Selective Oxidation of Toluene over the Ultrafine Composite Molybdenum-Cerium Oxide Particles

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(Received November 14, 1996)

The ultrafine composite Mo-Ce oxide particles exhibit higher catalytic activity for selective oxidation of toluene to benzaldehyde than the corresponding large oxide particles prepared by conventional precipitation method, which can be correlated to the higher reactivity of lattice oxygen ions in the ultrafine oxide particles.

In the past decades, metal oxides especially Mo-based and V-based oxides have been widely used as the selective oxidation catalysts for conversion of hydrocarbons to oxygenates, and the structure and catalytic properties of these oxides have been extensively studied. It has been demonstrated that the nature of oxygen species in the oxides is one of the most important parameters influencing catalytic selectivity. In oxidation of olefins and aromatics, the nucleophilic lattice oxygen ions(O^{2-}) are responsible for the selective oxidation, while electrophilic ionic oxygen species(O_2^-,O^-) may attack C=C and benzene ring because of the higher electron density in these regions, eventually leading to C-C bond cleavage and complete oxidation. [1,2] So for, great efforts have been made in improving the catalytic selectivity by adding some transition metal ions to molybdenum and vanadium oxides.[3] However, comparatively little results concerning the effect of oxide particle size on the nature of lattice oxygen ions and their reactivity have been available. Recently, we have prepared the ultrafine composite molybdenum-cerium oxide particles by a sol-gel method and studied their catalytic activity for selective oxidation of toluene to benzaldehyde. It has been found that by decreasing the composite oxide particles size to nano-scale the reactivity of lattice oxygen ions in the oxide particles can be increased, so that the catalytic activity for selective oxidation of toluene to benzaldehyde can be remarkably improved. Our results have indicated that the ultrafine composite oxide particles are the potentially new catalytic materials for selective oxidation reactions.

Composite Mo-Ce(I) oxide with the composition of Ce/Mo=1(mol/mol) was prepared by conventional precipitation method in which cerium nitrate aqueous solution was mixed with ammonium molybdate aqueous solution, and the precipitates formed were dried and calcined in air. Composite Mo-Ce(II) oxide catalysts were prepared by a sol-gel method. A mixed aqueous solution containing cerium nitrate, ammonium molybdate and citric acid with Ce/Mo=1(mol/mol) and (Ce+Mo) /citric acid =3(mol/mol) was kept in a water bath at 80 °C until gelation. Then, the as-prepared gel was dried at 120 °C for 4 h and calcined in air at 400 °C for 4 h. The morphology, particle size and structure of the above oxides were determined by transmission electron microscopy(TEM) and X-ray diffraction(XRD) techniques. The state of lattice oxygen species in Mo-Ce composite oxides was studied by using laser raman spectroscopy(LRS) and temperature-programmed reduction(TPR). Oxidation of toluene was carried out in a fixed-bed reactor under the conditions of 0.1 MPa, 400 °C, air/toluene=9(vol/vol) and F/W=1900 ml/g · h, and the reaction products were analyzed by an on-line gas chromatography. Under the above reaction conditions the oxidation reaction products on the above catalysts were mainly benzaldehyde, CO , CO_2 and H_2O.

Table 1. Catalytic properties of the composite Mo-Ce oxide particles for selective oxidation of toluene

Catalyst	MoO_3	CeO_2	Mo-Ce(I)	Mo-Ce(II)
Particle size(nm)	>200	10-20	>200	20-40
Surface area(m^2/g)	5.1	41.0	12.1	19.0
Conversion of toluene(mol%)	24.0	54.8	35.5	34.0
Benzaldehyde selectivity(%)	6.0	0.0	16.0	37.0
Benzaldehyde yield (10^{-6} mol/ m^2 · h)	23.4	0.0	40.2	56.4

TEM results showed that the particle size of Mo-Ce(I) oxide was larger than 200 nm, while that of Mo-Ce(II) oxide was in the range of 20-40 nm(Figure 1), which is in the nano-scale (<100 nm). This indicates that Mo-Ce particles prepared by the sol-gel method are actually the ultrafine particles. X-ray diffraction patterns revealed that molybdenum and cerium in the both Mo-Ce samples formed a solid solution having the sheelite-type structure of $Ce_2(MoO_4)_3$ with excess of CeO_2.

Table 1 shows the toluene conversion, benzaldehyde selectivity and benzaldehyde yields on CeO_2, MoO_3 and the two Mo-Ce catalysts. The main products on CeO_2 catalyst were only CO, CO_2 and H_2O, indicating that CeO_2 is an active component for complete oxidation of toluene. However, addition of cerium ions to molybdenum oxides leads to the increase in the specific activities for selective oxidation of benzaldehyde, as the composite Mo-Ce oxides show higher selectivity to benzaldehyde. In particular, the specific activity of ultrafine Mo-Ce(II) particle catalysts are higher than the corresponding large Mo-Ce(I) oxide particles prepared by the precipitation method. These results have revealed that ultrafine oxide particle catalysts

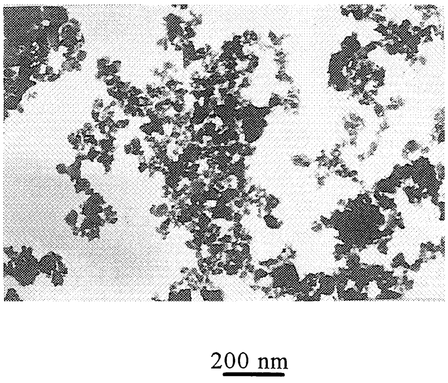

Figure 1. Transmission electron micrograph of the ultrafine composite Mo-Ce oxide particles.

have unique catalytic properties for the selective oxidation reaction.

As indicated previously, the lattice oxygen ions in molybdenum oxides are the main active species for selective oxidation of lower olefins and aromatics to aldehydes.[1,2] The effect of interaction between Mo and Ce on the nature of lattice oxygen species in the composite oxides were studied by LRS and TPR. It can be seen from Figure 2 that the raman band of Mo=O species in Mo-Ce(I) composite oxide appeared at 953 cm^{-1}. This vibration frequency is lower than that of Mo=O in MoO_3 (995 cm^{-1}).[4] The red shift of vibration frequency of Mo=O indicates a weaker chemical bonding between Mo=O in the Mo-Ce composite oxide due to the formation of Mo-Ce oxide solid solution. Our TPR profiles showed that H_2 consumption peaks of MoO_3 appeared at 670, 755 and 990 °C, while those of Mo-Ce(I) sample shifted to lower temperatures of 510, 715 and 860 °C, indicating that weaker bonding between Mo=O leads to a higher mobility of these lattice oxygen species. From the above results, we argue that the interaction between Mo-Ce increases the mobility of lattice oxygen ions and their reactivity for selective oxidation of toluene.

Moreover, it can be seen from Figure 2 that the vibration frequency of Mo=O species in Mo-Ce(II) was 928 cm^{-1}, which is much lower than that in Mo-Ce(I), indicating that Mo=O chemical bonding in the ultrafine oxide particles was still weaker than the corresponding large particles, so that the lattice oxygen ions in the ultrafine composite oxide particles have higher mobility. The higher specific activity for selective oxidation of toluene to benzaldehyde on the Mo-Ce(II) composite oxide may be correlated to the unique properties of lattice oxygen ions in the matrix of ultrafine oxide particles. The above results have confirmed the reactivity of lattice oxygen ions can be remarkably improved by decreasing the oxide particles size to nano-scale. Apparently, the ultrafine composite oxide particles are potentially new catalytic materials for selective oxidation reactions.

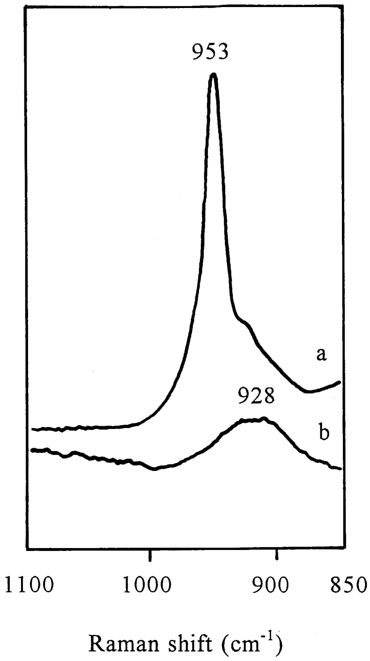

Figure 2. Laser raman spectra of Mo=O vibrations for the composite Mo-Ce oxides. (a) Mo-Ce(I), (b) Mo-Ce (II).

The financial support of the National Natural Science Foundation of China is gratefully acknowledged.

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