Catalytic Dehydration of 1-Propanol Over Silica Containing Sulfonic Acid Groups

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Mesoporous silica with strongly acid sulfonic sites were synthesized and used as catalytic supports for catalytic dehydration of 1-propanol. This porous material with a large surface area and high porosity were prepared by a simplified sol-gel in an acidic medium and impregnated easily by -SO 3H groups. The experimental results indicate that the very strong acidic sites contained on the surface are the seats of the reaction involving two molecules of n-propanol. By hydrogen bonding, ether compounds as well as the corresponding alkene are obtained in appreciable yield.

Keywords: Mesoporous silica, Dehydration, Catalysis, 1-Propanol, Ethers.

1. Introduction

Mesoscopically ordered mesoporous silica materials have attracted a wide interest since their discovery in the early 1990’s 1 due to their diverse potential applications areas; including catalysis, filtration and chromatography. Supramolecular surfactant aggregates are used as structure directing agents in organics during condensation, leading to mesoscopically ordered surfactant-inorganic composites. Silica mesoporous materials have opened the field of investigation in many organic reactions until then considered laborious and source of pollution. Used as catalyst supports when the surface is activated by redox, acidic or basic functional groups, these materials have active sites that can be the site of chemical reactivity of adsorbed organic molecules 2-5. In neutral medium, Bagshaw et al. 6 synthesized a variety of materials called MSU-X using polyoxyethylene (PEO) surfactants as structuring agents. These materials have a “wormhole” or cubic structure with a much larger pore diameter than that usually observed in MCM-41 7. Other studies of this type of materials are reported by Huo et al. 8, Ryoo et al. 9 and Richer and Mercier 10 which describes the textural properties. The wormhole channel motif is a potentially important structural feature for favorable catalytic reactivity, in part, because channel branching within the framework can facilitate access to reactive sites on the framework walls. Wormhole structures can also have relatively small fundamental particle sizes (<200 nm), which result in complementary textural mesoporosity for the more efficient transport of reagents to framework reaction centers 11. A number of studies have investigated the dehydration reaction of primary and branched alcohols, with obtaining the corresponding olefin as the major product and the formation of monoether. It has been known that alcohols undergo thermal decomposition in two ways:

\[
RCH_2CH_2 - OH \rightarrow RCH = CH_2 (alkene) + H_2O \quad (1)
\]

\[
RCH_2CH_3 - OH + RCH_2CH_2 - OH \rightarrow RCH_2CH_3 - O - RCH_2CH_2 (ether) + H_2O \quad (2)
\]

If the reaction is not sufficiently heated, the alcohols do not dehydrate to form alkenes, but react with one another to form ethers. The success of this procedure depends on the temperature. At 110° to 130°C an SN2 reaction of the alcohol conjugate acid leads to an ether product. At higher temperatures (over 150°C) E2 elimination takes place. These experiments were performed in the presence of metal oxides, microporous solids and commercial zeolites 12-16. Acid-catalyzed dehydration of small primary alcohols constitutes a specialized method of preparing symmetrical ethers. Recently, Almashhadani et al. 17 investigate the bimolecular dehydration of 1-propanol and methanol with catalysts to produce di-propyl ether by appropriated selection of the catalyst. More recently, great efforts have been made to explain the processes in heterogeneously catalyzed elimination 18. The ether formation (bimolecular reaction) from the hydration of alcohols on γ-aluminum oxide requires OH groups, oxygen and aluminum ions on the surface. The ether is formed from a surface alkoxide group and molecularly adsorbed alcohol. However, a competition exists between alkene and ether formations as investigated by Jain and Pillai 19 which the conclusion was drawn that both reactions are surface reactions but requiring different types of active sites.

Accordingly, the present work investigates the textural mesoporosity of samples of the mesoporous silica from non-ionic surfactants such as Di-block copolymers CnH2n+1-(EO)x as directing agents using tetraethylorthosilicate TEOS as silica source according to a simplified synthesis protocol. Mesoporous silica containing -SO3H acid groups are tested for the catalytic dehydration of 1-propanol.

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2. Materials and Methods

2.1 Chemicals

All surfactants are supplied by Acros Organics whose trade names and empirical formulas are: Polyoxyethylene (20) cetyl ether Brij®58: C_{16}H_{33}(OC_2H_4)_{20}OH; M=1151.5g/mol.; HLB:15.3 and cetyltrimethyl ammonium bromide CTAB: C_{16}H_{33}BrN; M=364.5g/mol. Tetraethylorthosilicate TEOS (Fluka) is used as silica source. For each synthesis, deionized water and prepared HCl (analytical reagent) 1mole.L⁻¹ by volumetric dilution of concentrated acid from Sigma-Aldrich. We use the 1-propanol: CH₃CH₂CH₂-OH at 99% (d=0.804) purity and commercialized by Riedel-de Haen (impurities noted: aldehyde CH₃COCH₃:0.05%, Free acid: 0.002%; water: 0.05%). PSS Poly-(4-styrene-sulfonic acid) solution C₈H₈O₃S (Mw~75,000, 18% in H₂O) and 0.002%; water: 0.05%).

2.2 Materials synthesis

The synthesis protocol adopted in this work consists of mixing of an aqueous solution of the non ionic surfactant with an aqueous HCl 1mol.L⁻¹ solution at constant stirring with an aqueous solution of the surfactant. The mixture of an aqueous solution of the non ionic surfactant was prepared by adding 120mL of HCl 1mol.L⁻¹ solution. An amount of TEOS was added by stirring for 24hours at room temperature. The mixture was kept under vigorous stirring for 24hours. The mixture was introduced in a closed glass tube and heated at 373K for 48hours without stirring. The precipitated solid product was recovered by filtration, washed and dried at 353K. For example, 2g of Brij®58 in 30 g of deionized water were stirred for 10min. before adding 120mL of HCl 1mol.L⁻¹ solution. An amount of TEOS was added to this homogeneous mixture and kept under vigorous stirring for 24hours. The mixture was introduced in a closed glass tube and heated at 373K for 48hours without stirring. 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Morphology and particle size of the final products were observed by using scanning electron microscopy FE-SEM (JEOL-350) operating at an acceleration voltage of 20-30kV. Transmission Electron Microscope (TEM, JEOL JEM-2010) was employed for microstructural observation. The surface acidic presence of the samples were identified by temperature programmed desorption of ammonia (NH₃-TPD) which was carried out in a quartz micro-reactor with a thermal conductivity detector (TCD). 50 mg of samples were pre-treated for 1h in Argon flow at 723K to remove strongly bound species then cooled to 373K and saturated with continuously flowing ammonia. Finally the samples were heated to 873K in 30mL/min of Argon flowing at 10K/min. The products of the dehydrogenation reaction of 1-propanol are analyzed by gas phase chromatography coupled to amass spectrometer (Perichrom2100 coupled with 5973 MSD Agilant NETWORK) with a polar column 25m in height and 0.22mm in diameter; stationary phase: Carbowax 20M Poly ethylene glycol polar; gas carrier Helium and flow rate: 1.0mL/min.

3. Results and Discussions

XRD patterns (Figure1) recorded on both samples from nonionic surfactants MS58 and MS78 samples show the presence of a single broad peak in the 2θ range of 1-4º indicates a poorly ordered structure as usually observed for mesostructured materials with worm-like pores. XRD pattern of Al-MCM41 sample shows two peaks indicating a more ordered pore network, which can be indexed in (100) and (200) reflections indicating an ordered 2D hexagonal mesostructure. If the correlation distance deduced from the main XRD peak can be attributed to the pore-pore distance, the \( D_{\text{pore-pore}} \) values are approximately very close (\( \approx 5nm \)) for the three samples. SEM observations done on MS58 and MS78 samples show distinct spherical particles with extremely varied size (2-7μm) indicating that nucleation and growth of silica particles are not independent of each other. The silica particles of Al-MCM41 material are distinct and uniform with a hexagonal morphology. Cubic arrangement and hexagonal disposition of pores are clearly observed by TEM for all samples as shown in Figure 2.

Figure 1. Low-angle XRD patterns of calcined samples: MS58, MS78 and Al-MCM41.

Figure 2. High resolution transmission HR-TEM of calcined samples: (a) MS58 (TEOS/Brij58); (b) MS78 (TEOS/Brij78) and (c) Al-MCM41 (TEOS/CTAB).
Nitrogen adsorption/desorption isotherms are type IV attributed to mesoporous materials for all samples with a different shape for Al-MCM41 showing no hysteresis loop which is characteristic of textural porous materials having a narrow pore distribution of uniform size (Figure 3). The other two isotherms show a hysteresis loop of H2 type with a slightly accentuated shape indicating regular spherical pores with narrow extremities. The textural and structural parameters of solid samples are given in Table 1. All samples exhibit high surface area (between 700-840 m²/g) and an average pores diameter around 3 nm. High volume pores is observed for Al-MCM41 sample (0.83 mL/g) and the calculated value of the wall thickness (1.40 to 2.10 nm) suggests a high relative thermal stability for these materials.

Surface acidity of the pure materials impregnated with the -SO₃H acid groups is identified using NH₃-TPD to evaluate the strength and type of acid sites. Often the temperature of maximum desorption (TPD peak) is used as a rough measure of the acid strength of the sorption sites. According to a study on the presence and nature of the acidic sites, among the limitations of the NH₃-TPD method is that it can distinguish sites by sorption strength only. Moreover, desorption may proceed simultaneously from sites of different type resulting in more or less overlapping TPD peaks. The results are summarized in Figure 4 with the presence of NH₃ desorption peaks for the pure samples, indicating the presence of acidic sites. In sample Al-MCM41 there are two peaks at about 200 and 450 °C, which last one is attributed probably to the presence of Brønsted acid sites due to the dispersion of aluminum in the matrix. The absence of this desorption peak at 450 °C in MS58 and MS78 suggests the absence of Brønsted acid sites as described by Notestein et al. giving its attribution to this type of acid sites. For the impregnated materials, desorption is visible around 350-450°C for both of MS58 and MS78 samples and much more assertive in Al-MCM-41. Therefore, an appearance of strong acid sites attributed to -SO₃H groups are distributed on the silica surface of each of the materials.

Table 1. Textural and structural parameters of material samples calcined at 823 K under air for 6 hours.

| Designation | Dₚore-pore/nm | S_BET/m².g⁻¹ | V_p/mL.g⁻¹ | ØBJH/nm | thickness/nm |
|------------|--------------|--------------|------------|----------|--------------|
| MS58       | 4.77         | 839          | 0.45       | 3.37     | 1.40         |
| MS78       | 5.04         | 779          | 0.35       | 3.12     | 1.92         |
| Al-MCM41   | 4.97         | 691          | 0.83       | 2.87     | 2.10         |

*Corresponding to the d value of the characteristic X-ray reflection of the calcined products. Calculated at ρ/ρ₀ = 0.99. Determined by the calculation method BJH applied on the desorption branch. Silica thickness calculated t=(Dₚore-pore - ØBJH)
Chromatography detected the constituents formed during the reaction in visibly distinct retention times and based on their polarity and molecular weight. It distinguishes the intense peak corresponding to propyl alcohol $(t_r = 1.62\ \text{min})$ as well as other constituents of significant molecular weight which are detected at longer times as illustrated in Figure 5 for MS58 solid impregnated with the acidic groups of -SO$_3$H. As each peak of a chromatogram becomes a “fingerprint” of the compound, identification by mass spectrometry leads to ether compounds (Figure 6). The mono-ether is easily identified as a product formed by dehydration of 1-propanol. Mass Spectrum MS of the Di-n-propyl ether shows the molecular ion at $m/z$ 102; the peak at $m/z$ 73 is the result of cleavage with a loss of an ethyl radical from either the n-propyl chains. Finally, the base peak at $m/z$ 43 corresponds to loss of neutral aldehyde molecule CH$_2$=O from the fragmentation at $m/z$ 73 in a reaction producing a propyl carbenium ion. The suggested mechanism of formation of Di-n-propyl ether illustrated in Figure 7 can be explained by the proton transfers suggested to be concerted.
Figure 6. Mass-spectrum generated by an MS-GC coupled for n-propanol/MS58-SO$_3$H at retention time $t_r=1.35$min.

Figure 7. Suggested mechanism of 1-propanol dehydration catalyzed by acidic groups –SO$_3$H.
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with the alcohol bonded between -SO3H groups as shown in the ethanol dehydration reaction 24,25. Nevertheless, as the ether yield seems less important, it is likely that the water is a reaction inhibitor because it competes favorably with the alcohol for the -SO3H groups, which are the proton donors and sites of catalysis in the solid. Often it has been observed that the rate of a catalytic reaction is strongly dependent on the concentration of -SO3H groups.

Furthermore, another reaction seems to take place when the masses of important fragments of the tri-n-propyl-ether molecule from the peak scanning located at retention time 1.80 min. Top peak at m/z 59 followed by second and third highest peaks at m/z 43 and 101 respectively. This is formed from the molecule of mono-ether by binding a propionate ion CH3CH2CH2O- by articulating on the acid surface. Other interactions are possible and lead to the formation of organic intermediates that we cannot identify. Probably the precursors of these reactions are propyl carbenium (+) and propionate ion (-); the first can be attributed to the formation of the corresponding alkene, and the second to the formation of the ethers. Table 2 gives the conversion rates of the propanol dehydration reaction as well as the percentages of selectivity of the final products. A longer reflux time and a large catalytic support mass lead to a higher conversion rate elsewhere. It also seems that there is no direct correlation between the textural properties of materials as catalyst supports, but it is the nature of their surface which has strongly acidic sites (Bronsted acid centers) due to the presence of sulfonic acid groups on basis of the conversion rates into ethers obtained for the three supports. However, the silanol groups also play a role in dehydrating the propanol molecule to promote the corresponding alkene.

Table 2. Results of the products from the dehydration reaction of 1-propanol in the presence of mesoporous catalytic supports functionalized with sulfonic groups. 10mL of 1-propanol; reflux temperature: 371K

| Sample | Weight /g | Time contact/hours | Conversion/ % | Selectivity (%) ethers propene Mono di others |
|--------|-----------|--------------------|---------------|-----------------------------------------------|
| MS58   | 0.062     | 12                 | 35.42         | 58.49 21.24 16.92 3.35                         |
| MS78   | 0.080     | 12                 | 38.82         | 66.26 18.56 10.64 4.54                         |
| Al-MCM41 | 0.150   | 24                 | 52.47         | 51.63 22.72 18.64 7.01                         |

4. Conclusion

Silica amorphous materials having strong acidic sites by incorporation of sulfonic acid groups are used as catalyst supports for the dehydration reaction of n-propanol. Organic intermediates formed during the reaction such as propyl carboxylation and propionate lead to the formation of mono- and di-ether compounds as well as the corresponding alkene. It is shown that the acidic sites are responsible for interactions that occur at the surface and include a bimolecular dehydration of the alcohol by association of hydrogen bonding from sulfonic acid groups. The propionate ion leads to promote molecules of ethers while carbenium ion favors the propylene molecule.

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