높은 표면적을 가지는 Sulfated Zirconia 상에서의 1-Butene의 골격이성질화 반응

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Skeletal Isomerization of 1-Butene over Sulfated Zirconia with High Surface Area

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INTRODUCTION

In the past few years, the skeletal isomerization of 1-butene has attracted a special attention as an alternative route to produce isobutene, which is a raw material for the synthesis of methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) [1]. In particular, MTBE is one of the octane-enhancers to replace tetra-ethyl lead in reformulated gasolines [2]. Isobutene has also been utilized in the current industry as the monomer in the production of polyisobutene and as one of the monomers for butyl rubber and polybutene manufacture [3].

The skeletal isomerization has been known to be a more demanding reaction than both the cis-trans and double-bond shift isomerization reaction, since it only proceeds on sites with high acid strength [4,5]. Thus, a large number of acid catalysts including halogen-modified metal oxide and zeolites (ZSM-5, FER, *etc.*) have been employed. The medium-pore zeolite ferrierite (FER topology) is of current interest since it shows an exceptional selectivity for the skeletal isomerization of 1-butene. The FER structure contains a two-dimensional pore system consisting of ten-membered rings (4.2×5.4 Å) intersected by eight-membered rings (3.5×4.8 Å) and this pore structure is considered to play an important role in achieving the high selectivity to isobutene in the skeletal isomerization [6].

In the extensive study of Hino and Arata [7], the sulfate addition to some freshly precipitated metal oxides such as Fe_2O_3, TiO_2 and ZrO_2 yielded solids with very strong acid. These solids, which have an acid strength higher than 100% H_2SO_4 ($H_0 = -11.9$), are called solid superacids. Since the first report by Holm and Bailey [8] in 1962, most attention has been paid to sulfated zirconia, because it obtained the highest acid strength among sulfated metal oxides ($H_0 \leq -16.04$). Jin *et al.* [9] ascribed the strong acidity of these solids to the electron withdrawing surface-bonded $(SO_4)^=$ anion, which creates a coordinatively unsaturated and electron deficient metal center that behaves as a strong Lewis acid site. The addition of sulfate to ZrO_2 yields a solid acid 10^4 times stronger than 100% H_2SO_4 [10].

In this work, pure zirconia with high surface area has been synthesized using the zirconium atrane complex. We have investigated the catalytic performance of this sulfated zirconia in the skeletal isomerization of 1-butene under various operating conditions, *i.e.*, temperature, time-on-stream (TOS) and acid strength. Finally, we have compared its catalytic activity to that of the conventional sulfated zirconia and suggested optimal conditions for the sulfated zirconia synthesized in this work.

EXPERIMENTAL

Preparation of Mesoporous Zirconia

First of all, zirconium atrane derivatives were prepared using zirconium propoxide and TEAH in THF according to the synthetic method of titanatranes described in the literature [11]. In a typical synthesis leading to the zirconia mesophase, 0.28 g of NaOH were dissolved in a TEAH solution containing 0.02 mol of the prepared Zr-atrane derivatives of TEAH and 2.20 g of cetyltrimethylammonium bromide (CTAB). Then, 60 ml of water were slowly added under vigorous stirring. The resulting mixture was stirred for 2 h and then allowed to cool at room temperature, which resulted in the formation of a pale yellow mesostructured solid. This was hydrothermally aged for 2 days. After aging, the solid was filtered off, washed with ethanol and air-dried. Finally, to obtain the mesoporous zirconia material, the surfactant was removed by calcining at 500 ^oC for 6 h under air atmosphere. The sample was characterized by the N_2 physisorption isotherm (Micromeritics ASAP2010 analyzer).

Skeletal Isomerization of 1-Butene

The skeletal isomerization of 1-butene in gas-phase was carried out in a fixed-bed flow reactor at an atmospheric pressure. The catalysts (0.1 g) were loaded into the reactor and pretreated at 500 °C before the reaction. After pretreatment, the reactor was cooled down to the reaction temperature. And then, 1-butene in He balance (ratio of He to 1-butene = 9:1) was streamed into the reactor at a flow rate of 10 ml/min.

Samples were taken out periodically during the course of reaction with Valco 16-port multiposition valve. The products were analyzed by an on-line GC (Hewlett Packard 5890 II) equipped with HP-PLOT capillary column and FID detector. These products were confirmed by using the authentic refinery gas test samples (Hewlett Packard P/N 5087-8755).

RESULTS AND DISCUSSION

The zirconia has been synthesized with the surfactant of CTAB by the zirconium atrane route. Figure 1(a) shows the N_2 physisorption isotherm of the prepared zirconia calcined at 500 °C. The isotherm is typical of Type IV according to IUPAC classification. The desorption isotherm presents a clear hysteresis, indicating the existence of some necking in the pore structure. According to the BET and BJH (Barrett-Joyner-Halenda model) analyses, the zirconia has a high surface area of 311.6 m^2/g, a pore volume of 0.48 cm^3/g and a narrow pore diameter distribution centered at 3.52 nm. Although calcined at a high temperature of 500 °C, the present zirconia has a higher BET surface area than any other zirconia reported previously. Therefore, this zirconia could be applied to the gas-phase reactions by virtue of its high thermal stability. Figure 1(b) illustrates the X-ray diffraction pattern of the prepared zirconia. The XRD pattern shows only one strong and broad reflection centered at 2θ of 1.43° (d spacing = 61.7 Å). A similar single peak diffraction with large d spacing was previously observed in both mesoporous silicas (disordered MCM-41, HMS and MSU) and mesoporous aluminas.

The activity of the present sulfated zirconia (SZ) was compared to that of the conventional SZ in the skeletal isomerization of 1-butene as shown in Figure 2. With respect to the conversion of 1-butene, a similar behavior is observed over the two catalysts. In other words, the conversion of 1-butene is high in the biginning and then it deceases rapidly with the reaction time. It is due to the rapid deactivation of the catalysts. The conventional SZ shows a much higher conversion than the present SZ during the initial stage of reaction. As the reaction proceeds, however, the conversion of 1-butene

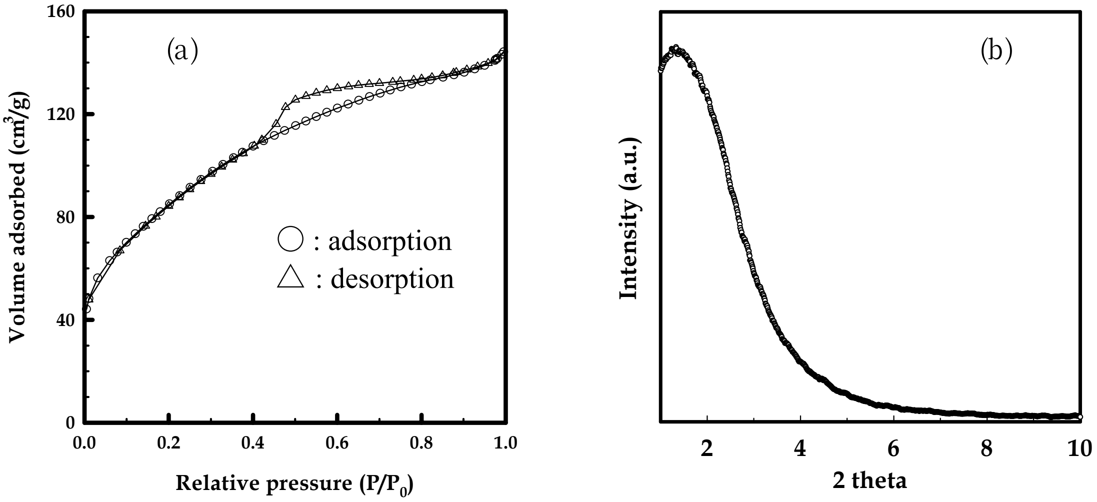

Figure 1. (a) N_2 adsorption-desorption isotherms and (b) XRD pattern of the present zirconia calcined at 500 °C.

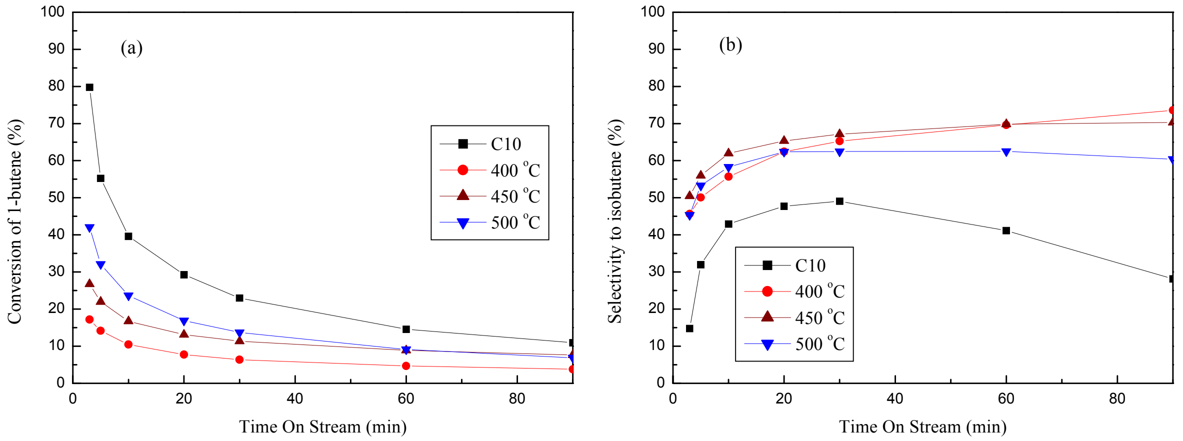

Figure 2. Conversion of 1-butene (a) and selectivity to isobutene (b) versus time-on-stream over the conventional sulfated zirconia (C10, 10 wt% sulfation, 450 °C) and the present sulfated zirconia (5M sulfation, 400 °C, 450 °C and 500 °C).

approaches each other between the two catalysts.

On the other hand, the selectivity to isobutene is observed very differently over the two catalysts. It rapidly increases until 30 min of TOS but, after then, decreases over the conventional SZ. This result indicates that coke deposits lead to a very rapid reduction of free space around the active sites, thus decreasing the effective pore size of the conventional SZ which has only micropores. In contrast, the selectivity to isobutene increases and is maintained at a higher level over the present SZ. This means that coke deposits have little effect on the selectivity to isobutene over the present SZ, having relatively large pore.

The effect of temperature in this reaction is also shows in Figure 2. As the temperature increases, the conversion of 1-butene increases. However, the selectivity to isobutene is observed to show a reversed trend. This feature is not unexpected because the high reaction temperature causes the cracking products to be formed in a large amount. Therefore, the reaction temperature is fixed at 450 °C.

It is well known that the number and strength of acid sites have an influence on this reaction. Before the catalytic reaction, the present zirconia is sulfated with sulfuric acids of 1, 3 and 5M respectively. The reaction results represented in Figure 3. The conversion of 1-butene increases with

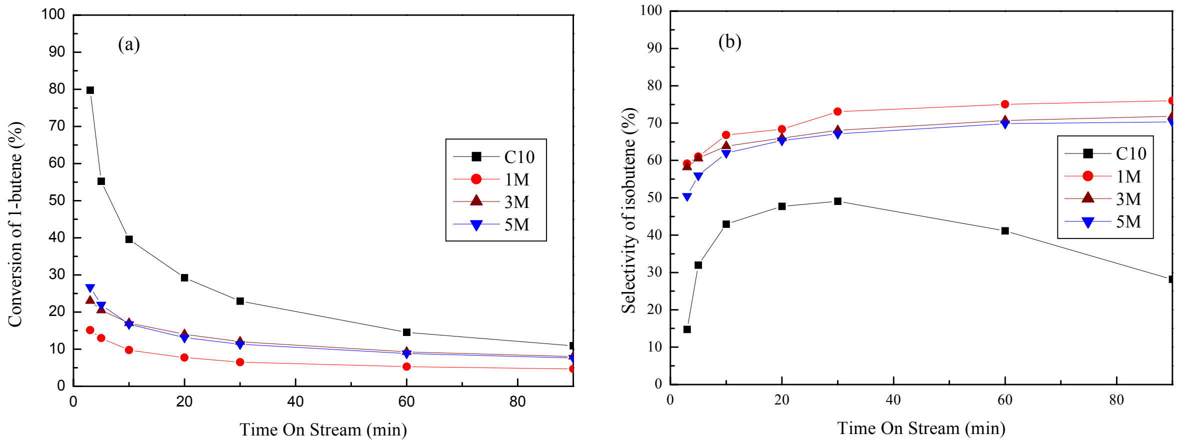

Fig. 3. Conversion of 1-butene (a) and selectivity to isobutene (b) versus time-on-stream over conventional sulfated zirconia (C10, 10 wt% sulfation) and the present zirconia sulfated with sulfuric acids of different concentration.

the sulfate concentration but its effect is negligible beyond the concentration of 3M. On the other hand, the selectivity to isobutene decreases with the sulfate concentration. Here again, the sulfate concentration has a negligible influence beyond the concentration of 3M. This result indicates that a relatively strong acid strength is required for the skeletal isomerization of 1-butene. In view of the yield of isobutene, the optimum acid strength is obtained with the sulfate concentration of 3M.

CONCLUSIONS

Zirconia with high surface area of 311.6 m^2/g has been prepared using zirconium atrane complex, after calcination at a high temperature of 500 °C. When applied to the skeletal isomerization of 1-butene, the present SZ showed higher and more stable selectivity to isobutene than the conventional SZ. This is attributed to the mesoporosity of the present SZ.

In addition, the reaction conditions over the present SZ were to give the reaction temperature of 450 °C and the sulfate concentration of 3M as the optimum conditions. This indicates that the intermediate conditions are required to suppress the cracking reactions.

ACKNOWLEDGMENTS

The authors greatly acknowledge the financial support from LG Caltex Oil Corp. and the partial aid from the Brain Korea 21 program sponsored by the Ministry of Education.

REFERENCES

1. Butler, A.C. and Nicolaides, C.P., *Catal. Today*, **18,** 443 (1993).
2. Hutchings, G.J., Nicolaides, C.P. and Scurrell, M.S., *Catal. Today*, **15,** 23 (1992).
3. Juguin, B., Torck, B. and Martino, G., in Imelik, B., Naccache, C., Coudurier, G., Ben Taarit, Y. and Vedrine, J.C. (Editor), *Catalysis by Acids and Bases (Studies in Surface Science and Catalysis, Vol. 20)*, Elsevier, Amsterdam, p. 253 (1985).
4. Damon, J.-P., Bonnier, J.-M. and Delmon, B., *J. Colloid Interface Sci.*, **55,** 381 (1976).
5. Damon, J.-P., Delmon, B. and Bonnier, J.-M., *J. Chem. Soc. Faraday Trans.*, **1**, 73 (1977).
6. Seo, G., Jeong, H.-S., Hong, S.-B. and Uh, Y.-S., *Catal. Lett.*, **36**, 249 (1996).
7. Hino, M. and Arata, K., *J. Chem. Soc., Chem. Commun.*, 1148 (1979).
8. Holm, Bailey, US Patent 3 032 599 (1962).
9. Jin, T., Yamaguchi, T. and Tanabe, K., *J. Phys. Chem.*, **90**, 4794 (1986).
10. López-Salinas, E., Hernández-Cortéz, J.G., Cortés-Jácome, Ma.A., Navarrete, J., Llanos, Ma.E., Vázquez, A., Armendáriz, H. and López, T., *Appl. Catal. A*, **175**, 43 (1998).
11. Menge, W.M.P.B. and Verkade, J.G., *Inorg. Chem.*, **30**, 4628 (1991).
12. Asensi, M. A., Corma, A. and Martinez, A., *J. Catal.*, **158,** 561 (1996).