Mesoporous cobalt oxide-supported palladium catalysts with high performance for *o*-xylene oxidation

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Abstract: The Pd-based catalysts have been widely studied for the combustion of volatile organic compounds, in which the roles of the Pd and the support are still not known clearly. In this study, mesoporous Co_3O_4 and CoO were prepared and used as support for the loading of Pd nanoparticles (NPs). The supported Pd samples performed much better than the supports for *o*-xylene combustion, in which the Pd/meso-CoO sample showed the best catalytic activity ($T_{90\%}$ = 173 °C). We conclude that the excellent catalytic performance of the Pd/meso-CoO sample was associated with its strong ability of *o*-xylene adsorption and oxygen activation, particularly the *o*-xylene adsorption ability.

Keywords: mesoporous CoO, supported Pd catalyst, *o*-xylene oxidation.

1. Introduction

Control of volatile organic compound (VOC) emissions is important since they are hazardous to the environment and human health. Catalytic combustion is regarded as one of the most promising pathways for VOC removal, in which the key issue is the availability of catalysts with good low-temperature activity and stability. The supported noble metal catalysts are highly efficient for VOC removal at low temperatures[1]. Although Pd-based catalysts have been widely studied for VOCs oxidation, the roles of the Pd and support are still not known clearly. Previously, we found that meso-CoO was rich in Co^{2+} species and showed a high catalytic activity for *o*-xylene combustion since it favored formation of highly active O_2^- and O_2^{2-} species[2]. In this work, we report catalytic properties of Pd/meso-CoO for *o*-xylene combustion.

2. Experimental

Ordered mesoporous Co_3O_4 and CoO were fabricated according to the strategy reported previously[2]. The meso-Co_3O_4 and meso-CoO-supported Pd samples were prepared using the PVA-protected reduction method. Physicochemical properties of the samples were characterized by means of the ICP–AES, XRD, TEM, BET, XPS, CO-TPR, O_2-TPD, *o*-xylene-TPD, and in situ DRIFT techniques, and their catalytic activities for *o*-xylene (1000 ppm) combustion were evaluated in a fixed-bed quartz microreactor at a space velocity (SV) of 40,000mL/(g h). Reactants and products were analyzed online by gas chromatography.

3. Results and discussion

The XRD results indicate that the meso-Co_3O_4 and meso-CoO samples possessed a highly ordered mesoporous structure with a cubic Ia3d symmetry. Pd loading did not induce a significant alteration in mesoporous architecture of the meso-CoO support. The Pd NPs were highly dispersed on the meso-Co_3O_4 or meso-CoO support. Pd particle sizes in Pd/meso-Co_3O_4 and Pd/meso-CoO were 3.6 and 3.7 nm, respectively. Surface areas of meso-Co_3O_4 and Pd/meso-Co_3O_4 were 94–95 m^2/g, much higher than those (ca. 65 m^2/g) of meso-CoO and Pd/meso-CoO. With the loading of Pd NPs, the O_{ads}/O_{latt} molar ratio increased, implying that the loading of Pd further enhanced the O_{ads} species concentration on the sample surface. The higher O_{ads} species concentration on the surface of the meso-CoO and Pd/meso-CoO samples demonstrate that the two samples exhibited better oxygen activation ability than the meso-Co_3O_4 and Pd/meso-Co_3O_4 samples. In other words, the meso-CoO-based samples possessed high oxygen activation ability. The reduction profile of the Pd/meso-CoO sample was rather similar to that of the meso-CoO sample. The loading of Pd significantly enhanced the *o*-xylene adsorption ability of the supports, with the Pd/meso-CoO sample showing the strongest ability of *o*-xylene adsorption.

The meso-CoO sample performed better than the meso-Co_3O_4 sample (the $T_{50\%}$ over the former was 21 °C lower than that over the latter); furthermore, the loading of Pd significantly enhanced the low-temperature catalytic activity of the meso-Co_3O_4 and meso-CoO samples, in which the Pd/meso-CoO sample showed the highest activity (the $T_{50\%}$ was 25 and 74 °C lower than that over the Pd/meso-Co_3O_4 and meso-CoO samples, respectively). Based on the characterization results, we conclude that the excellent catalytic activity of Pd/meso-CoO was associated with its good *o*-xylene adsorption and oxygen activation ability, particularly the *o*-xylene adsorption ability.

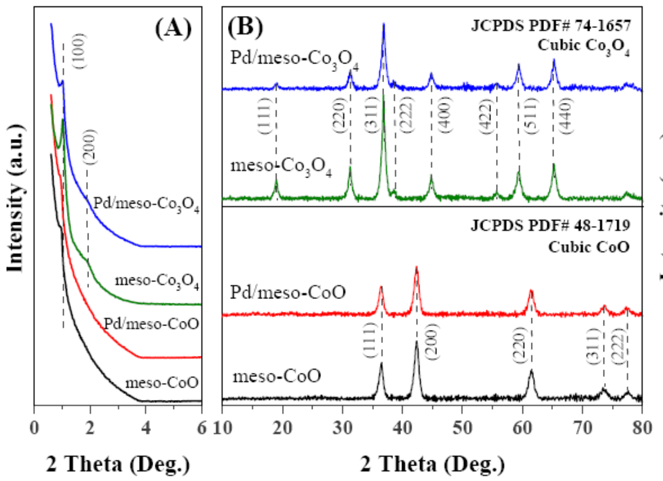

Figure 1. (A) Small-angle and (B) wide-angle XRD patterns of the samples.

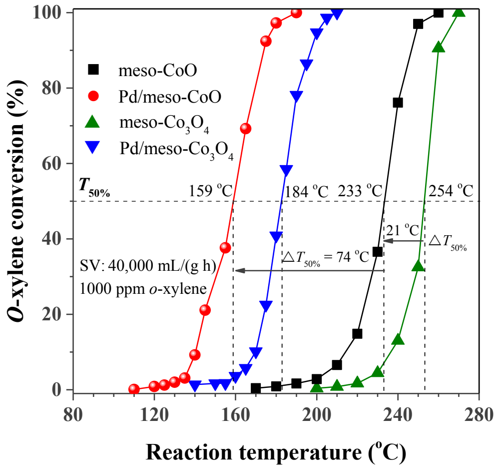

Figure 2. *o*-xylene conversion as a function of temperature over the samples at SV = 40,000 mL/(g h).

4. Conclusions

The Pd NPs were highly dispersed on the surface of meso-Co_3O_4 and meso-CoO. The supported Pd samples performed much better than their supports for *o*-xylene combustion, in which Pd/meso-CoO exhibited the highest catalytic activity ($T_{90\%}$ = 173 °C), giving rise to the reaction rate at 170 °C of 3.5 and 84 times higher than those over the Pd/meso-Co_3O_4 and meso-CoO samples, respectively. It is demonstrated that meso-CoO exhibited high ability of oxygen activation, and the loading of Pd NPs was beneficial for *o*-xylene adsorption. Therefore, it is concluded that the excellent catalytic performance of Pd/meso-CoO was related to its good *o*-xylene adsorption and O_2 activation ability, particularly the *o*-xylene adsorption ability.

References

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