Zirconium Atrane 복합체를 이용한 순수한 지르코니아의 합성 및 촉매 응용

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Novel Synthesis of Pure Zirconia by the Zirconium Atrane Complex and Its Catalytic Applications

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INTRODUCTION

Since the discovery of mesoporous silicates based on amphiphilic supramolecular templates [1], a large number of studies have been reported concerning the preparation conditions, synthesis mechanism, characterization, and use of these materials as catalysts and catalyst supports in various reactions [2]. This surfactant templating procedure was extended to the formation of non-silica mesoporous oxides [3], *e.g.*, titania, niobia, tantala, alumina, manganese oxide, ceria, hafnia, and zirconia. Among these non-silica oxides, zirconium oxide is of particular interest for acid catalysis [4]. However, due to the high reactivity towards water of zirconium alkoxides, another zirconium sources such as $ZrOCl_2$, $ZrCl_4$, $Zr(SO_4)_2$ have been utilized in the preparation of mesostructured or mesoporous ZrO_2 [5-8]. Therefore, a major concern in the synthesis of ZrO_2-based mesoporous materials is to achieve an adequate balance between the hydrolysis-condensation process involving the zirconium centers and the self-assembling reactions occurring between the resulting hydrolyzed inorganic entities and the surfactant. In practice, the high hydrolysis rate of Zr-alkoxides prevents the formation of stable mesostructures. Cabrera *et al.* [9] reported in recent years that ordered mesoporous materials were obtained by an atrane route, which is involved in the interaction between metal alkoxides and triethanolamine (TEAH). Here, TEAH ligand acts as a hydrolysis retarding agent. It was also suggested that the oxides such as Al_2O_3, TiO_2 and ZrO_2 could be prepared as ordered mesoporous materials by kinetically controlling the hydrolysis of the precursors (atranes). In this study we prepare pure zirconia with high surface area using the hydrolysis retarding agent, TEAH, and apply the synthesized material to the catalytic reaction.

EXPERIMENTAL

Synthesis and characterization of zirconia

First of all, zirconium atrane derivatives were prepared using zirconium propoxide and TEAH in THF according to the synthetic methods of titanatranes described in the literature [10]. A solution of $Zr(OPr^n)_4$ in THF was added dropwise to a solution of TEAH in THF. The mixture was then stirred for 2 hr. The volatiles were removed in vacuum for 1 hr using a rotary evaporator.

In a typical synthesis leading to the zirconia mesophase, 0.28 g of NaOH (0.007 mol) were dissolved in a TEAH (11.24 g, 0.0753 mol) solution containing 0.020 mol of the prepared Zr-atrane derivatives of TEAH and 2.20 g of cetyltrimethylammonium bromide (CTAB; 0.006 mol). Then, 60 mL of water (3.33 mol) were slowly added under vigorous stirring. Thus, the molar composition of the starting reagent mixture was 2:7.5:0.7:0.6:332 Si:TEAH:NaOH:CTAB:H_2O. The resulting mixture was stirred for 2 hr and was 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 calcination at 350 °C for 120 hr or 500 °C for 6 hr under air atmosphere. All the samples were analyzed and characterized by X-ray powder diffraction technique, TEM, FE-SEM (JEOL JSM6700F), and N_2 adsorption-desorption isotherms (Micromeritics ASAP2010 analyzer).

Skeletal isomerization of 1-butene

The skeletal isomerization of 1-butene was carried out in a fixed-bed quartz reactor. The catalyst was pretreated at 500 °C under a nitrogen atmosphere. The reaction was performed at 500 °C in a flow of 10% 1-butene/He. The products were analyzed by an on-line GC (HP 5890 II) equipped with HP-PLOT capillary column and FID detector.

RESULTS AND DISCUSSION

The strategy now reported involves two main procedural features, namely, the use of zirconium atrane complexes as the source of Zr reactive species and the use of a commercial alkyltrimethylammonium surfactant (CTAB and OTAB) as a template. It must be remarked that zirconium atrane solutions are easily and quickly prepared without additional purification or crystallization steps. On the other hand, it is the adequate control of kinetic parameters that finally makes it possible to produce the mesoporous material. In practice, we simply adjust (1) the mixing temperature (T_m), at which occur the hydrolytic and condensation processes involving the zirconium atrane complexes and (2) the aging conditions (temperature T_a and time t). It is also important in this context to emphasize that such kinetic factors affect the reactivity of both the inorganic and organic species involved in the self-assembling processes. Therefore, these factors were fixed from our preliminary study.

The present zirconia has been synthesized with the surfactant of CTAB by the zirconium atrane route. Figure 1 illustrates the nitrogen adsorption-desorption isotherm and pore size distribution of the material calcined under two different conditions; 350 °C for 120 hr and 500 °C for 6 hr, respectively. The corresponding BET isotherms are typical of type IV isotherm according to IUPAC classification. The isotherms show a single and well-defined step and a clear hysteresis in the desorption branch. This hysteresis loop indicates an 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 468m^2/g, a pore volume of 0.48cm^3/g and a relatively narrow pore diameter distribution centered at 3.52 nm, when the material was calcined at 350 °C for 120 hr. More interestingly, the material calcined at 500 °C for 6 hr has the similar results in the shape of isotherms and pore diameter (3.52 nm), except for the BET surface area and pore volume. When calcined at high temperature, the BET

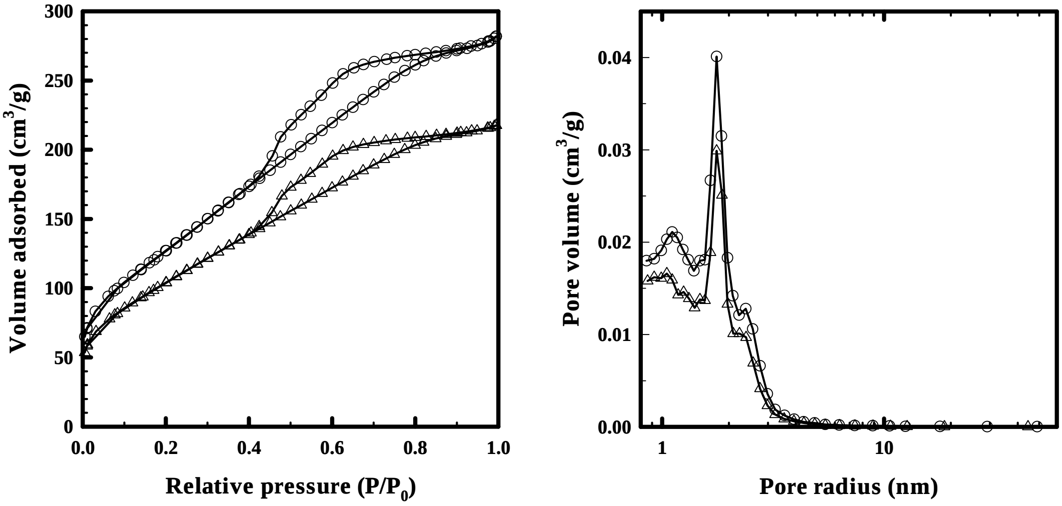

Figure 0. N_2 adsorption/desorption isotherm (left) and pore size distribution (right) of the zirconia synthesized with the surfactant CTAB by the zirconium atrane route. ○, calcination at 350 °C; △, calcination at 500 °C.

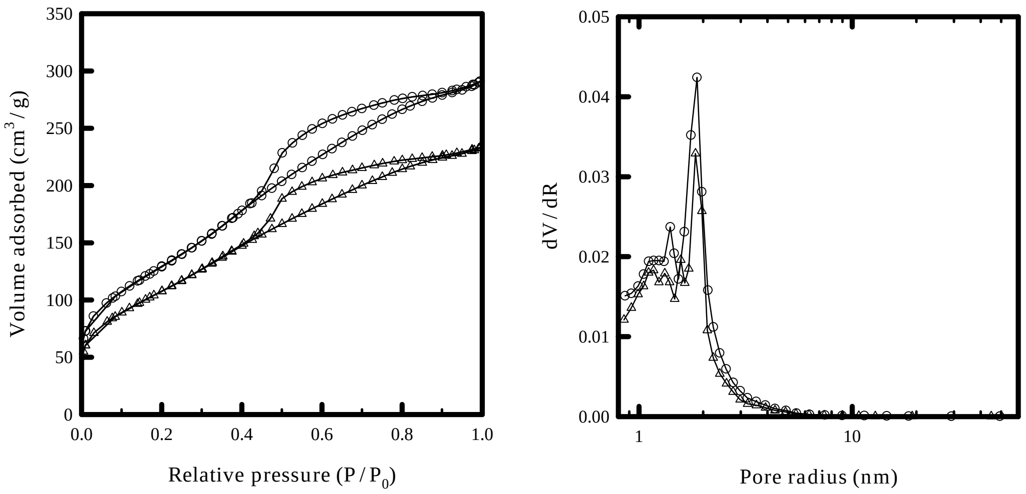

Figure 0. N_2 adsorption/desorption isotherm (left) and pore size distribution (right) of the zirconia synthesized with the surfactant OTAB by the zirconium atrane route. ○, calcination at 350 °C; △, calcination at 500 °C.

surface area and the pore volume decrease to 384m^2/g and 0.38cm^3/g, respectively. With respect to BET surface area, this result is very remarkable. Among many previous reports, the maximum surface area was 361m^2/g observed in the material suggested by Wong and Ying [3]. Even thermally stable mesoporous zirconia synthesized by Stucky and co-workers [8] had the BET surface area of 150m^2/g. Although calcined at high temperature of 500 °C, the present material has higher surface area than any other materials reported previously.

Also, the zirconia was prepared by the self-assembly between zirconium atrane complex and the surfactant of octadecyltrimethylammonium bromide (OTAB). The carbon chain length of this surfactant containing 18 C atoms, is longer than that of CTAB. Figure 2 shows the nitrogen adsorption-desorption isotherm and pore size distribution of the material calcined identically at two conditions operated in utilizing the surfactant CTAB. As expected, the results are similar to those observed in case of CTAB surfactant. BET and BJH (Barrett-Joyner-Halenda model) analyses indicate that zirconia has a high surface area of 474m^2/g, a pore volume of 0.49cm^3/g and a relatively narrow pore diameter distribution centered at 3.74 nm when the material was calcined at 350 °C for 120 hr. In regard to the pore diameter and pore volume, there is not much difference between both materials synthesized by CTAB and OTAB, respectively. When calcined at 500 °C for 6 hr, the material has lower values in all properties than the one calcined at 350 °C. The BET surface area, pore diameter and pore volume decrease to 395m^2/g, 3.68 nm and 0.40cm^3/g, respectively. However, these values are larger than those observed in the materials synthesized by CTAB, followed by calcination at the same temperature.

The present zirconia was applied to the skeletal isomerization of 1-butene. Before the reaction, the zirconia was sulfated with sulfuric acid. In the reaction mechanism, 1-butene is rearranged into tertiary carbocation on the acid sites and then the cation is transformed into isobutene, the final product. Figure 3 shows the results obtained over Ferrierite, the conventional sulfated zirconia (SZ) and the present SZ. The conventional SZ deactivates very fast. Also, the selectivity to isobutene increases until the reaction time of 30 minutes and, after then, it is decreasing. We compare the present material to the conventional sulfated zirconia in this reaction. As a result, the present SZ has slower deactivation than the conventional SZ. Also, the higher and more stable selectivity to isobutene is observed in the present SZ than in the conventional SZ. On the other hand, it is well-known that zeolite Ferrierite is very active in this reaction. The present SZ is comparable to Ferrierite in the

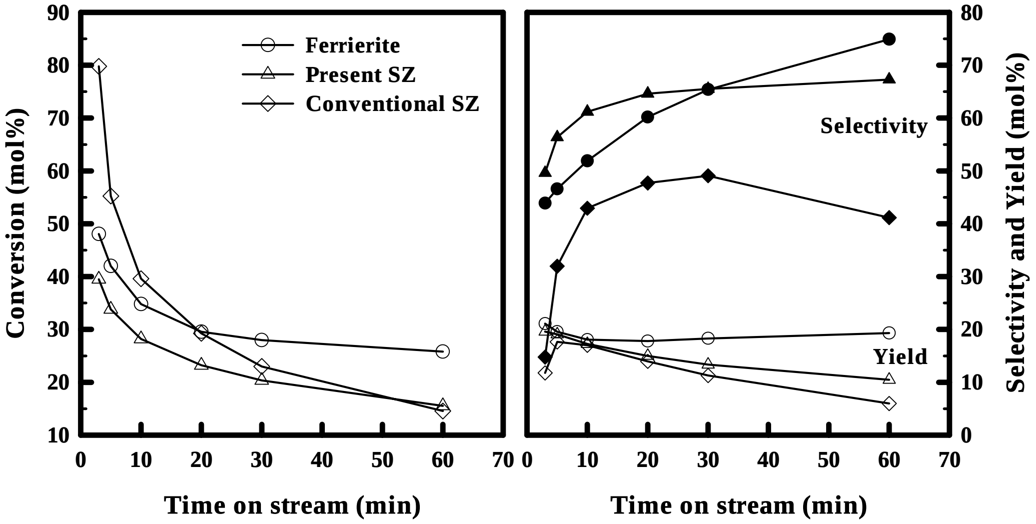

Figure 0. The conversion of 1-butene (left) and the selectivity and yield of isobutene (right) obtained over Ferrierite, the present sulfated zirconia (SZ) and the conventional sulfated zirconia (SZ) at 500 °C.

conversion of 1-butene and the selectivity to isobutene. We are studying the optimal reaction conditions for the present material.

CONCLUSIONS

We synthesized for the first time thermally stable zirconia with high surface area and wormhole-like pore structure by the zirconium atrane route. Also, the present sulfated zirconia (SZ) has been found to be more active than the conventional SZ when applied to the skeletal isomerization of 1-butene.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of SK Chemicals and the partial aid from the Brain Korea 21 Program sponsored by the Ministry of Education.

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