Selective Oxidation of Toluene Catalysed by Ultrafine Fe–Mo Oxide Particles†

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It has been found that by decreasing the size of both Fe_2O_3 and $Fe_2(MoO_4)_3$ particles in complex Fe–Mo oxide to nanometric order, the catalytic activity of the mixed oxide in toluene oxidation is remarkably improved.

Selective oxidation of hydrocarbons over metal oxide catalysts is currently the main method for the synthesis of organic oxygenate compounds. It has been found[1–8] that the nature of lattice oxygen ions is one of the most important parameters influencing catalytic selectivity. In past decades, considerable attention has been devoted to the design of highly selective oxidation catalysts, and great effort has been made to improve the reactivity of lattice oxygen ions by adjusting the composition and structure of oxide catalysts.

In the past decade, ultrafine oxide particles have attracted considerable research interest in the field of heterogeneous catalysis due to their unique physical and chemical properties, and many efforts have been devoted to the preparation and application of single-phase or supported oxides.[9–11] However, studies on ultrafine mixed-phase oxides are rather limited, although most important industrial catalysts are mixed-phase oxides.

In our previous study,[12] it was found that for selective oxidation of toluene in the absence of molecular oxygen over complex Fe–Mo oxides prepared by the sol–gel (sg) technique, both the highest yield for benzaldehyde and the optimum specific activity are achieved at a Fe:Mo atomic ratio of 1:1. The aim of this work is to study the behavior of complex Fe–Mo oxides with different particle sizes for the selective oxidation of toluene in the absence of molecular oxygen and to discover the effect of oxide particle size on the reactivity of lattice oxygen ions.

The results of TEM, XRD and Mössbauer spectroscopy are presented in Table 1. It can be seen that the size of pure Fe_2O_3 and $Fe_2(MoO_4)_3$ particles is in the range 10–20 and 20–40 nm, respectively. The size of Fe_2O_3 and $Fe_2(MoO_4)_3$ particles in Fe–Mo (sg) is about the same as that of pure Fe_2O_3 and $Fe_2(MoO_4)_3$ particles, respectively. The BET surface area of the Fe–Mo (sg) is 46.3 m² g⁻¹. Due to the molecular homogeneous distribution of various components in the sol–gel process,[13–18] it is possible to form ultrafine Fe_2O_3 and $Fe_2(MnO_4)_3$ particles from the Fe–Mo gel. Pure Fe_2O_3, $Fe_2(MoO_4)_3$ and Fe–Mo (sg) are actually ultrafine oxide particles (<100 nm). As shown in Table 1, Fe_2O_3 particles in a pure sample or in Fe–Mo (sg) exist in the highly dispersed superparamagnetic state. It can also be shown that the particle size of Fe–Mo (cp) prepared by the coprecipitation method is much larger than that of Fe–Mo (sg) prepared by the sol–gel process. The corresponding BET surface area is 2.7 m² g⁻¹, smaller than that of Fe–Mo (sg).

Table 1 also shows the total yield of benzaldehyde over various samples in the pulse microreactor. It can be seen that the benzaldehyde yield of Fe–Mo (sg) is much higher than that of pure $Fe_2(MoO_4)_3$ and Fe_2O_3 samples, suggesting that the effect of the particle size on the reactivity of lattice oxygen ions of mixed-phase oxides is more marked than that of single-phase oxides. This may be correlated with the interaction between ultrafine $Fe_2(MoO_4)_3$ and Fe_2O_3 in Fe–Mo (sg). It is also noteworthy that for complex Fe–Mo oxides, with increasing size of Fe_2O_3 and $Fe_2(MoO_4)_3$ particles, the benzaldehyde yield decreases rapidly, indicating that the particle size of the mixed-phase oxides has great influence on the reactivity of lattice oxygen ions. In particular, the specific activity of Fe–Mo (sg) is found to be much higher than that of Fe–Mo (cp). This reveals that the lattice oxygen ions in the ultrafine oxide particles have unique reactivity for selective oxidation of toluene to benzaldehyde.

For pure Fe_2O_3, $Fe_2(MoO_4)_3$ and Fe–Mo (cp), no new species appear in the XRD patterns or in the Mössbauer spectra after the reaction. This indicates that only the lattice oxygen ions on the surface of these samples participate in the reaction. However, for Fe–Mo (sg), newly appeared XRD patterns and two doublets in Mössbauer spectra are observed and can be assigned to crystalline β-FeMoO₄.[12] Since the various components of Fe–Mo (sg) have a homogeneous distribution and the particles are of ultrafine size, the interaction between Fe_2O_3 and $Fe_2(MoO_4)_3$ may be greatly increased, resulting in both the lattice oxygen ions on the surface and those in the bulk phase of Fe–Mo (sg)

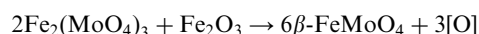**Table 1** The reactivity of lattice oxygen ions of various samples

Sample	Structure analysis by XRD and Mössbauer spectroscopy	Particle size/nm		Total benzaldehyde yield/μmol g⁻¹	Specific activity (a.u.)[c]
		$Fe_2(MoO_4)_3$	Fe_2O_3		
Fe_2O_3	Fe_2O_3[a]		10–20	0	0.0
$Fe_2(MoO_4)_3$	$Fe_2(MoO_4)_3$	20–40		1.0	0.2
Fe–Mo (sg)	$Fe_2(MoO_4)_3$, Fe_2O_3[a]	20–40	10–20	23.2	1.9
Fe–Mo (cp)	$Fe_2(MoO_4)_3$, Fe_2O_3[b]	200–400	40–80	0.7	1.0

[a]Superparamagnetic Fe_2O_3. [b]Magnetic Fe_2O_3. [c]Benzaldehyde per BET surface area.

participating in the reaction. The reaction mechanism for Fe–Mo (sg) is reported to be:[12]

$$2Fe_2(MoO_4)_3 + Fe_2O_3 \rightarrow 6\beta\text{-FeMoO}_4 + 3[O]$$

The above results reveal that the oxide particle size exerts great influence on the reactivity of lattice oxygen ions. By decreasing the size of both Fe_2O_3 and $Fe_2(MoO_4)_3$ particles in complex Fe–Mo oxide to nanoscale, the reactivity of lattice oxygen ions can be markedly improved.

Experimental

Fe_2O_3, $Fe_2(MoO_4)_3$ and Fe–Mo (sg) were prepared by the sol–gel method using citric acid as the complexing agent, and were calcined at 673 K for 4 h to afford the oxides.[12] Fe–Mo (cp) was prepared by the coprecipitation method. The precipitates formed were dried and calcined at 773 K for 8 h. The Fe:Mo atomic ratio of both Fe–Mo (sg) and Fe-Mo (cp) was 1:1. The pulse reactions of toluene over complex Fe–Mo oxide in the absence of molecular oxygen were carried out under the conditions of 623 K, 0.2 MPa, helium flow-rate 40 ml min^{-1}, and 1.45 μmol toluene per pulse.[12]

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