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Selective Oxidation of Isobutene over CsFeCoBiMnMoO$_x$ Mixed Oxide Catalyst

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Abstract: Mixed oxide catalyst $Cs_{0.1}Fe_2Co_6BiMnMo_{12}O_x$ was prepared by the coprecipitation method. Selective oxidation of isobutene was carried out in a fixed-bed reactor over $Cs_{0.1}Fe_2Co_6BiMnMo_{12}O_x$. The results showed that the catalyst had high catalytic activity. Under the optimum reaction conditions ($n(i\text{-}C_4^=):n(O_2)$=1:2–1:4, space velocity=180 h^{-1}, T=360 ℃), the yields of methacrolein and methacrylic acid can reach 80% and 8%, respectively. The total yield of liquid products (methacrolein, methacrylic acid and acetic acid) can reach about 90%.

Key words: mixed oxide, isobutene, selective oxidation, methacrolein, methacrylic acid

1. Introduction

Selective oxidation of lower alkanes by molecular oxygen is of great importance in the petroleum and petrochemical industries. The content of isobutene in the fraction of C_4 alkanes is about 45%–47%. The study of selective oxidation of isobutene has an important practical value, which can be used to produce methacrylic acid (MAA). MAA is the main materials for the production of methyl methacrylate (MMA). MMA is an important monomer, which is widely used for producing acrylic plastics (polymethyl methacrylate) or producing polymer dispersions for paints and coatings. Methacrylic polymer, which has the characteristics of good transparency and weather resistance, is used in many fields such as signboards, building materials, vehicles and lighting equipments. In 1932, ICI commercialized MMA by the acetone cyanohydrine (ACH) process [1], which most manufacturers in the world adopted even today. However this process uses the toxic hydrogen cyanide and produces ammonium bisulfate as a by-product, which also causes the environmental problem. For replacing this ACH process, many efforts have been continuously put into the development of new processes. One of the new processes is two step selective oxidation of isobutene to MAA *via* methacrolein (MAL). The first step is oxidation of isobutene to MAL. The catalysts utilized in the first step are always the multicomponent oxide catalyst of Mo-Bi. The second step is oxidation of MAL to MAA using P-Mo heteropoly acid structure catalysts. This new process has been developed for an environmentally friendly production of MMA and thereby the development of high performance oxidation catalysts is the key technology. In the past several years, the synthesis of MAA *via* selective oxidation of isobutene was reported in many literatures [2–5].

In this work, mixed oxide catalyst $Cs_{0.1}Fe_2Co_6BiMnMo_{12}O_x$ was prepared by the coprecipitation method. Selective oxidation of isobutene was carried out in a fixed-bed reactor.

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2. Experimental

2.1. Catalyst preparation

A certain amount of $CsNO_3$, $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$, $Mn(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were mixed by molar ratio (Cs:Fe:Co:Bi:Mo=0.1:2:6:1:12) with water under stirring at 60 ℃. The pale yellow thick liquid was evaporated to dry to get a catalyst in a water bath at 100 ℃, then the catalyst was continuously dried for 24 h at 120 ℃. The solid catalyst was calcined for 10 h at 250 ℃. Finally, the catalysts were calcined for 5 hours at 480 ℃, 500 and 520 ℃ respectively and are designated as $1^{\#}$, $2^{\#}$ and $3^{\#}$ corresponding to the different temperatures.

2.2. Characterization of catalysts

The characterization of H_2-TPR was carried out on a Chembet-3000 Adsorption Instrument (Quantachrome Co.). The sample (30 mg) was exposed to a 20 ml/min, 15% N_2/H_2 flow, and heated at a rate of 10 ℃/min. The final temperature was 800 ℃.

2.3. Catalytic reaction

The reaction was performed in a fix-bed microreactor at the temperature of 260–380 ℃. The weight of catalyst was 1.2 g. Before reaction, the catalysts were treated in an O_2 stream (10 ml/min) for 1 h at 300 ℃. The products were analyzed online by a gas chromatograph (GC 102 N) equipped with a porapak-Q column, FID detector and N-2000 workstation. The conversion and yield data were collected after reacting for 2-3 h to reach equilibrium.

3. Results and Discussion

3.1. The analysis of H_2-TPR

The TPR curves of the three catalysts are shown in Figure 1. It is shown that all the three catalysts have a series of reduction peaks in the range of temperature 370–750 ℃. The starting temperature of the $2^{\#}$ catalyst reduced by H_2 is about 400 ℃ which is lowest as compared to the other two samples. It means that the $2^{\#}$ catalyst is more reducible than the others. The highest activity of the $2^{\#}$ catalyst in the oxidation of isobutene also proves it. The temperature of the first reduction peak of the $1^{\#}$ catalyst (calcined at 480 ℃) shifts to higher temperature, starting around 450 ℃, and the apex temperature is around 649 ℃. The temperature of the reduction peak of the $3^{\#}$ catalyst (calcined at 520 ℃) is evidently higher than those of the other two, which means that the ability of oxidation of the $3^{\#}$ catalyst is weakest. From the above data, it can be seen that the single reduction peak does not belong to single oxides, because the synergistic effect takes place among the single oxides and the synergistic effect even can lead to hydrogen spillover [6]. But when the temperature of the calcination is over 520 ℃, the synergistic effect among the single oxides gradually decreases until the mixed oxides decomposes to single oxides. The analysis of H_2-TPR indicates the temperature of the calcination of the catalyst has an important effect on the catalytic performance. At different calcination temperatures, the multiply single oxides can lead to different synergistic effect, which is the same as the synergistic effect of the decomposed heteropoly compound catalyst [7].

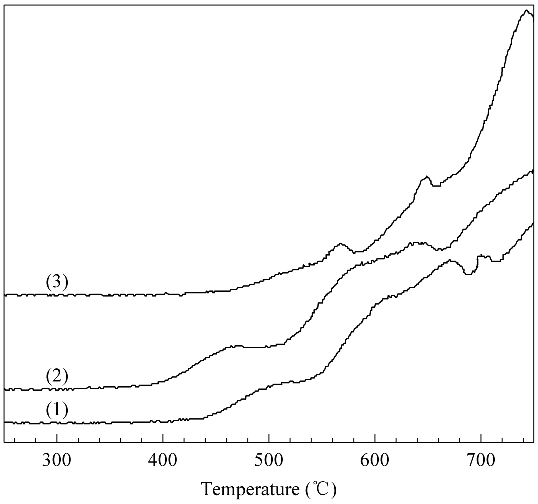


Figure 1. TPR profiles of different catalyst samples
(1) $1^{\#}$, (2) $2^{\#}$, (3) $3^{\#}$
($1^{\#}$, $2^{\#}$ and $3^{\#}$ are $CsFeCoBiMnMoO_x$ calcined at 480 ℃, 500 and 520 ℃ , respectively)

3.2. Effect of different reaction conditions

3.2.1. The effect of reaction temperature on the yields and selectivities of the products

Figure 2 shows the temperature effect on catalytic performance of three catalysts. The activity of the $1^{\#}$ catalyst increases greatly from 320 to 360 ℃. The conversion of isobutene is 34% at 320 ℃. At 360 ℃, it reaches 98%, but the selectivity of MAL has less change, it keeps at about 80%. The yield of MAL is 27.6% at 320 ℃, the maximum yield of MAL is 80% at around 360 ℃. At the same time, the yields of MAA and acetic acid (HAc) are 8% and 1.9% respectively. With the further increase of temperature, the selectivity of HAc increases. It is mainly due to the successive oxidation of the products. The optimum reaction temperature of the $2^{\#}$ catalyst is about 40 ℃ lower than that of the $1^{\#}$ catalyst. At 320 ℃, the conversion of isobutene is 99%, but the maximum yield of MAL is only 67%. At the same time, with the increase of temperature, the selectivity of MAL decreases greatly. The $3^{\#}$ catalyst displays some activity only at the higher temperature. At 380 ℃, the conversion of isobutene is only 42% and the yield of MAL is only 22%. It indicates that the catalytic performance of the $1^{\#}$ catalyst is the best. At 360 ℃, over the $1^{\#}$ catalyst, the yield of MAL can reach 80%, and the total yield of liquid products is about 90%.

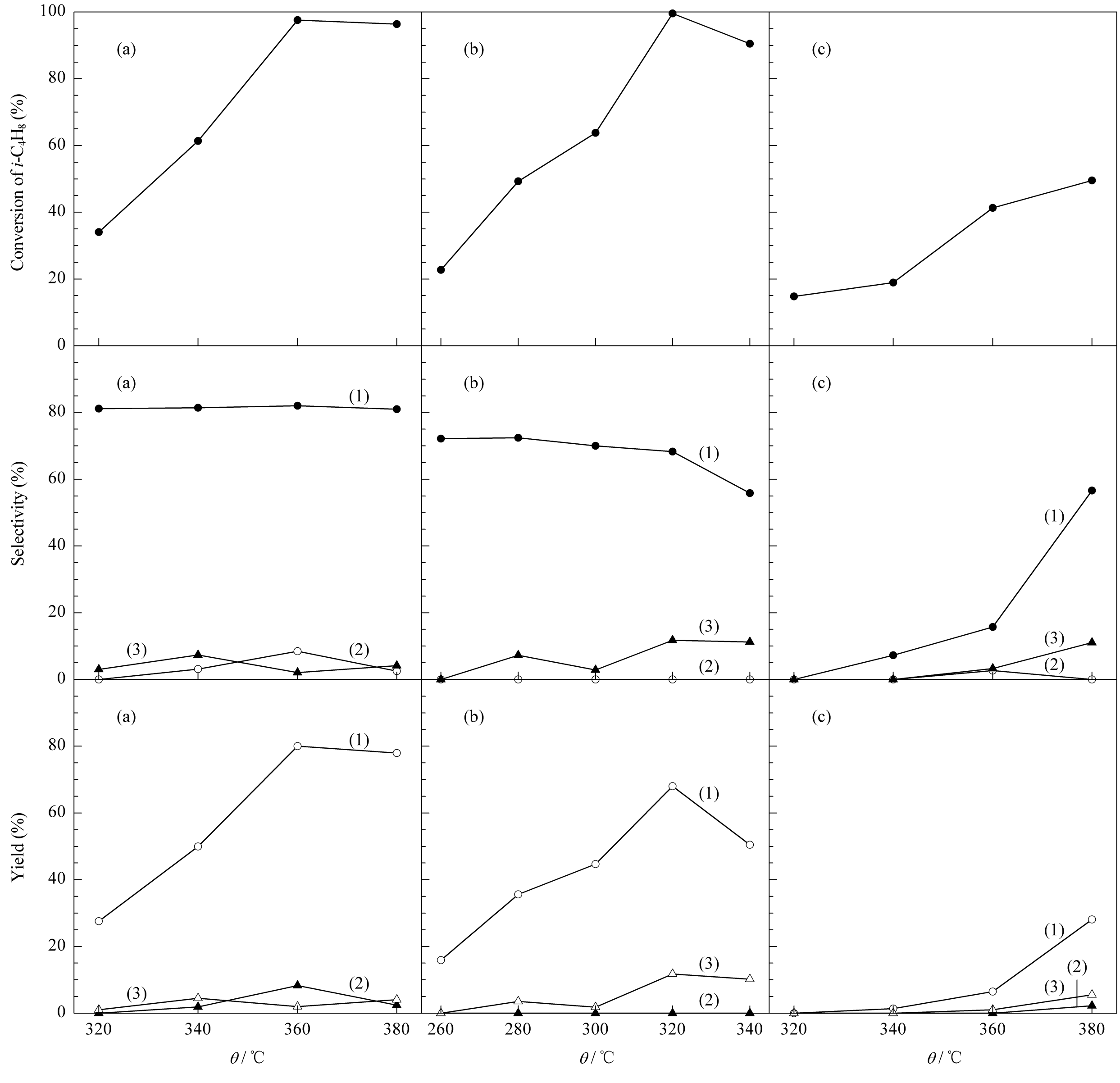


Figure 2. Effect of temperature on yields and selectivities of products of selective oxidation of isobutene over different CsFeCoBiMnMoO$_x$ catalyst samples

(a) $1^{\#}$, (b) $2^{\#}$, (c) $3^{\#}$; (1) MAL, (2) MAA, (3) HAc

Reaction conditions: catalyst weight 1.2 g, $n(i\text{-}C_4H_8):n(O_2)=1:2$, space velocity=180 h^{-1}

3.2.2. Effects of different oxygen concentrations and space velocity

Table 3 shows the effects of the oxygen concentration and space velocity on the oxidation of isobutene catalyzed by the 1# catalyst at 360 ℃. When the space velocity is 180 h^{-1}, $n(i\text{-}C_4H_8):n(O_2)=1:2$, the conversion of the isobutene is 97.55% and the yield of MAL reaches 80.01%. With the increase of the oxygen concentration, the conversion of the isobutene does not change, but the yield of MAL decreases and the yield of HAc increases accordingly. It illustrates that the high concentration of oxygen decreases the total yields of MAL and MAA. When the space velocity increasesto 500 h^{-1}, the conversion of the isobutene decreases drastically.

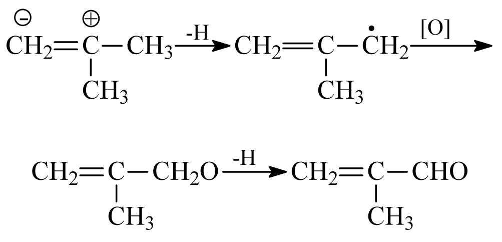
Table 1. Effects of different oxygen concentrations and space velocity on selective oxidation of isobutene over 1# catalyst at 360 ℃

$n(i\text{-}C_4H_8):n(O_2):n(N_2)$	Space velocity (h^{-1})	Conversion (%)	Yield (%)			Sum yield (%)
			MAA	MAL	HAc	
1:2:0	180	97.55	8.29	80.01	2.00	90.30
1:4:0	180	98.87	5.02	80.21	6.02	91.25
1:1:1.7	180	13.92	—	6.00	0.70	6.70
1:2:2.5	330	69.27	0.38	49.73	4.23	54.54
1:2:5.3	500	21.14	—	18.02	—	18.02

3.3. The discussion of the reaction mechanism

The important characateristics of the mixed oxides is the synergistic effect of the multiply functional active sites. However the synergistic effect of the functional sites is controlled by the different crystalline grains and the distribution of the different metallic cations [8]. The different calacination temperature can lead to different crystalline grain and different micro structure, which gives rise to different synergistic effect [9].

The reacting mechanism for the oxidation of isobutene to MAL was proposed as follows [10]:



$$\overset{\ominus}{CH_2}=\overset{\oplus}{\underset{CH_3}{C}}-CH_3 \xrightarrow{-H} CH_2=\underset{CH_3}{C}-\dot{C}H_2 \xrightarrow{[O]}$$

$$CH_2=\underset{CH_3}{C}-CH_2O \xrightarrow{-H} CH_2=\underset{CH_3}{C}-CHO$$

The catalyst for the selective oxidation of isobutene must have four functions: (1) the chemical adsorption of isobutene; (2) removal of the α-hydrogen atom of isobutene; (3) insertion of oxygen atom; (4) formation of the redox recycle. Over the mixed oxide catalyst, the function of Bi^{3+} cation may be for isobutene chemical adsorbption and oxygen insertion. The possible redox recycle is proposed in Figure 3 [4].

Fe^{3+}/Fe^{2+} and Mo^{4+}/Mo^{2+} must promote the exchange of oxygen between the surface and gas phase. The reaction mechanism of oxidation is characterized by redox mechanism. The oxygen of the products came from the catalyst but not directly from the gas phase [4]. The activity of catalyst is controlled not only by the gas oxygen but also the species of oxygen in the catalyst. However, the selectivities of the products were determined by the molecular of oxidation and the reactivity of the species of reacting oxygen. In the course of reaction, there are different active sites in the catalyst, such as the sites of absorption, desorption, dehydrogen, redox and so on. The rapid exchange of active species of oxygen plays a great role in the optimum of the synergistic effect of different active site.

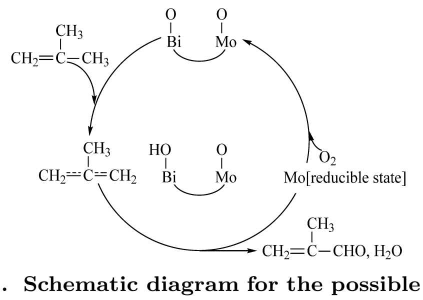


Figure 3. Schematic diagram for the possible redox recycle

4. Conclusions

The temperature of calcination and concentration of oxygen have great effect on the performance of the mixed oxide catalyst. The optimum temperature of calcinations and concentration of oxygen are the key to the best performance of the mixed oxide catalyst. When the mixed oxides calcined at 480 ℃ and under the optimum reaction conditions ($n(i\text{-}C_4^=):n(O_2)$=1:2–1:4, space velocity=180 h^{-1}, T=360 ℃), the yields of methacrolein and methacrylic can reach 80% and 8%, respectively. The total yield of liquid products (methacrolein, methacrylic acid and acetic acid) reaches about 90%. This indicates that it is a promising catalyst.

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