

# Enhancement of Isobutene Yield in the Oxidative Dehydrogenation of Isobutane on SBA-15 Doped with a Trace Amount of Chromium

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Recently the preparation of isobutene from isobutane via the oxidative dehydrogenation on various solid catalysts is going in our laboratory since isobutene is a starting raw material to prepare methyl methacrylate via C<sub>4</sub> direct oxidation process and C<sub>4</sub> oxidative esterification process. Although mesoporous silicas such as FSM-16 and MCM-41 doped with chromium, those silicas treated with an acid and calcium hydroxyapatite doped and un-doped with chromium showed favorable yield of isobutene while the maximum yield of isobutene was still up to 6.8% [1-4]. In the present study, it will be presented that the use of another mesoporous silica, SBA-16, doped with a trace amount of chromium (Cr-SBA-15) results in the great enhancement of isobutene yields up to 13.6%.

According to the reported paper [5], Cr-SBA-15 with various Si/Cr atomic ratios, which were adjusted in the preparation step, were prepared. Catalytic activity was examined using a fixed-bed continuous flow reactor at atmospheric pressure. The following reaction conditions were employed in the present study;  $W = 0.25$  g,  $T = 723$  K,  $P(\text{iso-C}_4\text{H}_{10}) = 14.4$  kPa,  $P(\text{O}_2) = 12.3$  kPa (both diluted with He) and  $F = 15$  ml/min. Under these conditions, no homogeneous gas phase reaction was observed. The reaction was monitored using online gas chromatograph equipped with a TCD.

Table 1 showed the catalytic activity at 0.75 h on-stream over Cr-SBA-15 with various Si/Cr atomic ratios. Rather stable activity was continued by 6 h on-stream. With increase of Si/Cr, the conversion of isobutane and the yield of isobutene were increased to finally reach 13.6% of the yield on Cr-SBA-15 with Si/Cr = 100. In order to confirm the reproducibility of the catalyst preparation, Cr-SBA-15 with Si/Cr = 100 was prepared three times to show the greater yields of isobutene again between 10.1 and 15.1 %. These results indicated that the present great yield of isobutene can be reproduced. XRD revealed that the Cr-SBA-15 with Si/Cr = 100 possessed mesoporous structure while the specific surface area was 1,300 m<sup>2</sup>/g, both characteristics to SBA-15. Elemental analysis on Cr in Cr-SBA-15 with Si/Cr = 100 showed that Cr content in the catalyst was less than ppm order. Therefore the most of chromium species was excluded during the preparation step and the reminding trace amount of Cr contributed to the improvement of the yield of isobutene.

Table 1 Catalytic activity on Cr-SBA-15

Catalyst Si/Cr	Conv.[%] i-C <sub>4</sub> H <sub>10</sub>	Select.[%]		Yield[%] i-C <sub>4</sub> H <sub>8</sub>
		i-C <sub>4</sub> H <sub>8</sub>	CO <sub>x</sub>	
1/1000	4.7	59.6	13.7	2.8
1/500	13.3	60.3	25.2	8.0
1/250	19.3	61.4	25.1	11.9
1/100 <sup>a</sup>	22.9	59.3	28.2	13.6
1/100 <sup>a</sup>	20.7	58.8	28.7	12.2
1/100 <sup>b</sup>	14.6	69.3	19.4	10.1
1/100 <sup>c</sup>	27.3	55.5	32.7	15.1

a : Lot A. b : Lot B. c : Lot C.

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