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Surface and catalytic properties of triflic acid supported zirconia: Effect of zirconia tetragonal phase

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ABSTRACT

In this paper, trifluoromethanesulfonic acid was successfully loaded over calcined crystalline zirconia. Zirconia was calcined at 200, 350, 500, 700 and 900 °C before trifluoromethanesulfonic acid was loaded. The catalysts were characterized by various sophisticated techniques such as FTIR, SEM, TEM, XRD and N_2 adsorption–desorption measurements. The acidic behavior of the catalysts has been studied by non-aqueous potentiometric titration and FTIR spectra of adsorbed pyridine. The results showed that the catalysts are highly acidic and exhibited high catalytic activity in the esterification of acetic acid with benzyl alcohol (95%) with very high selectivity to benzyl ester (96%). Furthermore, the tetragonal phase of zirconia was the only phase up to 500 °C, and completely vanished at 900 °C. These changes in crystalline structure was also found to be related to the number and strength of acid sites. Our results showed that, the number and strength of acid sites were optimum at 350 °C, at which only tetragonal phase is the metastable one. Moreover, the catalysts were capable of recycling for five times without appreciable deactivation at 100 °C.

1. Introduction

Acid catalyzed reactions are finding numerous applications in many areas of the chemical industry. These are extremely useful in many large volume applications, especially in fine chemicals manufacture and petroleum industry for alkylation and isomerization reactions [1–4]. At the same point, solid acids are considered to be more safe and eco-friendly than liquid acids such as, H_2SO_4, HCl, HF, $AlCl_3$, BF_3, $ZnCl_2$ and SbF_5 because of their specific features such as non-corrosive, non-toxic, easy to handle, easily recoverable, reusable and less expensive.

Metal oxides, in their supported or unsupported form, have been successfully used as catalysts for many acid catalyzed organic transformations such as dehydration [5], isomerization [6], acylation [7], oxidation [8], esterification reaction [9,10], Nitration [11], etc. Now-a-days metal oxide-based catalysts are active over a wide range of temperatures and having high resistance to thermal excursions. Moreover, the preparation methods, characterization tools and advantages of zirconia based solid acids have gained much attention in various organic transformations due to their non-toxicity, super acidity, simplified product isolation, high selectivity, reduction of wasteful byproducts and high activity at low temperatures [12–14].

The trifluoromethanesulfonic acid (Triflic acid, CF_3SO_3H) has a highly acidic nature and excellent thermal stability; it also has good resistance to reductive and oxidative dissociation, with no generation of fluoride ions. The using of triflic acid in heterogeneous catalysis by immobilization on a support is an interesting alternative to contribute to the field of clean processes. Actually, there are few works on this subject, though it can be mentioned its immobilization on some supports [15,17].

The esterification of carboxylic acids and alcohols is fundamental reaction in organic synthesis [18,19]. Esters, which include a wide category of organic compounds ranging from aliphatic to aromatic, are generally used in the chemical industry such as drugs, pharmaceuticals, food preservations, perfumes, solvents and cosmetics, [20,21]. Benzyl acetate finds numerous uses in perfumery, chemical industries, and food [22].

In order to perform a new contribution to the field of ecofriendly acid-catalyzed esterification reactions, triflic acid was immobilized on crystalline zirconia obtained by sol-gel method. The effect of the calcination temperature (200–900 °C) and crystalline structure of the support on the physicochemical, acidic and textural characteristics of the catalysts was studied. The catalytic behavior of the prepared materials in benzyl acetate synthesis was studied through the esterification of acetic acid with benzyl alcohol in a round flask

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glass reactor at atmospheric pressure. The results are correlated with the catalyst properties.

2. Experimental

2.1. Synthesis of catalysts

2.1.1. Synthesis of zirconia

Zirconium isopropoxide (Sigma–Aldrich, 25 g) was mixed with isopropanol (Sigma–Aldrich, 200 g) and stirred for 30 min to obtain a homogeneous clear solution under N_2 at room temperature. Then drops of 0.2 M NH_4OH aqueous solution were dropped slowly into the above mixture under vigorous stirring to catalyze the sol–gel reaction for 2 h. After that, the mixture was left under sonication at room temperature for 2 h, then the zirconia gel left to dry under vacuum overnight at room temperature. Finally, and after complete dryness of the sample it was calcined at 200, 350, 500, 700 and 900 °C for 4 h (Zr200, Zr350, Zr500, Zr700 and Zr900 °C, respectively).

2.1.2. Synthesis of zirconia supported Triflic acid

In three neck 50 ml round flask 2 g of precalcined zirconia was added to 20 ml dry toluene under N_2 atmosphere, the mixture was heated to reflux. Triflic acid, CF_3SO_3H, (1.5 ml, Sigma–Aldrich, 98%) was slowly injected drop wise to the mixture under vigorous stirring at 90 °C under nitrogen atmosphere, then the mixture was further refluxed under nitrogen atmosphere for 3 h. finally, the mixture was cooled, filtered, washed with acetone and dried at 100 °C for 24 h under vacuum. The samples were named TFA-$ZrO_2$200, TFA-$ZrO_2$350, TFA-$ZrO_2$500, TFA-$ZrO_2$700 and TFA-$ZrO_2$900.

2.2. Support and catalyst characterization

2.2.1. FTIR Spectra

FT-IR spectra of all calcined samples were recorded by using a Nicolet-Nexus 670 FTIR spectrophotometer (4 cm^{-1} resolution and 32 scans) in dried KBr (Sigma) pellets and a measuring range of 400–4000 cm^{-1}.

2.2.2. X-ray diffraction

X-ray powder diffraction patterns of samples were determined using an X'Pert Philips Materials Research Diffractometer. The patterns were run with copper radiation (Cu Kα, λ = 1.5405 Å) with the second monochromator at 45 kV and 40 mA with a scanning speed of 2° in 2θ/min.

2.2.3. Textural properties

The adsorption isotherms and the specific surface area (S_{BET}) of the various catalysts were determined from nitrogen adsorption studies conducted at −196 °C using a Quantachrome Autosorb-1-C system. The samples were previously degassed at 100 °C for 2 h.

2.2.4. TEM and SEM images

Transmission electron microscope (TEM) images and the particle size were obtained using a Jeol JEM-1230 operated at 120 kV. For TEM images the sample powder was dispersed in methanol by using ultrasonic radiation for 10 min, and a drop of the suspension was placed onto the carbon-coated copper grids.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were carried out using a Quantum DS-130S Dual Stage Electron Microscope.

2.2.5. Acidity measurements

2.2.5.1. Potentiometric titration. The total acidity of the solid samples was measured by means of potentiometric titration [23–25]. The solid (0.05 g) was suspended in acetonitrile (Merck), and agitated for 3 h. The suspension was then titrated with 0.1N *n*-butylamine (Merck) in acetonitrile at 0.05 ml/min. The electrode potential variation was measured with an Orion 420 digital A model by using a double-junction electrode.

2.2.5.2. FTIR spectra of chemisorbed pyridine. Lewis and Brønsted acid sites present on the surface of the catalyst were determined by FT-IR spectra of adsorbed pyridine. Prior to the pyridine adsorption [23], small portions of the calcined samples were degassed under vacuum at 100 °C for 3 h, followed by suspending in dry pyridine. The excess pyridine was removed by evaporation. The FT-IR spectra of the pyridine-adsorbed samples were obtained using a Nicolet-Nexus 670 FTIR spectrophotometer by mixing 0.005 g of the sample with 0.100 g KBr in a resolution of 4 cm^{-1}, and in a frequency range of 1400–1700 cm^{-1}. The ratio of Brønsted to Lewis acidity was determined based on the method in the literature [26].

2.2.6. Catalytic activity

The esterification of Acetic acid with benzyl alcohol was carried out using 0.1 g of the catalyst. In a typical run, a mixture of 1 mmol of acetic acid (Aldrich, 99.9%) and 1 mmol of benzyl alcohol (Sigma–Aldrich, 99.8%) were magnetically stirred and heated to attain the reaction temperature (100 °C) in a round bottomed glass flask (50 ml) fitted with a water cooled condenser. Then activated catalyst (0.1 g) was added and the mixture stirred for 2 h. The reaction mixture was then filtered and the products were analyzed by means of GC–MS (HP GCD system equipped with FID detector). The main product was found to be benzyl acetate with minor participation of dibenzyl ether. More experiments were designed by varying the molar ratios of the reactants, the reaction temperature and the reaction time to obtain various kinetic parameters. To check the catalyst reproducibility, all the experiment were repeated two times at the same reaction conditions, and each experiment was analyzed 3 times using GC–MS equipment. The uncertainty was found to be ±3% in most cases. The yield and selectivity (in percentages) were calculated based on the GC analysis using the following expressions:

$$\text{Yield\%} = \frac{100\,([\text{benzyl acetate}] + [\text{dibenzyl ether}])}{([\text{benzyl acetate}] + [\text{dibenzyl ether}] + [\text{acetic acid}])}$$

$$\text{Benzyl acetate\%} = \frac{100\,([\text{benzyl acetate}])}{([\text{benzyl acetate}] + [\text{dibenzyl ether}])}$$

3. Results and discussion

3.1. FTIR spectra

The infrared spectra of ZrO_2 200, TFA-ZrO_2 200, TFA-ZrO_2 350 and TFA-ZrO_2 500 are shown in Fig. 1**.** Inspection of Fig. 1 reveals the following: (i) the spectrum of the ZrO_2 200 displays strong and broad band between the region of 3700–3100 cm^{-1} centered at around 3450 cm^{-1} and another band at 1627 cm^{-1}, assigned to the stretching vibrations of hydroxo- and aquo-OH, and to the bending vibration of (H—O—H) and (O—H—O) present in the structure of ZrO_2 200 sample, respectively [27–29]. (ii) moreover, the weak unresolved band between 800 and 520 cm^{-1} is attributed to Zr—O stretching modes, FT-IR spectra of other unsupported zirconia samples calcined at different temperatures showed features similar to those observed for the ZrO_2 200 with different intensities, (iii) the FTIR spectrum of zirconia supported with triflic acid show additional bands, which are absent in pure unsupported zirconia, these at 1265, 1180, and 1033 cm^{-1}. The first two bands are due to the S═O stretching mode of the adsorbed triflic acid on Zirconia sup-