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Ultrafine La–Mo and Ce–Mo complex oxide particle catalysts for selective oxidation of toluene

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It has been found that by decreasing the particle size of La–Mo and Ce–Mo complex oxides to nanoscale, the reactivity of lattice oxygen ions and thus the selectivity for oxidation of toluene to benzaldehyde can be remarkably improved.

Selective oxidation of hydrocarbons to organic oxygenate compounds over metal oxide catalysts is one of the most important catalytic process in the chemical industry. It is well known that Mo-based and V-based oxide catalysts have been widely used for selective oxidation of hydrocarbons to aldehydes.[1] In the past decades, considerable attention has been devoted to the design of highly selective oxidation catalysts, and great efforts have been made in improving the catalytic selectivity by adding some transition metal oxides to the catalysts. It has been found that Bi, Sn, Fe and W oxides are effective promoters of Mo-based and V-based oxide catalysts for oxidation of toluene to benzaldehyde,[2–7] and that the preparation conditions, oxide composition and catalyst structure exert great influences on the catalytic properties. In recent years, ultrafine metal oxide particles have attracted much research interests in terms of materials science and heterogeneous catalysis.[8,9] These new catalytic materials are expected to have unique catalytic properties because of their nanoscale particle sizes.

Recently, it has been found that some rare earth species such as lanthanum and cerium exert an influence on the selective oxidation of toluene to benzaldehyde over V-based oxide catalysts.[10,11] For instance, Yan *et al.*[10] reported that adding cerium to vanadium oxide catalysts further increased selectivity for benzaldehyde. However, studies on lanthanum or cerium used as promoters of Mo-based oxide catalysts to improve the selectivity for benzaldehyde in oxidation of toluene are rather limited. On the other hand, although Mo-based oxide catalysts have been extensively investigated, relatively little work has been done on the preparation of ultrafine Mo-based oxide particle catalysts and their catalytic properties for selective oxidation of hydrocarbons to organic oxygenate compounds. In this work, we report our recent results on the preparation of ultrafine La–Mo and Ce–Mo complex oxide particles and their catalytic properties for the selective oxidation of toluene to benzaldehyde.

Ultrafine La–Mo and Ce–Mo complex oxide particle catalysts with different molar ratios of metallic ions (La/Mo or Ce/Mo) were prepared by the sol–gel method. Lanthanum nitrate, $La(NO_3)_3 \cdot 6H_2O$, or cerium nitrate, $Ce(NO_3)_3 \cdot 6H_2O$, ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$ (the total amount of metallic ions is 0.06 mol), and citric acid (0.02 mol) aqueous solutions were prepared separately and then mixed. The pH values of mixture solutions were adjusted to 1.0 for the La–Mo solution and 0.5 for the Ce–Mo solution. The above solutions were first kept in a water bath at 353 K until gelation was completed, and then the gels thus prepared were dried at 393 K for 4 h and calcined in air at 773 K for the La–Mo gel and 673 K for the Ce–Mo gel to afford the oxide catalysts.

The morphology, particle size and structure of the oxide catalysts were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM) and laser Raman spectroscopy (LRS) techniques. The Brunauer–Emmett–Teller (BET) surface areas of the samples were measured by using a Micromeritics ASAP-2000 instrument (N_2 adsorption at 77 K). The oxide catalysts were introduced into a U-type quartz fixed bed microreactor and their catalytic properties for the selective oxidation of toluene to benzaldehyde were evaluated under the following reaction conditions: 0.1 MPa, air/toluene = 9 : 1 (vol/vol), F (flow rate of feed gas)/W (catalyst mass) = 1900 ml $(\text{h g cat})^{-1}$. Reaction products were analyzed by on-line gas chromatography.

The image results show that the particle size are in the range of 40–80 nm for La–Mo oxide (La/Mo = 1.0) and 20–40 nm for Ce–Mo oxide (Ce/Mo = 1.0). This indicates that the La–Mo and Ce–Mo oxide catalysts prepared by the sol–gel method are ultrafine oxide particles (< 100 nm). The BET surface areas for La–Mo and Ce–Mo complex oxides are 21.3 and 19.0 $m^2\ g^{-1}$, respectively. The XRD patterns of La–Mo and Ce–Mo samples show that the rare earth oxide and molybdenum oxide in both samples form complex oxides having the structures of $La_2Mo_2O_9$ and $Ce_2(MoO_4)_3$ with an excess of CeO_2, respectively.

The toluene oxidation reaction was used as a probe to evaluate the catalytic properties of the ultrafine La–Mo and Ce–Mo complex oxide particle catalysts. Under our reaction conditions the reaction products on the above catalysts were mainly CO, CO_2, H_2O and benzaldehyde. The specific activities for selective oxidation of toluene to benzaldehyde (benzaldehyde yield per specific surface area of catalysts) over La–Mo and Ce–Mo complex oxide catalysts with different molar ratios of metallic ions are shown in Fig. 1. Both rare earth oxides

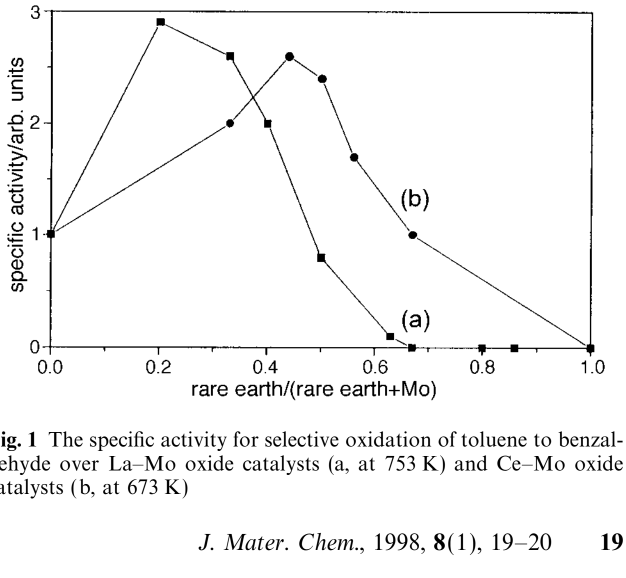

Fig. 1 The specific activity for selective oxidation of toluene to benzaldehyde over La–Mo oxide catalysts (a, at 753 K) and Ce–Mo oxide catalysts (b, at 673 K)

Table 1 The structure and catalytic properties of Ce–Mo complex oxide particle catalysts (Ce/Mo = 1.0) with different particle sizes

preparation method	phase structure by XRD	particle size/nm	conversion of toluene (%)	benzaldehyde selectivity (%)	Mo=O LRS band/cm^{-1}
sol–gel	$Ce_2(MoO_4)_3$, CeO_2	20–40	34.0	37.0	928
precipitation	$Ce_2(MoO_4)_3$, CeO_2	>100	35.5	16.0	953

are inactive for the selective oxidation of toluene to benzaldehyde. However, addition of lanthanum and cerium to molybdenum oxides leads to an improvement of the specific activities for the selective oxidation. It can be seen that with increasing rare earth/(rare earth + Mo) atomic ratios, the specific activities are first increased and then decreased remarkably. Obviously, the composition of the complex oxides has a great influence on the catalytic properties of the ultrafine oxide particle catalysts. The maximum catalytic activities are reached in the vicinity of La/(La + Mo) = 0.2 and Ce/(Ce + Mo) = 0.5 for La–Mo and Ce–Mo oxide catalysts, respectively.

For comparison, the catalytic properties of the ultrafine Ce–Mo oxide particles prepared by the sol–gel method and the corresponding larger oxide particles with the same composition prepared by a conventional precipitation method are listed in Table 1. It is interesting to note that the conversions of toluene on the ultrafine Ce–Mo oxide particles and the corresponding larger particles are very similar, but the selectivities to benzaldehyde are different, which can not be accounted for by the difference in particle size or specific surface area. Apparently, the nature of the active species for the selective reaction over the ultrafine and larger oxide particles should be taken into consideration. Haber[12] demonstrated that the lattice oxygen species (Mo=O) in molybdenum-based oxide catalysts are the main active species responsible for selective oxidation of aromatics. The state of the lattice oxygen species in the above ultrafine and large Ce–Mo oxide particles were studied by using LRS. As presented in Table 1, the vibrational frequency of Mo=O in the large Ce–Mo oxide particles is at 953 cm^{-1}, while that of Mo=O in the ultrafine Ce–Mo oxide particles shifts to 928 cm^{-1}. This red shift indicates that chemical bonding between Mo=O in the ultrafine Ce–Mo oxide particles is weaker than that in the corresponding large particles, so that the lattice oxygen ions have higher reactivity. The higher selectivity for oxidation of toluene to benzaldehyde on the ultrafine particle catalyst may be correlated to the higher reactivity of their lattice oxygen ions.

The above results have shown that besides the composition of oxides, the oxide particle size exerts a great influence upon the catalytic selectivity of complex oxide catalysts. By decreasing the particle size to nanoscale, the reactivity of lattice oxygen ions and thus the selectivity for oxidation of toluene to benzaldehyde can be remarkably improved. The ultrafine complex oxide particles may be potentially new catalytic materials for selective oxidation reactions.

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