

# SULFATED MESOPOROUS ZIRCONIA, AN ACTIVE CATALYST FOR N-BUTANE ISOMERIZATION

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## SUMMARY

A zirconia/surfactant composite was synthesized using  $Zr(OPr)_4$  as the metal precursor and hexadecyl-trimethyl-ammonium bromide (CTAB) as the template in an aqueous solution containing sulfate ions. The mesoporous structure of  $ZrO_2$  with a hexagonal packing order was well preserved after calcination at  $540^\circ C$  to remove the organics from the composite. The resulting material was found to be an active and highly selective catalyst for n-butane isomerization to i-butane at  $105^\circ C$ .

## INTRODUCTION

The usage of supramolecular assemblies of organic amphiphiles as structure directing reagents for the formation of M41S-type materials has been expanded in recent years to the syntheses of numerous non-siliceous metal oxides with ordered mesoporous structures. Beside others, zirconia/surfactant composites with hexagonal packing orders analogue to that of MCM-41 were obtained (e.g. [1,2]). However, these composites usually suffered from an inadequate thermal stability. A removal of the templates from the composites by calcination without destroying the inorganic pore wall structure was hardly possible [1]. Recently, it was found that adding sulfate ions into the synthetic precursors had a reinforcing effect on the bonding of the inorganic species of the composites. The thermal stability of the zirconia pore walls could be significantly improved this way, which enabled the calcination at elevated temperatures while preserving the mesoporous structure of zirconia [2]. Since then, zirconia with well defined mesopores became available to be tested as a catalyst.

On the other hand, sulfated zirconia (SZ) is known to be extraordinarily active for n-butane isomerization at temperatures as low as RT [3]. The conventional SZ catalysts possess generally a bulk tetragonal crystalline phase with specific surface areas of  $80-100\text{ m}^2/\text{g}$ . Should sulfate containing mesoporous zirconia be active for the reaction, with its unique textural properties such as large surface areas and porous structures, the new material would be a desired complementary to the conventional SZ catalysts.

## EXPERIMENTAL SECTION

A hydrogel was prepared by mixing solution A containing 2.5 g of CTAB, 5.99 g of 70 wt.%  $Zr(OPr)_4$  in propanol, 24.4 g of 37 wt.% hydrochloric acid in 115 g of water and solution B with 1.69 g of  $(NH_4)_2SO_4$  in 23 g of water. The formation of the mesostructured

ZrO<sub>2</sub>/CTAB composite occurred then in a sealed bottle under autogeneous pressure at 100°C within 3 days. The recovered solid was washed, dried at 110°C overnight and calcined at 540°C in flowing air for 16 h. Characterization was done by XRD, SEM, TEM and N<sub>2</sub> adsorption. The catalytic test was carried out in a flow type fixed bed reactor at 105°C with a feed of 1 vol.% n-butane in N<sub>2</sub> at a total flow rate of 30 cm<sup>3</sup>/min over 200.0 mg of the catalyst.

## RESULTS AND DISCUSSION

XRD at small angles shows that the as-synthesized sample possesses the expected mesostructural feature with a signal at  $d \cong 45 \text{ \AA}$ . After the calcination at 540°C, the observed diffraction signal has shifted to  $d \cong 35 \text{ \AA}$ , indicating a strong shrinkage of the pore diameters. Simultaneously, the diffraction signals in the  $2\theta$  range of 4-6° becomes more significant upon calcination, proving a hexagonal structure (Fig.1). For both as-synthesized and calcined samples, XRD at wide angles does not find diffraction of any crystalline zirconia phases. The catalytic performance of the material in n-butane isomerization to i-butane is depicted in Fig.2. Comparing to the catalytic behavior of the conventional SZ catalysts under the same reaction conditions, the mesoporous zirconia shows a pronounced resistance against deactivation. Detailed characterization including spectroscopic data as well as discussions about the catalytic test results will be presented.

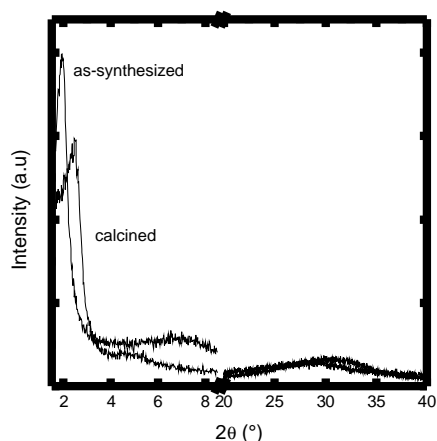


Fig.1: XRD of mesoporous zirconia.

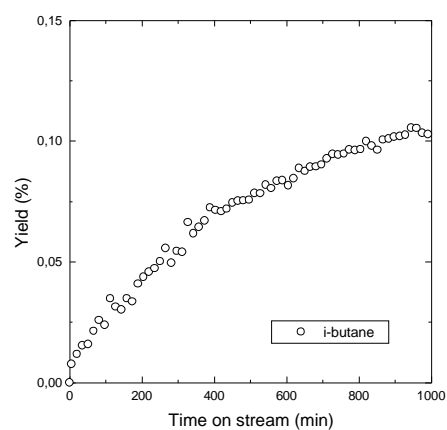


Fig.2: Catalytic activity of mesoporous zirconia.

## REFERENCES

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