

Benzylation of Toluene Over Sulphated Mesoporous Zirconia

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Abstract: Mesoporous materials have attracted the attention of chemists and material scientists due to their commercial application in chemical separations and heterogeneous catalysis. Conventional hazardous liquid acid can be replaced by sulphated zirconia by virtue of super acidic character. In the present work Mesoporous Zirconia catalysts were prepared by template assisted sol gel process and modified with Sulphate process. The prepared catalysts were characterized by various characterization techniques such as XRD, IR, surface area, pore volume measurements and TG. The catalytic activity was evaluated for liquid phase benzylation of toluene. Effort is made to correlate activity with textural properties of materials. Preliminary studies reveal that they can be effectively used as heterogeneous catalyst for the alkylation of aromatics.

Key words: Heterogeneous catalysis, Sulphated zirconia

Introduction

The environmental concern and the drive towards a “clean technology” urge the replacement of the liquid acids by eco-friendly solid acid catalysts. During the past decade, much attention has been paid to the replacement of homogeneous catalysts by solid acid catalysts such as zeolites Al_2O_3 , TiO_2 , clays, metal oxides and modified silica. The use of sulphated zirconia(SZ) has attracted the attention of scientific community due to its the super acidic properties induced in these materials by the presence of SO_4^{2-} ions and these properties have been exploited in a variety of reactions [1-4]. High surface area coupled with high acidity makes it a potential catalyst for many reactions generally catalysed by strong acids. The catalytic activity of sulphated zirconia significantly depends upon the preparation method and the activating treatment [5-7]. Conventional preparations of SZ lead to microporous material suitable for reactions of small molecules in the vapor phase[8]. If conventional sulphated zirconia is calcined at high temperatures, the micropores collapse and larger pores are formed with wider pore-size

distributions [9-10]. If a method could be found that would form mesoporous sulphated zirconia with narrow pore-size distributions and a regular, well-defined structure it could be used in the selective reactions of larger molecules. The present work involves the synthesis of mesoporous sulphated zirconia by neutral template assisted solgel method, its characterization and evaluation of its catalytic activity.

Materials and Methods

Preparation of catalysts

Zirconia was prepared by sol gel process. About 10 g of zirconium oxy chloride was dissolved in 200ml of water and then NH_3 solution was added till the pH attain 11. The formed sol was stirred for 24 hours to form a gel and $\text{Zr}(\text{OH})_4$ was precipitated. It was then filtered and dried at 110°C for 4 hour and calcined at 500°C to get ZrO_2 .

Mesoporous zirconia $-\text{ZrO}_2(\text{M})$ was prepared by template assisted sol gel route. 3 g of Hexadecyl amine(HDA) was dissolved in 250mL of water. 10 g of zirconium oxychloride was added to the above solution and the rest of the procedure was done as above. For the preparation of sulphated zirconia, 2g of zirconia was refluxed with 30.mL 2M H_2SO_4 for 6 hours. It was filtered and dried at 110°C and calcined at 500°C to get sulphated zirconia.

Instrumentation

XRD patterns of the prepared catalysts were recorded in Bruker AXSD8 Advance X-Ray Diffractometer using Ni filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) in the range 2θ from 2 to 80. FTIR spectra of the samples were recorded using Nicolet FTIR 380 spectrometer using KBr pellets in the range of $400- 4000 \text{ cm}^{-1}$ in the transmission mode. Surface area measurements were performed at liquid nitrogen temperature with a Micromeritics Tristar 3000 surface area and porosity analyzer. Prior to the measurements the samples were degassed for one hour at 90°C followed by degassing at 300°C for 3 hours. TG- DTA analysis of the dried sample were done Perkin Elmer Pyris Diamond TGA-DTA analyzer in nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 900°C .

Catalytic testing.

The liquid- phase benzylation of toluene using benzyl chloride was carried out in a 50 ml double necked flask fitted on a magnetic stirrer cum heater with a spiral condenser. Toluene and benzyl chloride in a specific molar ratio was added to 0.1 g of the catalyst in the R.B flask accompanied by constant stirring. The product was analysed using a Chemito 8610 Gas Chromatograph equipped with a flame ionization detector and OV -17 column.

Results and Discussions.

Characterization.

XRD pattern of the prepared catalysts were given in figure-1. Usually zirconia shows polymorphism with monoclinic, triclinic and cubic phases . But in the present systems there are four strong diffraction peaks at 2θ value 30.1, 34.90, 50.40, and 60.35 were observed which can be indexed to the (111), (200), (220), and (311) diffraction planes of the tetragonal zirconia by the standard JCPDS data. Furthermore, there is no characteristic diffraction peak of monoclinic zirconia, m-ZrO₂, indicating its absence from the present catalyst systems.

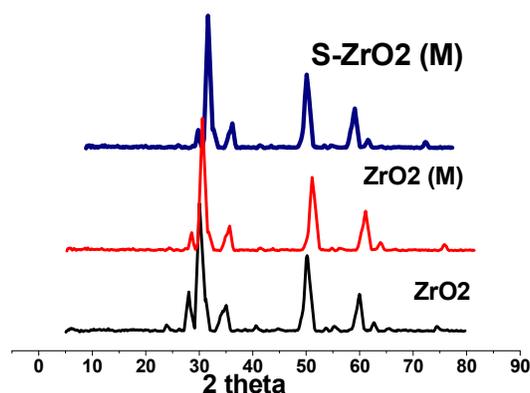


Fig 1. XRD pattern of S-ZrO₂ , ZrO₂(M) and ZrO₂

The sulphate process does not alter the basic XRD pattern of zirconia. But the sulphate doping imparts special stabilization to the catalytically active tetragonal phase at high calcination temperatures by prevention of agglomeration of zirconia particles.

FTIR of Catalysts were given in figure-2. The bands around 1626 cm⁻¹ and 3400 cm⁻¹ corresponds to the bending and stretching modes of the -OH groups molecules present in the

sample. The existence of these bands points to the presence of Bronsted acidity in the samples even after high temperature calcination. The protonic site generation is believed to occur through the interaction of sulphate groups with water. The presence of Bronsted sites in spite of the high calcination temperature employed is consistent with earlier reports. The increase in Bronsted acidity during sulphation may be ascribed to the generation of S-OH groups or to the acidity enhancement of the surface -OH groups.

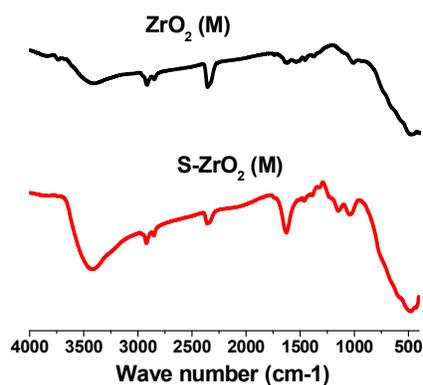


Fig 2. IR spectra of ZrO_2 and $S-ZrO_2(M)$

In comparison with pure zirconia the spectrum of acid treated samples shows peaks in the range $1000-1300\text{ cm}^{-1}$. The peaks at 1026 , 1158 and 1236 cm^{-1} are typical of the S-O mode of vibration of a chelating bidentate sulphate ion co-ordinated to a metal cation. The band around 1375 cm^{-1} arises from the highly covalent character of the S=O on a highly dehydrated oxide surface.

The results of surface area and porevolume measurements were tabulated on the table. The zirconia prepared without the surfactant HDA has lower surface area and pore diameter. Its pore diameter is only 22 \AA . But the pore diameter of zirconia prepared by template method has a pore diameter of 37 \AA indicate that the pores are in mesoporous range. Up on sulphation process a small increase in surface area is noted which may be due to dissolution agglomerated particles.

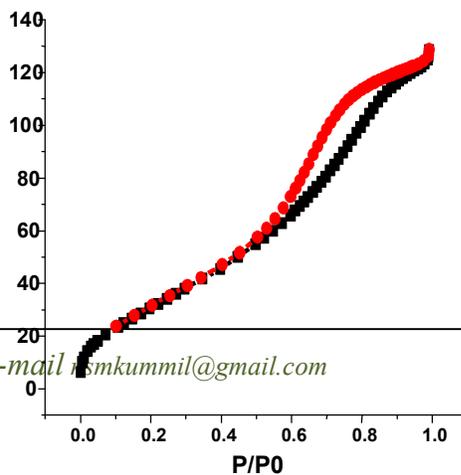
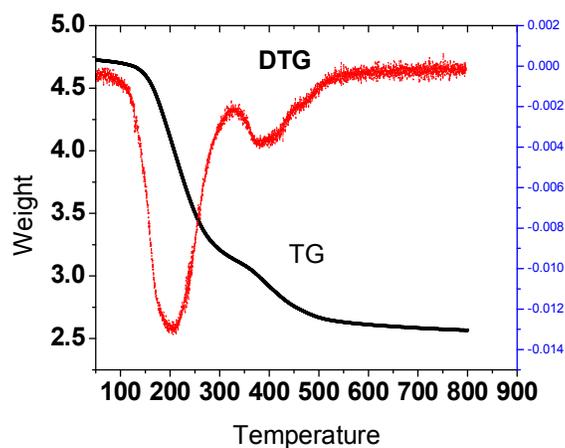


Fig-3 adsorption isotherm of $ZrO_2(M)$

Adsorption isotherm of mesoporous zirconia is given in figure-3. The adsorption isotherm is of type-IV characteristic of mesoporous material with hysteresis loop H1 corresponds to open cylindrical pores.

The Thermogram of uncalcined $ZrO_2(M)$ is given in figure-4. The weight loss up to $200^{\circ}C$ is due to loss of physisorbed water. The weight loss from $200-350^{\circ}C$ is due to loss of surfactant HDA. The weight loss from 350 to $550^{\circ}C$ may be due to the conversion of $Zr(OH)_4$ to ZrO_2 . The weight loss above $550^{\circ}C$ is negligible which indicates the extra stability of this material at higher temperature.

Fig-4 TG and DTG of uncalcined $ZrO_2(M)$

Benzylation of toluene

liquid phase benzylation of toluene using benzyl chloride as benzylating agent were carried out over prepared catalysts and the products were analyzed in GC as the procedure in section 2.3 and results were tabulated in table-1. Ortho and para methyl diphenyl methanes are obtained as products. They are industrially important compounds used as pharmaceutical intermediates, heat

transfer fluids, aromatic solvents, fragrances, monomers for polycarbonate resins and fine chemicals.

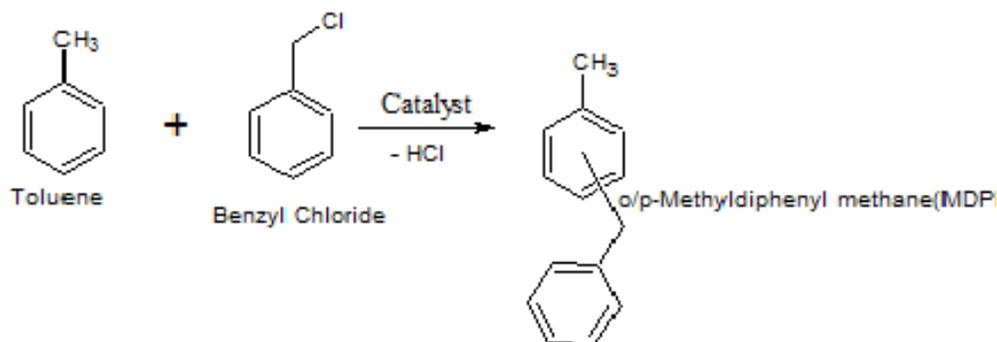


Table-1 Textural and catalytic activity of catalysts

Temperature-90⁰C, Benzyl Chloride to toluene ratio-1:15,Catalyt amount-0.1gTime-1 h

Catalysts	Surface Area (m ² /g)	Pore diameter (A ⁰)	Conversion (%)	Selectivity (%)	
				P-methyl diphenyl methane	O-methyl diphenyl methane
ZrO ₂	62	22	44.8	71	29
S -ZrO ₂	68		56	65	35
ZrO ₂ (M)	142	37	80.6	68	32
S-ZrO ₂ (M)	147	38	90.2	66	34

All the catalysts showed reasonable activity. As it can be seen the unmodified ZrO₂ shows lower conversion. The mesoporous Zirconia showed higher conversion than that of ZrO₂ which may be

due to its higher surface area and pore diameter which in turn result greater accessibility of active sites. The activity depends on both surface area and the number and distribution of acidic sites. The catalytic activity was improved to a greater extent after sulphation process due to the increase of acidic sites. Sulphated mesoporous Zirconia showed maximum activity. The selectivity of ortho product increases with surface area and pore diameter.

Conclusions

Mesoporous zirconia catalyst were prepared by template assisted sol gel route and modified by sulphation process. The prepared catalysts were characterized by various physicochemical methods like XRD, FTIR, Surface area measurements and TG analysis. From the XRD it is clear that major phase formed was tetragonal. The success of sulphation process was evaluated from FT-IR as the FT-IR spectrum consists of characteristic peaks of S=O. The mesoporous nature of zirconia is evident from adsorption isotherms. Catalytic activity of the prepared catalysts were evaluated for benzylation of toluene. Mesoporous zirconia showed higher conversion than bare zirconia. Sulphation process improved the catalytic activity which may be due to the additional surface area and additional acidic sites created during sulphation process. The ortho product selectivity increases with surface area and pore diameter. Sulphated mesoporous zirconia showed maximum conversion probably due to reasonable surface area and higher amount of acidic sites.

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