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Journal of Molecular Catalysis A: Chemical 225 (2005) 71–78

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Modified zirconia solid acid catalysts for organic synthesis and transformations

Benjaram M. Reddy*, Pavani M. Sreekanth, Vangala R. Reddy

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad – 500007, India

Received 8 July 2004; received in revised form 1 September 2004; accepted 1 September 2004

Abstract

A series of sulfate, molybdate and tungstate promoted ZrO_2 catalysts were prepared by wet impregnation method. To incorporate these promoters to $Zr(OH)_4$, sulfuric acid, ammonium heptamolybdate, and ammonium metatungstate were used as precursors, respectively. Further, a Pt promoted Mo-ZrO_2 catalyst was also prepared separately by impregnating with hexachloroplatinic acid. The surface and bulk properties of various promoted ZrO_2 catalysts were investigated by means of X-ray powder diffraction, BET surface area, ammonia-TPD, and Raman spectroscopy techniques. The unpromoted ZrO_2 when calcined at 873 K exists in the crystalline form with monoclinic phase dominating over the tetragonal phase. Incorporation of various promoters into $Zr(OH)_4$ shows a strong influence on the bulk and the surface properties. Addition of promoters enhanced the tetragonal zirconia phase and the surface acidity. In the case of Pt/Mo-ZrO_2 catalyst, a complete tetragonal ZrO_2 phase is observed. The ammonia-TPD results indicate that the impregnated sulfate ions show a strong influence on the acidity of ZrO_2, which is followed by molybdate. The prepared catalysts were evaluated for various organic synthesis and transformation reactions in the liquid phase. All catalysts exhibit good catalytic activity for synthesis of diphenylureas, coumarines and 1,5-benzodiazepines, acylation of alcohols, phenols and amines, and protection of carbonyl compounds. In particular, the sulfate and molybdate promoted catalysts exhibited excellent catalytic activity.

Keywords: Zirconium oxide; Solid superacid; Sulfate; Molybdate; Tungstate; Diphenylureas; Coumarines; 1,5-Benzodiazepines; Tetrahydropyranylation; Acylation

1. Introduction

Acid catalysts play a predominant role in organic synthesis and transformations. Many organic reactions such as alkylation, acylation, isomerization, nitration, esterification, and rearrangements like pinacol, Beckman, etc. are accomplished by acid catalysts. All these acid catalyzed reactions are mostly carried out by employing conventional mineral acids like H_2SO_4, HNO_3, and HF or Lewis acids such as $AlCl_3$ and BF_3. In view of environmental and economical reasons, there is an ongoing effort to replace the conventional catalysts with newer solid acids. This is mainly due to the distinct advantage of solid acid catalysts such as non-toxicity, non-corrosiveness, ease of handling, less expensive, and easy to recover and reuse [1–6]. In this direction, various solid acid systems were introduced which include hetropolyacids, ion exchange resigns (Amberlyst and Nafion-H), zeolites, and clays. The main disadvantage associated with hetropolyacids is that they are fairly soluble in polar solvents and loose their activity at higher temperatures by loosing structural integrity. To prevent this there are some attempts to immobilize them in silica or activated carbon matrix, which however limits the accessibility and efficiency of the catalysts. Ion exchange resigns pose various problems like poor thermal stability and low specific surface area. Styrine based resins like Amberlyst is stable up to 393–413 K and its acid strength and surface area are not very high ($H_0 = -2.2$, SA = $0.4\,m^2\,g^{-1}$). Nafion-H exhibits better thermal stability (533–553 K) and acidity than

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* Corresponding author. Tel.: +91 40 2716 0123; fax: +91 40 2716 0921.
E-mail addresses: mreddyb@yahoo.com, bmreddy@iict.res.in (B.M. Reddy).

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doi:10.1016/j.molcata.2004.09.003

Amberlyst but possesses less surface area ($H_0 = -12$ to -13, SA = 0.02 $m^2\,g^{-1}$) [5]. Although clays and zeolites are quite reliable, activities of these materials are much lower than the conventional homogeneous acids due to pore blocking and hydration. In view of these reasons there is an ongoing effort to develop stronger solid acid systems which are water tolerant, stable at high temperatures and suitable for both liquid and vapor phase conditions. Metal oxide based catalysts offer several advantages over zeolite and clay-based catalysts. These are active over a wide range of temperatures and more resistant to thermal excursions.

Among the solid superacid catalysts reported, sulfated zirconia gained much attention due to its high activity to catalyze many reactions even at low temperatures [10–12]. However, it gets deactivated rapidly at higher temperatures and in reducing atmosphere by forming H_2S and SO_x. Also it forms sulfuric acid at high temperatures if there is water in the reaction medium leading to the down stream contamination. Arata and Hino reported that the solid superacids could be synthesized by incorporating WO_3 or MO_3 into Zr- or Ti-hydroxides under certain preparation conditions [13,14]. Activity of these oxides depends on various parameters such as nature of precursors, precipitation procedure, concentration of dopant, and calcination temperature [8]. In the case of sulfated catalysts, nature of sulfating agent and sulfation procedure also play a crucial role [15]. Variation in any of these parameters can drastically affect the resultant catalytic activity of these materials. Many research groups have studied these systems and explored them in petroleum industry, particularly for isomerization of light alkanes [16–18]. However, these catalysts are not exploited in the areas of fine chemicals synthesis. Therefore, a comprehensive investigation was undertaken on promoted zirconia catalysts for organic synthesis and transformation reactions in the liquid phase. In this study sulfate, molybdate and tungstate promoted zirconia catalysts were prepared and characterized by various physico-chemical techniques namely, X-ray diffraction, BET surface area, ammonia-TPD, and Raman spectroscopy. The prepared catalysts were evaluated for various commercially important organic reactions.

2. Experimental section

2.1. Catalyst preparation

Zirconium hydroxide was prepared from an aqueous solution of $ZrOCl_2$ (Aldrich, GR Grade) by adding dilute NH_4OH drop-wise from a burette up to pH 8. The obtained precipitate was washed several times until free from chloride ions and dried at 393 K for 48 h. To prepare sulfated ZrO_2, a 0.5 M sulfuric acid solution (30 ml) was pored into the finely powdered $Zr(OH)_4$, dried at 393 K for 12 h and calcined at 923 K for 4 h. To impregnate molybdate and tungstate promoters (6 mol%), the desired quantity of ammonium heptamolybdate and ammonium metatungstate were dissolved in excess water separately and to which the powdered $Zr(OH)_4$ was added. The excess water was evaporated on a water-bath with vigorous stirring, oven dried at 383 K for 12 h, and calcined at 923 K for 4 h in air atmosphere. To prepare Pt/Mo-ZrO_2 catalyst (0.5 wt.% Pt), the powdered Mo-ZrO_2 sample was added to the 5% solution of hexachloroplatinic acid ($H_2PtCl_6 \cdot xH_2O$). The excess water was evaporated on a water-bath and the resulting sample was oven dried at 393 K for 12 h and calcined at 973 K for 4 h.

2.2. Catalyst characterization

The powder X-ray diffraction patterns of various samples have been recorded on a Siemens D-5000 diffractometer by using Cu Kα radiation source and scintillation counter detector. The XRD phases present in the samples were identified with the help of JCPDS data files. A conventional all glass volumetric high vacuum (up to 1×10^{-6} Torr) system was used for BET surface area measurements. The BET surface areas were measured by nitrogen physisorption at liquid nitrogen temperature by taking 0.162 nm^2 as the area of cross section of N_2 molecule. Raman spectra were recorded at ambient temperature on a DILOR XY spectrometer equipped with a CCD detector. The spectra were recorded in the range of 4000–100 cm^{-1} and a spectral resolution of 2 cm^{-1} using the 514.5 nm exciting line from an argon ion laser (Spectra Physics, USA).

The temperature programmed desorption (TPD) measurements were carried on an AutoChem 2910 instrument (Micromeritics, USA). A thermal conductivity detector was used for continuous monitoring of desorbed ammonia and the areas under the peaks were integrated using GRAMS/32 software. Prior to TPD studies, the samples were pretreated at 473 K for 1 h in a flow of ultra pure helium gas (40 ml min^{-1}). After pretreatment, the sample was saturated with 10% ultra pure anhydrous ammonia gas (balance He, 75 ml min^{-1}) at 353 K for 2 h and subsequently flushed with He (60 ml min^{-1}) at 373 K for 2 h to remove the physisorbed ammonia. The heating rate for the TPD measurements, from ambient to 1023 K, was 10 K min^{-1}. All flow rates mentioned are at normal temperature and pressure (NTP).

2.3. Catalyst evaluation

All chemicals and solvents used in this study were commercially available and used without further purification. All the reactions were carried out in the liquid phase batch mode. These were carried out by taking a mixture of reactants, catalyst and a suitable solvent (some reactions were carried under solvent free conditions) in a round bottom flask provided with a condenser and stirred/refluxed for appropriate times. Completion of the reaction was monitored by TLC. After completion of the reaction, catalyst was recovered by simple filtration and reused. The products were recovered from the filtrate, concentrated on a rotatory evaporator and chromatographed on a silica gel column to offered pure