

Synthesis and Characterization of Super-Acid Supported on MCM-41

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Abstract

Tetra-flouro-ethane sulfonic acid supported on ordered mesoporous material, covalently anchored with acid groups was synthesized. The catalyst supported on MCM-41 was prepared by the pore volume impregnation method using an aqueous solution containing 10 wt% super-acids. The catalyst characterization was performed by physical (X-ray powder diffraction, nitrogen adsorption and desorption isotherms) and chemical (reactivity on the glycerol etherification) methods. A sample was used in the etherification of glycerol with isobutylene and the experimental results are compared with those obtained by using other type of catalyst on the same experimental conditions.

Key words: silica, impregnation, surfactant, etherification.

Introduction

Super-acids supported on mesoporous molecular sieves (MMSs) exhibit exceptional chemical and physical properties that have suggested a large number of applications, such as aromatic alkylation, isomerisation, oligomerization, acylation of arenes [1]. Here we investigate such a catalytic system for the etherification of glycerol with isobutene. Because of the support properties such as regular pore structure, high surface area, narrow pore size distribution, adjustable pore size, highly dispersed active sites and uniform distribution of these on silica pore these catalysts are similar to the sulfonic-acid group incorporated in macroporous ion exchange resins that have been successfully used in such application [2].

MCM-41 has thin walls of amorphous silica allowing the pore size to be varied from 2 to 10 nm, and chemical properties can be manipulated [3]. The supported catalyst was prepared by pore volume impregnation method. The increase in the chain length of the surfactant was found to be effective in the pore size control of MMSs, including silica with two-dimensional hexagonal arrays of cylindrical pores like MCM-41 template by alkyl-ammonium surfactants- C_{16} [4]. Glycerol etherification with isobutene is realized in presence of acid catalyst to yield a mixture of mono-, di-, and tri-tert-butyl glycerol ethers (MTBG, DTBG, and TTBG, respectively) [2].

Experimental details

The silica support of MCM-41 was prepared, followed by the impregnation of silica support and the catalyst characterization. The obtained catalyst was used in the etherification of glycerol with isobutylene to yield tert-butylated derivatives. Then the results are compared with results obtained using other type of catalyst (heteropolyacid silicotungstic acid-STA and CT 175 Purolite ion exchange resins) on the same conditions.

Catalyst preparation

The surfactant solution was first prepared. The powder of cetyl-tri-methyl-ammonium bromide was dissolved in de-ionized water to make a 20 % wt solution. This solution mixed by 2 h. Then Amberjet 4400 OH anion-exchange resin was added into the solution to exchange Br ions with OH ions. The ion-exchange process was performed by 24 h under vigorous agitation. The resulting solution was filtered and ready to use on silica preparation. The surfactant is the most important on preparation procedure because it defines the structure and porosity of silica, and the calcination procedure has the same cause.

The fumed silica Cab-O-Sil M5 was added to the tetra-methyl-ammonium silicate aqueous solution and de-ionized water, the mixture was stirred vigorously for 1 h. Two drops of antifoam agent (0.2 wt% of surfactant) was added. After this, the surfactant solution was added under stirring. Then pH was adjusted to 11.5 by adding acetic acid under agitation. If the pH of the solution is higher than 11.5 then acetic acid was added drop-wise, else maximum 5 drops of surfactant was added to adjust the pH. Mixing for 1 h and then the synthesis solution was taken into the polypropylene bottle and placed into an autoclave at 373 K for 6 days.

After the solution was cooled to room temperature, the resulting solid was recovered by filtration, washed with de-ionized water, filtered again and dried in an oven at 348 K under ambient air for 24 h. Then the solid was ground very thin, followed by taking it into the glass cell for calcinations. The pre-dried solid was heated at a constant rate from room temperature to 813 K over 17 h under helium flow and held for 1 h under the same conditions, followed by calcinations at 813 K for 5 h with air to remove the residual surfactant, then cooled at a constant rate (4 degrees/min) from 813 K to room temperature under air flow.

Impregnation of the silica support with super-acid

Supported catalyst was prepared by pore volume impregnation method using aqueous solution containing 1,1,2,2-tetrafluoroethanesulfonic acid (TFESA). Those silica spheres MCM-41 were impregnated with 10 wt% super-acid. Before impregnation, the adsorption capacity of the silica support was checked. Alternatively, the value of the adsorption volume from the adsorption-desorption isotherm calculated with BET method could be used. The adsorption capacity was checked by the difference between the initial amount of water and the amount of water remaining after adsorption.

$$\text{Adsorption Capacity} = V_{\text{adsorbed water}} = V_{\text{initial water}} - V_{\text{non-adsorbed water}}$$

The resulting mixture (super-acid and water) was added over silica under continuous stirring for a good and uniform distribution in the silica pores. The impregnated silica was dried overnight at 393 K in an oven.

Results and discussion

Characterizing the pore structure of silica materials is important to check its physical properties and structure. Liquid nitrogen isotherms provide the data to characterize the pore structure of silica. Liquid nitrogen isotherms provide the data to characterize the pore structure of silica and check the pore size, the pore volume and the isotherm type. The typical adsorption/desorption isotherms of the pure silica and the impregnated silica are shown in figure 1.

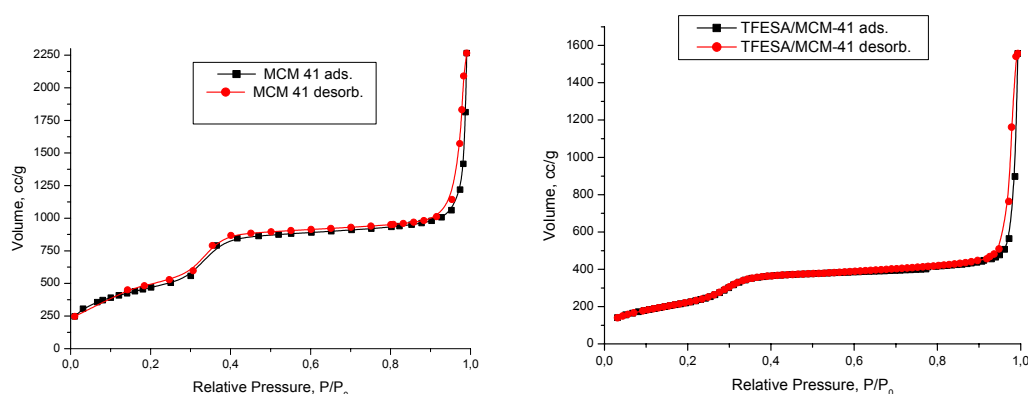


Fig.1. The typical adsorption/desorption isotherms of pure silica MCM-41 and impregnated silica.

These isotherms are comparable and follow the type IV without hysteresis curves, characteristic for the mesostructured silica pores with ordinary structure.

The adsorption/desorption isotherms show four different regions. The first zone at low relative pressure p/p_0 (gap 0-0.3 for silica MCM-41) is specific to the highest nitrogen physical adsorption yield, associated with a thin-layer adsorbed over the silica surface (at external surface and in mesoporous area). The second zone (gap 0.3-0.38 for silica MCM-41) describes an increase of pressure corresponding to a multi-layer adsorption given by the contribution of the external surface and mesoporous area. The third zone (gap 0.38-0.93 for silica MCM-41) reflects the adsorbed nitrogen yield growing significantly, that suggests a nitrogen capillary condensation on the mesoporous area. The lowest difference between adsorption and desorption curves for pure silica MCM-41 gives an indication of the pore diameter uniformity, without obstructions. The fourth zone, at relative pressure close to 1, suggests an increase of the volume of adsorbed nitrogen associated with nitrogen condensation in the interparticular spaces.

The pore size distributions for the pure silica MCM-41 and the impregnated silica are shown in figure 2.

The pore size for this impregnated silica MCM-41 samples are equal to 25 Å, but for the pure silica the pore size is biggest, around 27 Å. These suggest the impregnation process has partially affected the structure of the pure silica, probably with increasing of walls thickness because of the super-acids grafted on the surface leading to a decrease of the pore size.

The XRD measurements for the pure silica MCM-41 and the impregnated silica samples are shown in figure 3.

The D_{100} , D_{110} and D_{200} peaks corresponding to 2θ angles of 2.5°, 4.4° and 4.8° confirm the amorphous hexagonal structure of the support silica MCM-41 as honeycomb type. A small shift of the first diffraction peak to lower 2θ and the lower intensity of impregnated silica compared to the pure silica is indicative of a decrease in the pore diameter values. The flattening of the peaks corresponding to 2θ angles equal to 4.4° and 4.8° confirm some obstruction of the tubular channels of the pure silica caused by the impregnation process.

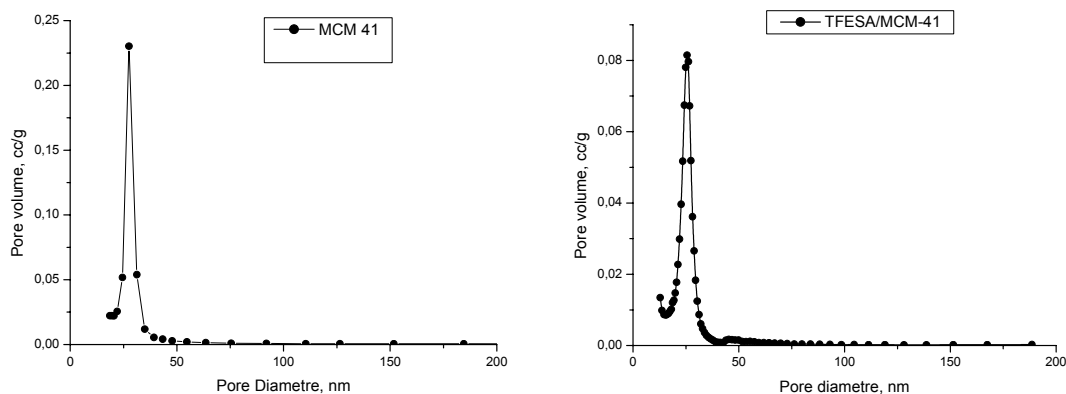


Fig.2. The pore size for pure MCM-41 silica and impregnated silica

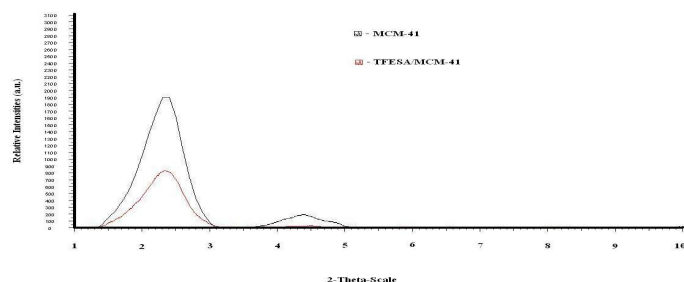


Fig.3. The XRD for pure silica MCM-41 and impregnated silica samples

The glycerol etherification with isobutene in presence of acid catalyst to yield a mixture of mono-, di-, and tri-tert-butyl glycerol ethers (MTBG, DTBG, and TTBG, respectively) was tested with the 10 wt% TFESA/MCM-41, STA and CT 175 Purolite catalysts.

The reaction has been performed in a 600 mL stainless steel Berghoff autoclave equipped with mechanical stirring. The autoclave is electrically heated, with automatic temperature control. For all experiments performed the concentration of the catalyst respect the amount of glycerol loaded in the reactor was 4 wt%, the amount of glycerol is 130 g, running for 5 h at 373 K, at isobutene/glycerol molar ratio of 3/1 and without the pH correction of the glycerol phase. The concentration of the emulsifier in the reaction mixture was of 0.1 wt%.

The Ammonium quaternary salt ($C_{27}H_{42}ClNO_2$) was added to the reaction mixture as emulsifier and the stirring rate was enhance and then maintained at 1200 rot/min. The analyses of the reaction products were performed by gas-chromatography.

Figure 4 show the glycerol conversion, the yields of the obtained ethers in the presence of the emulsifier over 10 wt% TFESA/MCM-41, STA and CT 175 Purolite catalysts.

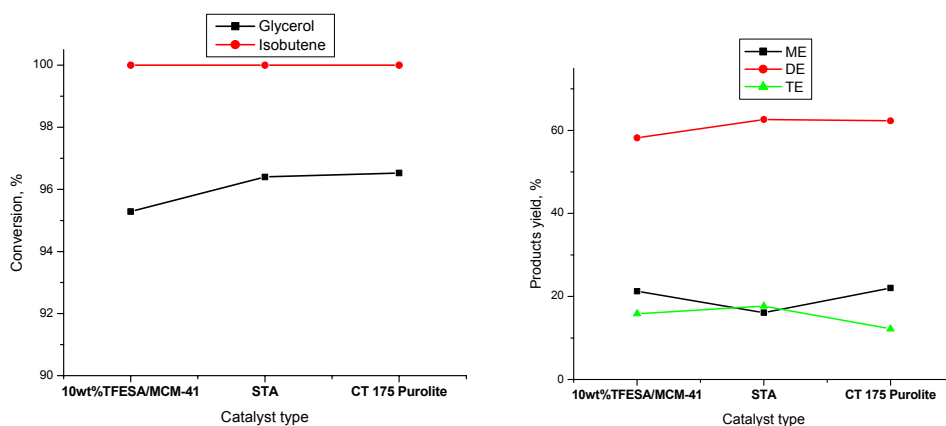


Fig.4. The glycerol conversion and the yields of ethers obtained by using different catalysts

The glycerol conversions are almost the same for the three cases around 96 %, but smaller with 1 % when the reaction is performed in presence of 10 wt % TFESA/MCM-41 as catalyst (95.3 %), and the isobutene conversion are the same using all type of catalysts, that is about 100 %.

The MTBG is an undesired product on the glycerol etherification reaction, this means we must obtain the lower percent for this kind of product. The lower percent for the MTBG was obtained when we used the heteropolyacid STA as catalyst, about 16 %, and the higher percent for using the ions exchange resins CT 175 Purolite, about 22 %. When we used 10 wt % TFESA/MCM-41 as catalyst, an intermediate value, around 21%, was observed. The percent for the DTBG product is 58% for using 10 wt % TFESA/MCM-41 as catalyst and 4 % higher when the reaction is performed in presence of the heteropolyacid and ion exchange resins. The TTBG product is the most desired product for the glycerol etherification with isobutene. The yield in tri-ether is approximately 2 % smaller when the reaction is performed in presence of 10 wt % TFESA/MCM-41silica as catalyst then in the case were heteropolyacid STA (about 18%) is used, but 4% higher then ion exchange resins CT 175 Purolite is employed. A possible explanation for these results is the difference between the pore size, the structure and the acidity for the catalysts used, which affects the mass transfer of isobutene molecules to the active acid sites, making isobutene molecules ready to completing the glycerol conversion to tri-ether.

Conclusions

The adsorption/desorption isotherms are comparable and follow the type IV without hysteresis, characteristic for mesostructured silica pore dimension with ordinary structure. The surfactant is the most important on preparation procedure because it is define the structure and porosity of silica. The impregnation process has partially affected the structure of the pure silica MCM-41; probably increasing the wall thickness, because of the super-acids doped on the surface reduced the pore size. XRD measurements confirm the amorphous hexagonal structure of MCM-41 silica support. A small shift of the first diffraction peak to lower 2θ and lower intensity of the impregnated silica compared with the pure silica is indicative of a decrease in the pore diameter values. The yield of the desired etherification products is dependent on the size of the accessible

surface area for the reactants, on the pore size, on the number of acid active sites and, at the same time, on the mass transfer.

References

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Sinteza si caracterizarea superacidului depus pe MCM-41

Rezumat

Acidul tetrafluoretansulfonic depus pe material mezoporos ordonat, ancorat covalent prin grupe acide a fost preparat. Catalizatorul MCM-41 suportat a fost preparat prin metoda impregnarii volumice a porilor, folosind o solutie apoasa ce contine 10gr % super-acid. Caracterizarea catalizatorului a fost realizata folosind metode fizice (Difractie de raze X, Izoterme de adsorbție-desorbție cu azot lichid) si chimice (reactivitatea in reactia de eterificare a glicerinei). O proba de catalizator este folosita in reactia de eterificare a glicerinei cu izobutena si rezultatele experimentale sunt comparate cu cele obtinute prin folosirea altor tipuri de catalizatori in aceleasi conditii de reactie.