

Dehydroisomerization of n-butane over metal promoted sulfated zirconia

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Abstract

The dehydroisomerization of n-butane to isobutene over Pt/metal/sulphated zirconia catalysts was studied at 550 °C and 1 Atm. Sulfated zirconia catalysts (SZ), promoted with Al, Mn, Cu and Ni, were synthesized by coprecipitation. The catalysts were characterized by AAS, ICP-MS, TGA, and XRD. Effects of metals, sulfur content, and crystallite size of the samples on the selectivity and yield to isobutene were investigated. The increase in crystallite size and sulfur content caused an increase in the selectivity of total butenes. The presence of platinum and second metal improved the catalytic stability and isomerization selectivity of SZ catalyst for n-butane isomerization. SZ catalyst with aluminum showed much higher selectivity towards isobutene than the unpromoted ones.

Key Words: Sulfated zirconia, n-Butane, Catalyst Characterization, Dehydroisomerization.

Introduction

Isobutene is an important intermediate in the petrochemical industry, mainly used for the production of polymers (butyl rubber, polybutene, and isoprene). Isobutene is also reacted with methanol or ethanol to produce MTBE (methyl-tert-butyl-ether) or ETBE (ethyl-tert-butyl-ether), both of which are useful as gasoline additives.

Sulfated zirconia is known to possess super acidity and good properties for catalyzing n-alkane isomerisation at ambient temperature (Hino et al., 1979, Hino and Arata, 1980). Fast deactivation was always observed, primarily due to coke deposition (Song and Sayari, 1996, Li and Gonzales, 1998, Xia et al., 1999). To improve the life time of SZ catalyst, the presence of hydrogen and/or addition of a small amount of Pt was suggested and used (Garin et al., 1991). Hollstein et al. (1990) and Hsu et al. (1992) first noticed that SZ doped with 1.5 wt.% Fe and 0.5 wt.% Mn was 2 to 3 orders of magnitude more active in n-butane isomerization at low temperature than unpromoted SZ. Coelho et al. (1995) reported a comparable enhancement upon the addition of Ni to SZ. Miao et al. (1996) found that sulfated oxides of Cr-Zr, Fe-Cr-Zr, and Fe-V-Zr binary and ternary metal containing catalysts were 2 to 3 times more active than SZ for n-butane isomerization. Unfortunately,

these transition metals-promoted SZ catalysts deactivated rapidly during the reaction (Jatia et al., 1994, Song et al., 1996, Yori and Parera, 1996).

The purpose of this study is to examine the catalytic activity in the dehydroisomerization reactions. Thus, we prepared nano-crystalline promoted sulphated zirconia catalysts, in which Al, Mn, Cu, and Ni metals were used as promoters. We investigated the influence on the isomerization activity of the sulfur content.

Experimental

Materials

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were procured from Lachema. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (40% Pt), H_2SO_4 (96%), and aqueous ammonia (25%, Merck) were all from Merck. They were used without any further purification.

Catalyst preparation

Sulfated zirconia (SZ) samples were prepared by coprecipitation. An aqueous solution of 1 N sulfuric acid was added dropwise into $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Then, 1 mol $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 1 mol metal (M) nitrate were dissolved in water. Aqueous ammonia was added to the solution until the final pH of 9-10 reached. The precipitate was then filtered and washed with distilled water. After drying the mixed hydroxide at 110 °C for 24 h, it was immersed in 1 N sulfuric acid at a rate of 15 mL g⁻¹ of hydroxide for 1 h with continuous stirring at room temperature. Sulfated $\text{M}(\text{OH})\text{-Zr}(\text{OH})_4$ was again filtered without washing, dried, and calcined at 650 °C in flowing dry air (30 mL min⁻¹) for 3 h. Pt/SZM catalysts (1 wt.% Pt) were prepared by impregnation method. Sulfated $\text{M}(\text{OH})\text{-Zr}(\text{OH})_4$ were impregnated with an aqueous solution of H_2PtCl_6 . After drying at 110 °C for 24 h, it was calcined at 650 °C in flowing dry air (30 mL min⁻¹) for 3 h. Considering the fact that the amount of Al added has an influence on the catalytic activity of n-butane isomerization, various amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were added. Molar ratio of Zr-Al and Zr-Mn were 1.0/0.1, 1/0.5 and 1.0/1.0, respectively. The catalysts are termed according to composition, where SZAl (1.0) describes a material with 1 mol Al and SZ is the unpromoted sulfated zirconia and SZM is metal promoted sulfated zirconia.

Catalyst characterization

The amount of metal deposited was measured using a Varian Spectra Fast Sequential -220 atomic absorption spectrometer with an air-acetylene flame. In some elements, the actual metal loadings were determined using a Thermo Elemental X Series ICP-MS. The bulk sulfur (wt.%) retained in sulfated zirconia samples after calcination at 650 °C for 2 h was analyzed by a Thermo Finnigan Flash EA 1112 Series elemental analyzer. The thermal decomposition behavior of the samples was analyzed by a thermo gravimetric analyzer (TG-60WS-Shimadzu). All the samples were heated from room temperature to 1000 °C with a heating rate of 10 °C/min under flowing air.

The crystal phases were determined by X-ray diffraction using a Rigaku D/Max-2200 diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.5405$) radiation. Samples were scanned from 10 to 60 at a rate of 0.5°/min (in 2 Θ). The sizes of the crystalline domains (ZrO_2) were obtained via the Scherrer equation ($t = C\lambda / B\cos\Theta$) where λ is the x-ray

wavelength (A°), B is the full width at half maximum, Θ is Bragg angle, C is a factor depending on crystallite shape (taken to be one), and t is the crystallite size (A°).

The acidic properties of the catalysts were investigated by n-butylamine desorption using a Shimadzu TGA-60WS thermo gravimetric analyzer.

Catalyst testing

Catalysts were examined for their selectivity and activity in n-butane dehydroisomerization. For this purpose, 0.65 g of sample was mixed with 5 g of quartz of the same size and placed into a quartz reactor with a 4 mm inner diameter. The activities of the catalysts were compared at 550 °C, at atmospheric pressure and with a weight hourly space velocity (WHSV) of 10 h⁻¹.

Prior to the reaction, the catalyst was reduced with hydrogen mixture (10.3% H₂/N₂). A reactant stream (n-C₄/H₂ = 1/2) contains n-butane (BOC, 99.5%) and 10.3% H₂/N₂. The reactor effluent was analyzed by an on-line gas chromatograph fitted with an Al₂O₃ column. After 10 min on stream, the reactor effluent was analyzed by direct injection into GC and then at intervals of 30 min (namely, at 40, 70, and 100 min and so on).

The conversion and selectivity were calculated from the reaction product on the basis of the carbon balance: the total molar amount of carbon in the effluent was assumed to be equal to the molar amount of carbon in the n-butane fed to the reactor. The coke formed on the catalyst during the dehydroisomerization test was neglected. The total amount of n-butane fed to the reactor equals $C_{nb_{in}}$.

$$C_{nb_{in}} = \Sigma C_1 * \frac{1}{4} + \Sigma C_2 * \frac{2}{4} + \Sigma C_3 * \frac{3}{4} + \Sigma C_4 + C_6 * \frac{6}{4} + C_7 * \frac{7}{4} \quad (1)$$

where C_i = molar amount of product containing carbon in the reactor effluent, including hydrocarbons, CO, and CO₂. The conversion of n-butane equals X_{nb} .

$$X_{nb} = 100 * \frac{C_{nb_{in}} - C_{nb_{out}}}{C_{nb_{in}}} \quad (2)$$

where $C_{nb_{in}}$ = amount of n-butane fed to the reactor calculated according to Eq. (1) and $C_{nb_{out}}$ = amount of n-butane in the reactor effluent. The selectivity to a specific product, for example, n-butenes, S_{nb} was calculated as

$$S_{nb} = 100 * \frac{C_{nb}}{C_{nb_{in}} - C_{nb_{out}}} \quad (3)$$

where C_{nb} = amount of n-butenes, 1-butene, cis-2-butene, and trans-2-butene in the reactor effluent.

The yield of a specific product was obtained by multiplying n-butane conversion by the corresponding selectivity. Experimental repeatability was around $\pm 14\%$, which was calculated from 4 repeated experiments performed at a representative reaction condition with fresh catalysts of the same type and used as a measure of repeatability.

Results and Discussion

The physicochemical properties of SZM catalysts are listed in Table 1, showing that the presence of Pt did not change sulfur content and weight loss. However, by comparison of thermal analysis of catalysts, obtained after

reaction, weight loss % reduced with additional Pt. This result was interpreted as the addition of Pt to SZ reduced the amount of coke (Kimura, 2002).

Table 1. Physicochemical properties of SZ catalysts.

Sample Code	ZrO ₂ Crystallite size (nm)	Sulfur content (%)	Weight Loss (%) before reaction	Weight Loss (%) after reaction
SZ	10.2	2.6	17.12	3.29
SZAl(1.0)	23.1	4.2	34.39	10.46
SZAl(1.0)Pt	24.7	4.4	32.18	7.98
SZNi(1.0)	20.5	1.0	22.69	*NM
SZCu(1.0)	20.5	0.9	20.20	*NM
SZMn(1.0)	22.9	3.2	26.48	8.79

*NM: Not Measured

The diffraction patterns of sulfated zirconia (SZ) are shown in Figure 1. The SZ crystal showed the presence of only tetragonal phase with well-defined most intensive peaks corresponding to the planes with hkl (111), (202), and (311) (Lajavardi, 2000).

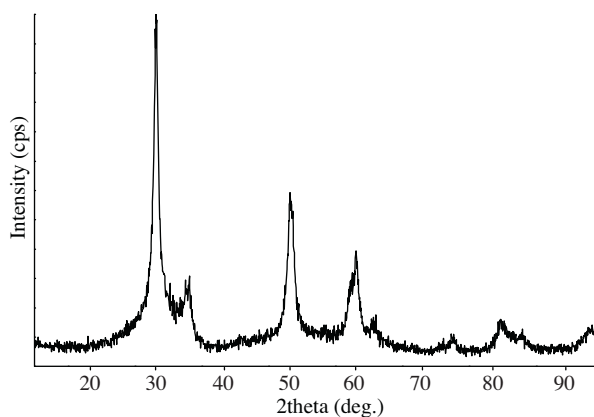


Figure 1. X-ray diffraction pattern of SZ catalysts.

Five catalysts samples, namely SZ, SZAl(1.0), SZNi(1.0), SZCu(1.0), and SZMn(1.0), were chosen to investigate the effect of promoter in the catalytic activity of metal-promoted sulfated zirconia for n-butane dehydroisomerization. XRD patterns showed that the crystalline phase in all samples was mainly the tetragonal phase of zirconium. The width of the diffraction peak showed that the particle sizes of zirconia in SZNi and SZCu were smaller than those in SZAl(1.0) and SZMn(1.0).

Amine adsorption method on acid sites of solid catalysts is a well-known technique to determine the acidity of the catalyst. The use of *n*-butylamine as a molecular probe for the characterization of catalysts has been reported (Fernandes et Al., 1999, Milburn et al., 2001). Catalysts were treated with *n*-butylamine vapors in a desiccator for adsorption and then the weight loss curves of adsorbed *n*-butylamine were recorded by Thermo gravimetric (TG) analysis at the heating rate of 10 °C min⁻¹. Based on weight loss values of *n*-butylamine treated catalysts, the amount of adsorbed *n*-butylamine was calculated quantitatively. A link between the Al promoter content and the total acidity can be found (Table 2). Whereas SZ had lower acidity, addition of Al yielded to higher acidity. Moreover, Table 2 shows correlations between acidity and activity. A good correlation between acidity and n-butane conversion was found for all SZAl catalysts.

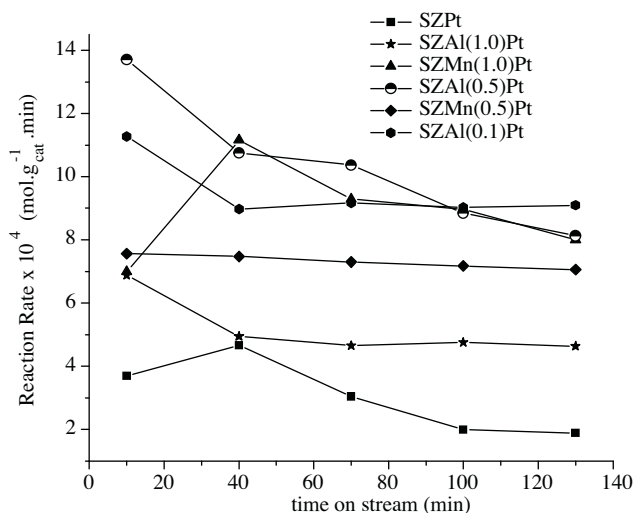
Table 2. Initial activity, conversion (X) and catalysts selectivities (S) of butenes on average during 10 min for n-butane isomerization at 550 °C.

Catalysts	S(%) (iC4=)	S(%) (C4=)	X (%)	Activity (10^{-4} . mol.g _{cat.} ⁻¹ . min ⁻¹)	Total acidity ^b (au)
SZ	17.41	40.41	12.02	3.3	4.82
SZPt	25.5	34.46	13.47	3.7	5.67
SZAl(1.0)	28.44	68.5	17.15	4.7	6.30
SZAl(0.1)Pt	11.63	4.8	41.04	11.3	8.52
SZAl(0.5)Pt	18.74	7.65	49.88	13.7	10.43
SZAl(1.0)Pt	42.97	30.24	25.11	6.8	7.12

^areaction condition: n-butane/H₂= 1/2

^b Number total of sites (au) calculated for 10 mg of catalyst

The influence of metal and Pt on catalytic activity for SZ is shown in Figure 2. For SZPt, the activity in isomerization declined strongly over the first 40 min of reaction. The addition of metal caused an increase in Butenes selectivity compared to SZPt catalyst. Very low activity was found for SZNi(1.0)Pt and SZCu(1.0)Pt catalysts. In the case of SZMnPt catalyst, a considerable increase was observed on the catalytic activity when the molar ratio of SZ/Mn increased. The catalytic activity remained stable during reaction time with SZ/Mn(0.5)Pt. However, the maximum activity was obtained with SZ/Mn(1.0)Pt at the 40th minute of the reaction.

**Figure 2.** Isomerization rate vs. time on stream at various SZ catalysts (550 °C, 1 atm., n-butane/H₂ = 1/2).

It was seen that SZAl(0.5)Pt exhibited the highest catalytic activity than other catalysts. The catalytic activity increased with molar ratio of SZ/Al catalysts. However, when the molar ratio of SZ/Al was increased from 0.5 to 1.0, the catalytic activity reduced. SZAl(1.0)Pt improved isobutene selectivity and stability of catalytic activity with time. Additionally, SZAl(1.0)Pt catalyst showed the highest isobutene yield (10.79%). It indicates that there is an optimum for SZ catalyst under a given molar ratio of Zr/Al.

As shown in Table 1, SZAl(1.0) and SZAl(1.0)Pt contain more sulfur than SZ alone. More sulfur meant more catalytically active sites under the same condition (Hua, 2000). This might be the main reason why SZAl(1.0)

and SZAl(1.0)Pt showed much higher catalytic activity than SZ. The catalytic activity and selectivity of samples are shown in Table 2. When the Al content in SZ increased from 0.1% to 1%, isobutene selectivity remarkably increased while conversion decreased. On the other hand, isobutene selectivity and conversion increased as both Al and Pt modified in SZ catalyst increased to 25.56% and 8%, respectively. When Pt and Al were singly added to SZ, isobutene selectivity and conversion increased. However, the addition of Pt alone decreased the selectivity of isobutane while Al caused to increase. Løften et al. (2005) reported that the unpromoted catalyst (SZ) had a higher activity compared to the promoted samples (FeMnSZ). There were reports that Iron and manganese acted as inhibitors. Gao et al. (1998) provided the activity of FeMnSZ catalyst (also 1.5 wt.%Fe, 0.5 Wt.%Mn) was 2-3 times higher than the activity of unpromoted and aluminum promoted SZ at 35 °C. At 250 °C however, they found that the FeMnSZ catalyst was less active than unpromoted SZ and exhibited a much poorer stability than both aluminum promoted and unpromoted SZ.

Further addition of Pt led to an increase in activity as well as acidity. Eswaramoorthi et al. (2003) observed that bimetallic Ni-Pt/Zeolite β catalysts containing 0.1% Pt show better activity and selectivity for n-heptane than Ni only containing catalysts. In general, the higher activity of Metal-Pt catalysts can be accounted by the presence of Pt enhancing the reduction of metal cations forming more metal particles, the metal particles serving as support for the Pt atoms and the generation of further acidity due to the best metal–acid balance between bimetallic particles and acid sites of the support. Further, the threshold of any metal addition and platinum as promoter is found to enhance the branching selectivity and olefin selectivity. The enhanced activity can tentatively be accounted in terms of better metal–acid balance between catalytically active bimetallic (metal–Pt) nanoparticles formed and acid sites of the support.

Conclusions

SZ, SZM, and SZMPt samples have been tested for their activity in n-butane dehydroisomerization. The presence of platinum and metal improved the catalytic stability and isomerization selectivity of SZ catalyst for n-butane isomerization. However, SZMn(1.0)Pt catalyst showed the higher maximum isobutane selectivity (9.8%). Molar ratio of SZAl(1.0)Pt improved isobutene selectivity and stability of catalytic activity with time. Additionally, SZAl(1.0)Pt catalyst showed the highest isobutene yield (10.79%). Isobutene selectivity and conversion increased as both Al and Pt modified in SZ catalyst increased to 25.56% and 8%, respectively. The increase in crystal size and sulfur content caused an increase in selectivity of butenes. Moreover, the catalytic activity was found to be correlated with the total acidity of the samples.

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