Oxidative Dehydrogenation of Isobutane on Mesoporous Silica Catalysts Introduced with Binary Metallic Cations

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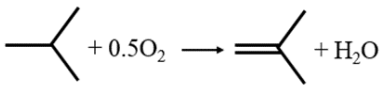
Abstract: The oxidative dehydrogenation of isobutane to isobutene was examined using SBA-15 introduced with chromium and molybdenum via a direct synthesis method, by which both metallic cations could be introduced into the framework of SBA-15. Although, in the present reaction, it has been already reported that it was difficult to obtain the yield of isobutene greater than 8% using various Cr-introduced mesoporous silicas, the present binary system afforded the yield of 9.6%. In order to explain the high catalytic activity, the results obtained by various characterization producers were correlated to the catalytic activity.

Keywords: Oxidative dehydrogenation, Isobutane, Mesoporous silica.

1. Introduction

In our laboratory, the oxidative dehydrogenation of isobutane to isobutene (eq. (1)) has been examined on various mesoporous silicas introduced with chromium cations since isobutene is expected as one of the most possible candidates as a raw material for the production of methyl methacrylate.[1]



(1)

It has been already reported that chromium-introducing mesoporous silica catalysts sometimes showed favorable activity for the oxidative dehydrogenation. Particularly, when employing a template ion exchange method for an introduction of chromium cations in various mesoporous silicas such as FSM-16 and MCM-41,[2,3] the yield of isobutene was significantly improved to 8%. However, since further enhancement of the catalytic activity beyond 8% of the yield of isobutene and the decrease of the loading of chromium is undoubtedly desired, the development of a more active catalysts should be needed. In the present study, another mesoporous silica, SBA-15, was employed as a support, while chromium and/or molybdenum were introduced into the framework of SBA-15 via a direct synthesis method.[4]

2. Experimental

All the catalysts, SBA-15 introduced with molybdenum cation (Mo-SBA-15), with chromium cation (Cr-SBA-15) and with both cations (Mo,Cr-SBA-15) were prepared using the direct synthesis method, in which $Cr(NO_3)_3 \cdot 9H_2O$ and/or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were mixed with TEOS in an aqueous starting solution with pH adjusted to 1.5, which was followed by the hydrothermal treatment.[4] Catalytic activity tests were carried out in a fixed-bed continuous-flow reactor at atmospheric pressure. Each catalyst (0.25 g, 0.85–1.70 mm) was pretreated with 12.5 mL/min of O_2 gas flow at 723 K for 1 h. Catalytic activity tests were examined at 723 K by flowing 15 mL/min of a mixed gas consisted of P(He) = 74.6 kPa, P(i-C_4H_{10}) = 14.4 kPa, and $P(O_2)$ = 12.3 kPa. These reaction conditions were used unless otherwise stated. Under these conditions homogeneous oxidation was not observed. X-ray diffraction (XRD), N_2 adsorption-desorption measurement and NH_3 temperature-programmed desorption were used for characterization of the catalysts.

3. Results and discussion

The catalytic activities on various catalysts at 6 h on-stream are shown in **Table 1**. The atomic ratios of Si/Mo and Si/Cr in the preparation solution are described in parenthesis in column of the Catalyst. The yields of isobutene on SBA-15 and three kinds of SBA-15 introduced with Mo (Mo-SBA-15; Si/Mo = 10, 100 and 1000) were less than 1.2% while that on SBA-15 introduced with Cr (Cr-SBA-15 (Si/Cr = 50)) reached to 4.8%, as reported for other mesoporous silicas.[2,3] It is noteworthy that the yield was further improved on introducing both of Mo and Cr in SBA-15 to be 6.3% on Mo,Cr-SBA-15 (Si/Mo, Si/Cr = 100). It is generally known that the enhancement of $P(O_2)$ in the reactant gas decreases the selectivity to isobutene together with the increase of the conversion of isobutane, resulting in the decrease of the yield of isobutene. However, in the present case, the yield was further enhanced to 9.6% on Mo,Cr-SBA-15 (Si/Mo, Si/Cr = 50) upon adjusting $P(O_2)$ to 24.6 kPa.

Table 1 Catalytic activities on various catalysts

Catalyst	Conv.(%)		Select.(%)		Yield(%)
	O_2	iso-C_4H_{10}	CO_x	iso-C_4H_8	iso-C_4H_8
Mo,Cr-SBA-15 (Si/Mo,Si/Cr=50)	30.6	11.2	32.5	53.8	6.0
Mo,Cr-SBA-15 (Si/Mo,Si/Cr=100)	43.9	12.6	33.7	50.3	6.3
Mo,Cr-SBA-15 (Si/Mo,Si/Cr=1000)	17.6	7.6	26.2	49.2	3.8
Cr-SBA-15 (Si/Cr=50)	62.6	16.7	49.6	29.0	4.8
Mo-SBA-15 (Si/Mo=10)	1.6	1.3	13.0	71.5	0.9
Mo-SBA-15 (Si/Mo=100)	4.1	1.0	7.1	71.2	0.7
Mo-SBA-15 (Si/Mo=1000)	7.2	1.7	17.6	57.3	1.0
SBA-15	6.7	3.6	55.0	33.4	1.2

XRD of all catalysts detected a main peak at 2θ ~ 0.9 degrees together with two smaller peaks at 2θ ~ 1.4 and 1.6 degrees, which could be indexed as (100), (110), and (200) reflection, respectively, associated with P6 mm hexagonal symmetry typical of SBA-15.[4] Specific surface areas of those catalysts estimated from N_2 adsorption-desorption measurement ranged from 520 m^2/g on Mo,Cr-SBA-15 (Si/Mo, Si/Cr = 100) to 872 m^2/g on Mo,Cr-SBA-15 (Si/Mo, Si/Cr = 1000) and no correlation between the specific surface area and the catalytic activity was observed. Therefore physical nature such as structure of the catalysts may not explain the difference on those catalysts. Therefore, in order to detect differences on chemical property, particularly on acidic nature of the catalysts, NH_3 temperature-programmed desorption were used. Smaller acidity (0.039 mmol/g) was detected from Mo-SBA-15 (Si/Mo = 10), while no information on acidic nature was not obtained from other catalysts. In order to explain the unique catalytic activity for the oxidative dehydrogenation of isobutane on Cr-introduced mesoporous silica catalysts via chemical nature of the catalysts, the contribution of Cr^{6+} converted from Cr^{3+} has been pointed out in our previous studies using XPS and XAFS.[2,3] Furthermore, it has been suggested that strong acidic sites that cannot be detected using NH_3-TPD have been noted when using solid-state ^1H MAS NMR. In order to find out the factor for the enhancement of the catalytic activity, further study is now in progress.

4. Conclusions

Single metallic system, SBA-15 introduced with Cr or Mo cations, showed a lower yield of isobutene than 4.8% detected from the oxidative dehydrogenation of isobutane. However, binary metallic system, SBA-15 introduced with both of Cr and Mo cations, showed rather greater yield as 6.3%, which was further improved to 9.6% by adjusting $P(O_2)$. Since the enhancement of the catalytic activity could not be explain using the results via XRD and N_2 adsorption-desorption measurement, some contribution of chemical nature of the catalysts to the catalytic activity were suggested in the present study.

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