) 434