Characterization of acidic and redox properties of Ce–Mo–O catalysts for the selective oxidation of toluene

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Abstract

The surface acidic and redox properties of CeO_2, MoO_3, mechanically mixed CeO_2–MoO_3 and co-precipitated Ce–Mo–O catalysts were characterized by using microcalorimetric adsorption of ammonia and isopropanol (IPA) probe reaction, and the surface properties of these catalysts were correlated with their selectivity for the oxidation of toluene to benzaldehyde and benzoic acid. With the presence of O_2, IPA converted to propylene and diisopropyl ether on acidic sites while converted to acetone on redox sites. It was found that CeO_2 exhibited mainly the redox property while MoO_3 the surface acidity. The IPA probe reaction showed that the mechanically mixed CeO_2–MoO_3 exhibited the surface acidic property, similar to that of MoO_3, indicating that the surface of CeO_2 might be covered by MoO_3 in the mixture upon the calcination at 773 K. On the other hand, the co-precipitated Ce–Mo–O catalyst showed the equivalent acidic and redox properties, and thereby the selectivity to benzaldehyde was greatly enhanced on it as compared to the other catalysts studied in this work.
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1. Introduction

The surface acidity/basicity and redox properties of metal oxides play the important roles in catalytic selective oxidation reactions. The surface acidity/basicity can be titrated by basic and acidic probe molecules, as well as by the probe reaction of isopropanol (IPA) conversion [1–3]. On the other hand, the redox property of a metal oxide catalyst can be characterized by using the techniques of TPR/TPO (temperature-programmed reduction/temperature-programmed oxidation) [4]. It is generally true that IPA undergoes the dehydration reaction to produce propylene (PPE) and diisopropyl ether (DIPE) over acidic sites while undergoes the dehydrogenation reaction to produce acetone (ACE) over basic sites [1]. When O_2 is present, IPA can be oxidatively dehydrogenated to ACE. Thus, the oxidative dehydrogenation of IPA may become a probe reaction to characterize the redox properties of metal oxide catalysts. In addition, the presence of O_2 does not seem to affect the dehydration reactions of IPA. Thus, the conversion of IPA with the presence of O_2 may become a probe reaction to characterize the surface acidity and redox properties simultaneously. In this way, the surface acidity and redox property of a metal oxide catalyst can be compared directly, and the dehydration and oxidative dehydrogenation reactions occur on a bi-functional (acidic and redox) surface in a competitive way.

In this work, we studied the surface acidity and redox properties of CeO_2, MoO_3 and two binary oxides Ce–Mo–O prepared via different methods. The surface acidity and redox properties were characterized by microcalorimetric adsorption of ammonia, TPR and IPA probe reactions. These catalysts were also tested for the selective oxidation of toluene to benzaldehyde and benzoic acid, and the catalytic behavior was correlated with the surface acidity and redox properties of the catalysts.

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2. Experimental

CeO_2 and MoO_3 were prepared by calcining $(NH_4)_2Ce(NO_3)_6$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, respectively, at 773 K for 5 h. One binary oxide was prepared by mechanically mixing the two single oxides, and termed as CeO_2–MoO_3. Another binary oxide was prepared by the co-precipitation [5]. Specifically, $(NH_4)_2Ce(NO_3)_6$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ with the molar ratio of 1/1 were dissolved to form an aqueous solution, which was adjusted with NH_4OH solution to pH = 7–8. The solution was evaporated with a rotatory evaporator. The sample was dried and then calcined at 773 K for 5 h. The co-precipitated sample thus obtained was termed as Ce–Mo–O. All the samples were pressed, crashed and sieved to collect the particles with the sizes between 20 and 40 meshes. The mechanically mixed sample was obtained by simply mixing the CeO_2 and MoO_3 with the particles of 20–40 meshes (molar ratio of 1/1).

The surface areas were measured by N_2 adsorption at the temperature of liquid N_2 employing the BET method. The phases present in the catalysts were determined by X-ray diffraction (XRD) using the X′TRA diffractometer equipped with a Cu target and graphite monochromator. TPR measurements were performed by using a quartz U-tube reactor loaded with about 50 mg of a sample. A mixture of N_2 and H_2 (5.13% H_2 by volume) was used and the flow rate was maintained at 40 ml/min. The hydrogen uptake was monitored using gas chromatography with a thermal conductivity detector (TCD). The reducing gas was first passed through the reference arm of the TCD before entering the reactor. The reactor exit was directed through a trap filled with $Mg(ClO_4)_2$ (to remove product water) and then to the second arm of the TCD. The temperature was raised at a programmed rate of 10 K/min from 303 to 1173 K.

Microcalorimetric measurements for the adsorption of NH_3 were carried out using a Tian-Calvet heat-flux apparatus. The microcalorimeter was connected to a gas handling and volumetric adsorption system, equipped with a Baratron capacitance manometer (MKS, USA) for precision pressure measurement. The differential heat of adsorption versus adsorbate coverage was obtained by measuring the heats evolved when doses of a gas (2–5 μmol) were admitted sequentially onto the catalyst until the surface was saturated by the adsorbate. Ammonia with a purity of 99.99% was used. Before microcalorimetric measurements, the samples were typically dried under vacuum, calcined in 66.7 kPa O_2, and evacuated, respectively, at 673 K for 1 h. The microcalorimetric adsorption was performed at 423 K.

The probe reaction was carried out in a fixed-bed glass tube reactor. About 100 mg sample was loaded for the reaction. Isopropanol was introduced to the reaction zone by bubbling air through a glass saturator filled with isopropanol maintained at 295 K. Isopropanol and reaction products were analyzed by an on-line gas chromatograph, using a PEG 20M packed column connected to an FID. Each catalyst was pretreated by heating in air at 673 K for 1 h and then cooled in air flow to the reaction temperature.

The reaction of selective oxidation of toluene was performed by using a U-tube fixed-bed reactor loaded with a sample of about 0.5 g with 20–40 meshes. The reaction was performed at 673 K. The reactants were fed into the reactor by flowing air (62 ml/min) through a glass saturator filled with toluene maintained at 330 K. The tail gas was analyzed by using an on-line gas chromatograph. The organic compounds were separated by an FFAP capillary column and detected by an FID while CO_2 was detected by using a Hayesep D packed column and a TCD.

3. Results and discussion

Fig. 1 presents the XRD patterns for CeO_2 (23 m^2/g), MoO_3 (4 m^2/g), co-precipitated Ce–Mo–O (1.2 m^2/g) and mechanically mixed CeO_2–MoO_3. It is clearly seen that the mechanically mixed sample (after calcination at 773 K) displayed the phases of CeO_2 and MoO_3. No phase change occurred upon the mixing and calcination. The co-precipitated sample exhibited totally different phases. The MoO_3 phase was hardly seen in this sample. The phase of CeO_2 was apparently there and a new phase $Ce_2Mo_4O_{15}$ was formed. Thus, the co-precipitated sample was a mixture of CeO_2 and $Ce_2Mo_4O_{15}$.

Fig. 2 shows the TPR profiles. The CeO_2 exhibited two reduction peaks around 696 and 820 K, corresponding to the reduction of surface Ce^{4+} to Ce^{3+}. The high temperature reduction peak around 1125 K was due to the reduction of bulk Ce^{4+} [6]. The TPR profile of MoO_3 displayed two reduction peaks around 973 and 1040 K, which may be due to the reduction from MoO_3 to MoO_2 and a peak with the temperature higher than 1173 K, which may be attributed to the reduction from MoO_2 to Mo [7]. The mechanically mixed sample CeO_2–MoO_3 had the TPR profile that looked like the overlap of the two TPR profiles of pure CeO_2 and MoO_3. The co-precipitated Ce–Mo–O catalyst displayed totally different TPR profile. Three peaks can be observed for this profile around 880, 1100 and over 1200 K. The peak around 880 K may be due to the reduction of cerium species. This peak shift to higher temperature compared to that of
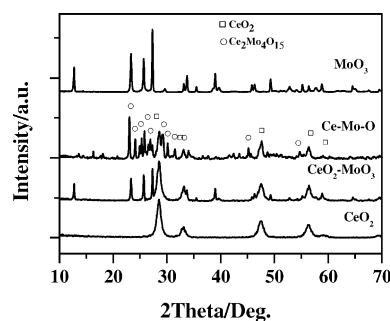

Fig. 1. X-ray diffraction patterns.