

Methanol dehydration reaction to produce clean diesel alternative dimethylether over mesoporous aluminosilicate-based catalysts

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Due to its good burning characteristics and high cetane number, dimethylether (DME) is considered as a highly attractive and clean alternative to diesel fuel. This ether can be produced by methanol dehydration reaction over solid acid catalysts. In the present study, activities of mesoporous aluminosilicate catalysts prepared by the hydrothermal synthesis route and containing Al/Si atomic ratios ranging between 0.03 and 0.18 were tested in methanol dehydration. The optimum Al/Si ratio was 0.09 for DME synthesis. Activity of silicotungstic acid (STA) impregnated aluminosilicate was also tested. This STA impregnated catalyst showed very high DME yield values at temperatures as low as 250 °C. DME selectivity approached unity for all the aluminosilicate catalysts over 300 °C.

Key Words: DME, aluminosilicate, silicotungstic acid, methanol dehydration.

Introduction

The demand for the development of alternative clean energy sources has risen with the increase in the rate of depletion of oil reserves. Moreover, the increase in the rate of global warming and the emission of pollutants from the diesel engines of buses and trucks initiated new research for the production of clean fuels.^{1–3}

Being less polluting and having good burning properties, alcohols and ethers are considered as alternative fuels and fuel additives.^{1,4–9} Among these, dimethylether (DME) is an attractive compression-engine fuel

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alternate with a very high cetane number (55-60) and good burning characteristics, causing low NO_x emissions. DME has been shown to be non-toxic and environmentally benign. Low concentrations of gaseous DME have hardly any odor and cause no negative health effects.^{1,8-9} As an automotive fuel, DME is advantageous in many ways when compared to petroleum-derived diesel fuel. No particulate matter or smoke emissions, no SO_x , and low CO_2 emissions result from the combustion of dimethylether in diesel engines. In addition, the use of DME results in low engine noise and high fuel economy.^{1,9}

DME is produced either by direct synthesis starting from synthesis gas or by dehydration of methanol in the presence of solid-acid catalysts. Different types of solid acid catalysts, Na modified H-ZSM-5¹⁰ zeolites, $\gamma\text{-Al}_2\text{O}_3$, and phosphorus modified $\gamma\text{-Al}_2\text{O}_3$ ¹¹, Amberlyst 35¹², and Nafion⁸ have been tested in DME synthesis by dehydration of methanol.

Heteropolyacids (HPAs) show higher catalytic activity than conventional solid-acid catalysts. Being stronger than usual mineral acids, such as H_2SO_4 and HCl , HPAs are active at milder experimental conditions and lead to a low proportion of side reactions. Due to their very strong acidity, heteropolyacids were tested as catalysts in dehydration of alcohols.¹³⁻¹⁵ The main drawbacks of heteropolyacids are that they are nonporous and their surface area values are extremely low (less than $1 \text{ m}^2/\text{g}$). Moreover, due to their solubility in polar solvents, heteropolyacids are preferred in vapor phase reactions. In order to increase the surface area of heteropolyacid-based catalysts, they can be impregnated on high surface area supports. By doing so, HPAs are dispersed over the large surface area of the support and their catalytic activity is significantly enhanced.^{16,17} Our recent studies had indicated that, among the HPAs, silicotungstic acid (STA) showed the highest activity as compared to tungstophosphoric acid and molybdophosphoric acid in ethanol dehydration to produce ethylene and diethylether.^{15,16}

Silicate structured mesoporous materials having high surface areas and narrow pore size distributions¹⁸⁻²⁰ have attracted significant attention of catalysis researchers. In order to improve the catalytic performance of these materials, metals or metal oxides were incorporated into their structures by one pot or impregnation procedures.²⁰⁻²⁴

In the present study, activities of mesoporous aluminosilicate type catalysts having different Al/Si ratios and the activity of a STA impregnated aluminosilicate catalyst were investigated in DME synthesis by dehydration of methanol. Activities of the aluminosilicate type catalytic materials synthesized following a hydrothermal synthesis route were also compared with the activity of a commercial mesoporous aluminosilicate catalyst.

Experimental studies

Catalyst synthesis

Mesoporous aluminosilicate catalysts were synthesized by a direct hydrothermal synthesis route, designed by the modification of the procedure described in our earlier publications^{22,23} for pure MCM-41. Synthesized aluminosilicate materials contain different Al/Si atomic ratios. In this one-pot hydrothermal synthesis procedure, cetyltrimethylammonium bromide (CTMABr) was used as the surfactant, sodium silicate as the Si source, and aluminum nitrate as the Al source. After dropwise addition of the sodium silicate solution to the surfactant solution, a predetermined amount of aluminum nitrate solution was added to the synthesis solution dropwise

and by continuous mixing. The pH of this solution was adjusted to 11. Hydrothermal synthesis was then carried out in a Teflon-lined stainless-steel autoclave at 120 °C. After hydrothermal synthesis, the solid product was filtered, washed with deionized water, dried in a vacuum oven at 40 °C for 24 h, and calcined in a quartz tubular reactor placed in a temperature controlled furnace (Carbolite) by heating it at a rate of 1 °C/min, up to 550 °C, and keeping it at this temperature for 8 h. Calcination was achieved in a flow of dry air (Oksan), with a flow rate of about 1 dm³/min. The catalysts prepared following this procedure and containing Al/Si ratios of 0.1 and 0.2 in the synthesis solution are denoted by the symbols AlSi1 and AlSi2, respectively.

In our earlier study¹⁵ it was indicated that STA was highly active in an ethanol dehydration reaction. Based on that study, activities of pure STA (Sigma-Aldrich) and STA impregnated aluminosilicate were also tested in a methanol dehydration reaction. Considering that pure STA had a very low surface area, novel catalysts were prepared in our recent work by impregnating STA on a suitable support such as MCM-41 or aluminosilicate.¹⁶ Details of the preparation procedure of STA impregnated aluminosilicate (STAMAS) were given previously.¹⁶ In the preparation of this catalyst, a commercial mesoporous aluminosilicate (Sigma) containing an Al/Si atomic ratio of 0.03 (AlSi(C)) was used as the supporting material. In the impregnation procedure, a solution of STA was prepared in ethanol and aluminosilicate was added to this solution and this mixture was continuously mixed at 30 °C for 44 h. The weight ratio of STA to aluminosilicate was 0.5 in this mixture. This mixture was then dried at 80 °C for 48 h in an oven. The final product was calcined at 200 °C for 8 h in a tubular furnace in a flow of dry air with a flow rate of about 1 dm³/min. The catalyst was then heated up to 350 °C in the reaction system.

Catalyst characterization

The synthesized aluminosilicate and STA impregnated aluminosilicate catalysts were characterized using different techniques. X-ray diffraction (XRD) analysis was carried out using the Rigaku D/MAX2200 diffractometer with a CuK radiation source. The 2θ scanning range was between 1° and 50° and its step size was 0.01°. Energy dispersive spectroscopy (EDS) analysis was carried out to determine the chemical compositions of materials by energy dispersive spectroscopy-JSM-6400 (JEOL) equipped with a NORAN system. Nitrogen adsorption analysis of the catalysts was carried out at 77 K using Micromeritics-ASAP2000 equipment present in the Department of Chemical Engineering of METU, to determine the average pore diameters, pore size distributions, pore volumes, and surface area values. FTIR of the pure and the impregnated STA catalysts was obtained using a Bruker FTIR-IFS66/S instrument. Pyridine adsorption-DRIFTS studies were done in order to detect the presence of acid sites, by a Perkin Elmer Spectrum1 FT-IR instrument.

Methanol dehydration experiments

The catalytic activities of aluminosilicates, STA, and STA impregnated aluminosilicate catalysts were tested in vapor phase methanol dehydration reaction. Fresh catalyst was placed into a stainless steel tubular reactor having an internal diameter of 1/4 inch and supported from both ends using quartz wool. In order to investigate the effect of the reaction temperature on the activity of the catalyst, the reactor was placed into a tubular furnace, which was heated to a predetermined temperature. At least 4 successive data points were taken at each temperature and the average of these data points was used in the evaluation of conversion and selectivity

values. Results of these successive measurements made at a certain temperature were highly reproducible within a reaction period of about 3 h. A syringe pump (Cole Parmer) was used to send liquid methanol (99.9%, Merck) with a flow rate of 2.1 mL/h through an evaporator in which the temperature was kept at 150 °C. In the evaporator, vapor phase methanol was mixed with the carrier gas Helium (99.999 %, Air Products) in 1:1 molar ratio, adjusting the total vapor flow rate as 44.2 mL/min. A Varian CP 3800 Gas Chromatograph equipped with a Poropak T column and a TCD detector was used to analyze the composition of the reactor effluent stream.

Results and discussion

Catalyst characteristics

The physical properties of the aluminosilicate catalysts, having different Al/Si atomic ratios, are presented in the Table. The Al/Si atomic ratios of these materials were evaluated by EDS analysis. EDS results and Al/Si ratios of the synthesis solutions were quite close to each other. EDS analysis of the catalysts synthesized with solutions containing Al/Si ratios of 0.1 and 0.2 gave Al/Si ratios of 0.09 and 0.18 in the final product. These results indicated that the incorporation of alumina into the synthesized catalyst was highly successful.

Table. Physical properties of aluminosilicate catalysts.

Catalyst	BET Surface Area (m ² /g)	BJH Ads. Surface Area (m ² /g)	BJH Ads. Pore Volume (cc/g)	BJH Ads. Pore Diameter (nm)	Lattice Parameter <i>a</i> (nm)	d ₁₀₀ (nm)	Al/Si (atomic) (EDS)
AlSi(C)	903	1339	0.96	2.9	4.4	3.9	0.03
AlSi1	673	1008	1.8	2.7	4.4	3.8	0.09
AlSi2	414	463	1.25	2.4	4.2	3.6	0.18

For mesoporous aluminosilicate materials, alumina can be located on either inner wall of pores or external surfaces of the particle, by providing accessible acidic sites. If alumina is within the bulk of the material, instead of being on the surface, its catalytic effect will be diminished. Another important property affecting the activity of H-ZSM-5 type catalytic materials is reported to be their crystallinity.²⁸ As it was discussed by Bressel et al.,²⁸ H-ZSM-5 type catalysts containing high Al contents (about 8.1%) have low crystallinity. The mesoporous aluminosilicate catalysts, as the ones synthesized in our work, are not crystalline and are expected to have thick amorphous walls. In our study, increasing the alumina content of the mesoporous aluminosilicate catalyst resulted in a decrease in its surface area (Table). Similar results are reported in the literature.²⁷ Commercial aluminosilicate (AlSi(C)) containing an Al/Si atomic ratio of 0.03 has a BET surface area of 903 m²/g, while the materials synthesized in this work contain Al/Si ratios of 0.09 and 0.18 and have BET surface area values of 673 and 414 m²/g, respectively. MCM-41-like materials are expected to contain well ordered hexagonal pores in an amorphous lattice. The low angle XRD patterns corresponding to aluminosilicate catalysts, are given in Figure 1. These results indicated some deformation of the MCM-41 like mesoporous structure of the synthesized materials by increasing the Al/Si ratio. A sharp Bragg peak was observed at a 2 θ value of about

2.30° for all aluminosilicate samples. This peak and its reflection at about 4° are characteristic peaks for the ordered mesoporous structure of MCM-41-like materials. Nitrogen adsorption results are close to type IV isotherms, also indicating a mesoporous structure (Figure 2). Pore size distributions of these materials also showed quite narrow mesopore size distributions (Figure 3), giving average pore diameters in the range of 2.4-

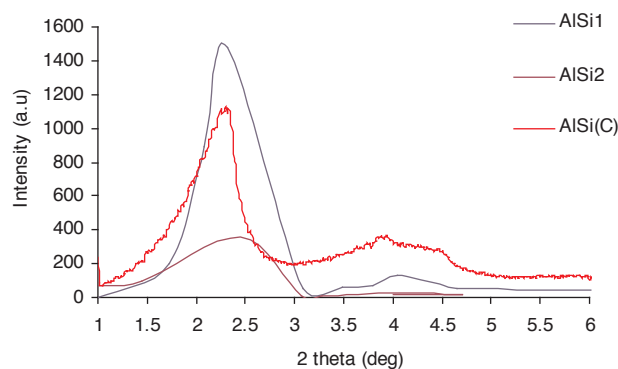


Figure 1. XRD plots of aluminosilicate catalysts with different Al/Si ratios.

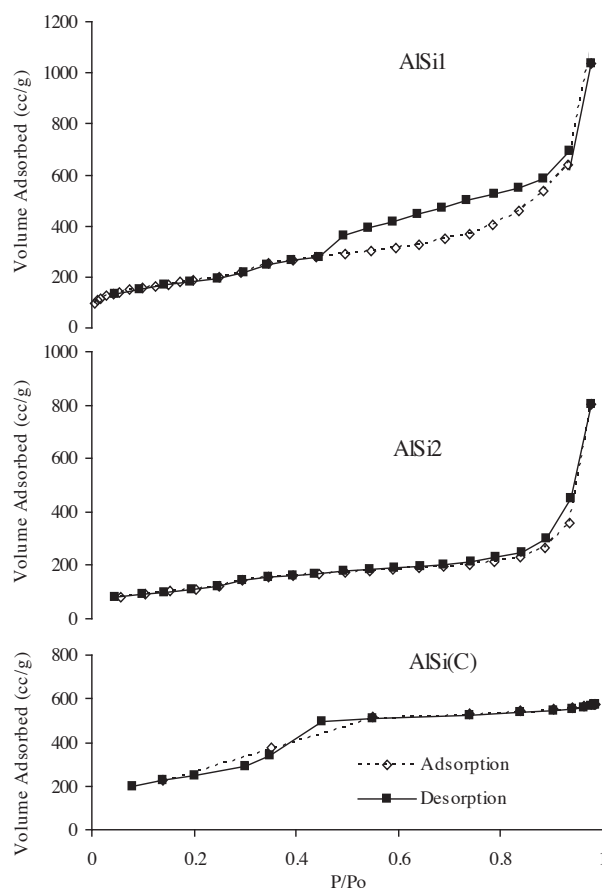


Figure 2. N_2 Adsorption isotherms for aluminosilicate catalysts with different Al/Si ratios.

2.9 nm. Pore size distributions also indicated the presence of macropores having diameters over 20 nm in the materials containing high Al/Si ratios. The aluminosilicate particles having diameters of 100-150 nm are seen in the SEM photograph of AlSi1 in Figure 4.

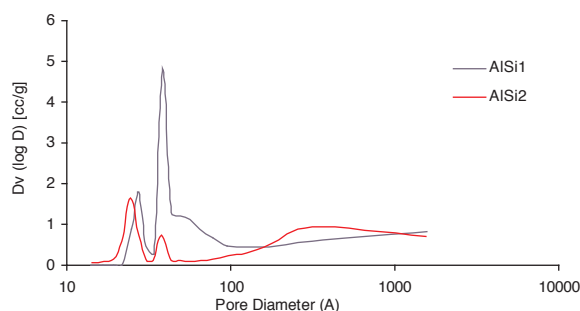


Figure 3. Pore size distributions of synthesized aluminosilicate catalysts with different Al/Si ratios.

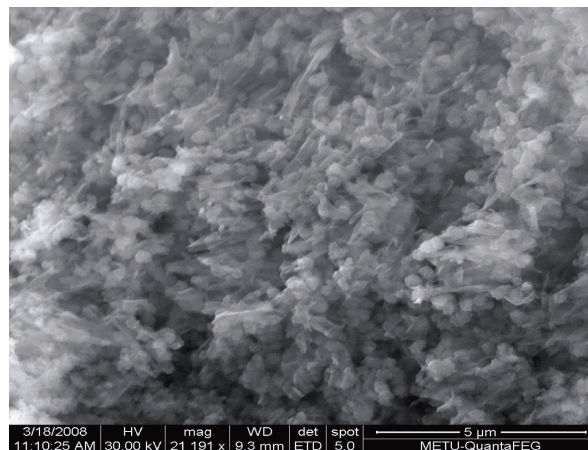


Figure 4. SEM photograph of AlSi1.

In the case of STA impregnated aluminosilicate catalyst, XRD analysis gave Bragg peaks of silicotungstic acid at 2θ values of 2.28° , 3.96° , and 4.44° , as reported in our earlier publication.¹⁶ For this catalyst, the characteristic d_{100} value was 3.87 nm and the lattice parameter evaluated from $a = 2d_{100}/\sqrt{3}$ was 4.47 nm. Two XRD peaks observed at 2θ values of 25.5° and 34.74° are characteristic peaks of pure silicotungstic acid. As shown in Figure 5, sharp peaks corresponding to the Keggin structure of pure heteropolyacid were not observed in the XRD patterns of the impregnated catalyst. This indicates good dispersion of STA within the mesoporous aluminosilicate support, forming small STA grains.

The BET surface area and BJH adsorption surface area values of STAMAS were 690 and 823 m²/g, respectively, from nitrogen adsorption analysis. The type IV adsorption isotherm¹⁶ indicated the mesoporous structure of STAMAS. Its BJH adsorption pore volume was 0.81 cm³/g and pore wall thickness was 1.41 nm as indicated in our earlier publication.¹⁶

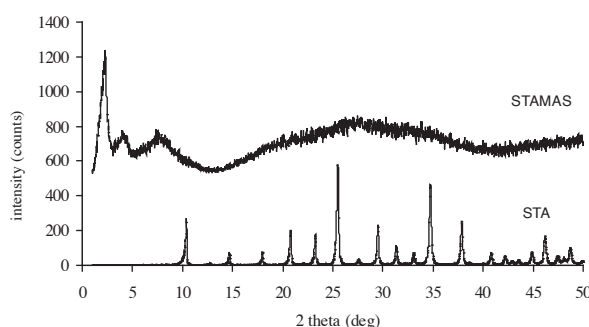


Figure 5. XRD plots of pure silicotungstic acid and STAMAS catalysts (XRD of STAMAS is adapted from Varisli et al.¹⁶).

Surface acidity of the catalyst is expected to play an important role in the methanol dehydration reaction. In order to investigate the acidic characteristics of the new catalyst, DRIFTS analysis of fresh and pyridine adsorbed catalysts was carried out. The differences in the spectra obtained with the pyridine adsorbed and fresh catalysts were analyzed to get information about the acid sites. Typical results obtained for STA, STA impregnated aluminosilicate, and the support aluminosilicate are given in Figure 6. DRIFTS bands observed at 1447 cm^{-1} and 1598 cm^{-1} correspond to the Lewis acid sites. Bands observed at 1540 cm^{-1} and 1640 cm^{-1} correspond to Bronsted acid sites and the band observed at 1489 cm^{-1} was reported to be due to both Lewis and Bronsted acid sites.^{16,26} As shown in Figure 6, pure STA and STAMAS catalysts have both Bronsted and Lewis acid sites. The ratio of the intensities of the bands observed at 1447 cm^{-1} to 1540 cm^{-1} gives information about the relative magnitudes of Lewis and Bronsted acid sites. As expected, pure STA has a large band at 1540 cm^{-1} , which corresponds to Bronsted acid sites. However, in the case of STAMAS intensity of the band corresponding to Lewis acid sites (at 1447 cm^{-1}) was higher than the band corresponding to Bronsted acid sites (at 1540 cm^{-1}). This is due to the Al content of STAMAS. DRIFTS studies of the pyridine adsorbed AlSi1, AlSi2, and AlSi(C) samples were also carried out and the results are presented in Figure 7. These mesoporous aluminosilicate catalysts synthesized in this study contain both Bronsted and Lewis acid sites. The intensity of bands at 1540 cm^{-1} is as strong as the intensity of bands at 1447 cm^{-1} for AlSi1 and AlSi2 catalysts, indicating the presence of significant amounts of Bronsted acid sites as well as Lewis acid sites. However, for AlSi(C), the intensity of the band corresponding to Lewis acid sites was much higher than that of the band corresponding to Bronsted acid sites.

Methanol dehydration results

Methanol dehydration reactions were carried out in a temperature interval of $200\text{--}400\text{ }^{\circ}\text{C}$ and at a space time of 0.14 sg/cm^3 , over the aluminosilicate catalysts. Results of a blank test carried out in the absence of catalyst indicated that there was no non-catalytic dehydrogenation of methanol at these reaction conditions. In the case of experiments carried out with pure STA and STA impregnated aluminosilicate (STAMAS), the temperature range was selected as $180\text{--}300\text{ }^{\circ}\text{C}$ with a space time of 0.27 sg/cm^3 .

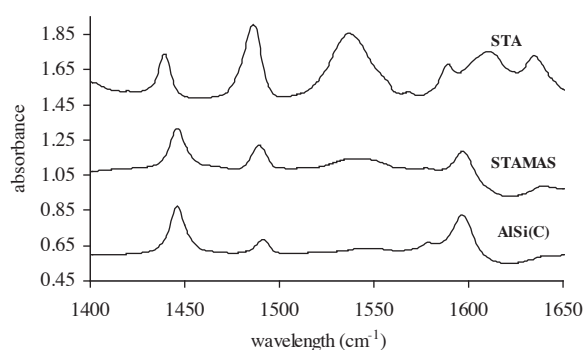


Figure 6. Pyridine adsorption DRIFT analysis of pure silicotungstic acid STAMAS catalyst and the support AlSi(C). (DRIFT spectra of STAMAS are adapted from Varisli *et al.*¹⁶).

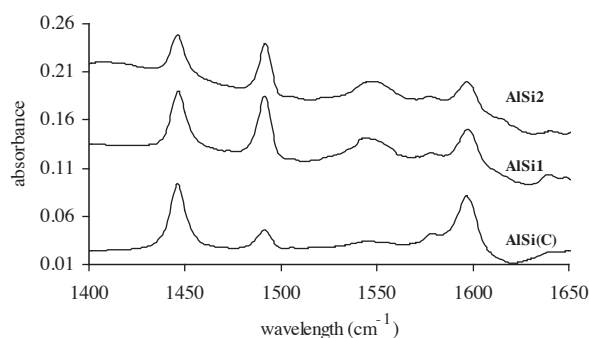


Figure 7. Pyridine adsorption DRIFT analysis of synthesized aluminosilicate catalysts.

The results showed that aluminosilicate catalysts have good activity in methanol dehydration reactions at temperatures higher than 200 °C (Figure 8). An increase in the reaction zone temperature favored the dehydration reaction for each catalyst and coke formation was not observed in the studied temperature range for aluminosilicate based catalysts. AlSi(C) having an Al/Si molar ratio of 0.03 gave lower conversions than AlSi1 and AlSi2 catalysts, for which Al/Si molar ratios were 0.09 and 0.18, respectively. A methanol conversion of 0.6 was obtained with AlSi(C) at 400 °C. In the cases of AlSi1 and AlSi2, methanol conversion values of about 0.78 and 0.72 were obtained at the same temperature. The Bronsted acidity of AlSi(C) was much lower than that of the other catalysts. As discussed in our earlier publication,¹⁶ an increase in Bronsted acidity resulted in higher catalytic activity in the ethanol dehydration reaction. As discussed in the previous section, the ratio of intensities of the pyridine adsorbed DRIFTS bands corresponding to Bronsted and Lewis acid sites was higher for AlSi1 and AlSi2 catalysts than AlSi(C). These results are consistent with the higher activity of AlSi1 and AlSi2 than AlSi(C) in methanol dehydration. It was interesting to observe that the catalyst containing an even higher Al/Si ratio (AlSi2 containing an Al/Si ratio of 0.18) was less active than AlSi1. This lower activity of AlSi2 is thought to be mainly due to the much lower surface area of AlSi2 than AlSi1. A further increase in Al/Si ratio over 0.09 caused a significant reduction in surface area and probably did not cause an increase in the total number of surface sites per unit mass of the catalyst. This excess alumina is probably placed within the bulk of the synthesized material rather than being on the surface. These results indicated that there is an optimum in the Al/Si ratio of the catalyst for methanol dehydration. In fact the presence of such an optimum Al/Si ratio was also reported by Xu et al.²⁹ for DME synthesis over solid acid catalysts.

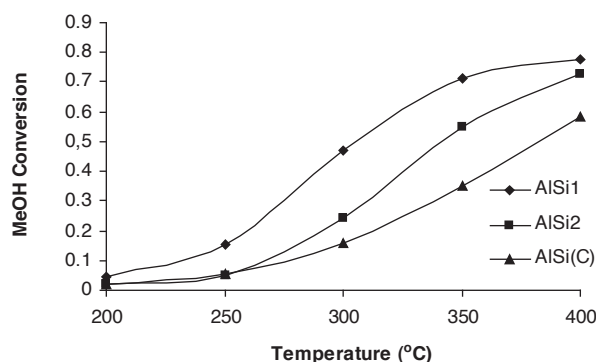


Figure 8. Conversion of methanol over different aluminosilicate catalysts.

DME was produced as the main product of the methanol dehydration reaction (Figure 9). Experiments carried out with aluminosilicates having different Al/Si molar ratios showed that DME formation was observed even at temperatures as low as 200 °C. The selectivity of DME, which was defined as the ratio of moles of methanol converted to DME to the total moles of converted methanol, was increased with an increase in temperature reaching a level of 0.99 over 300 °C. The effect of the alumina content of the catalyst on product selectivity was also investigated in these experiments. The selectivity value of 0.61 was obtained with AlSi(C), which had the lowest alumina content. Increasing the molar ratio of Al to Si from 0.03 to 0.09 and then to 0.18 caused a decrease in DME selectivity for temperatures less than 300 °C. However, above 300 °C DME selectivity values obtained with all these catalysts approached one. Although the AlSi(C) catalyst showed the highest DME selectivity at low temperatures its activity was less than that of the other catalysts. As discussed

above, this low activity of this catalyst is related to its lower Bronsted acidity. As a result, this catalyst gave the lowest DME yield values, which were evaluated by multiplying the selectivity values by the corresponding conversion values of ethanol.

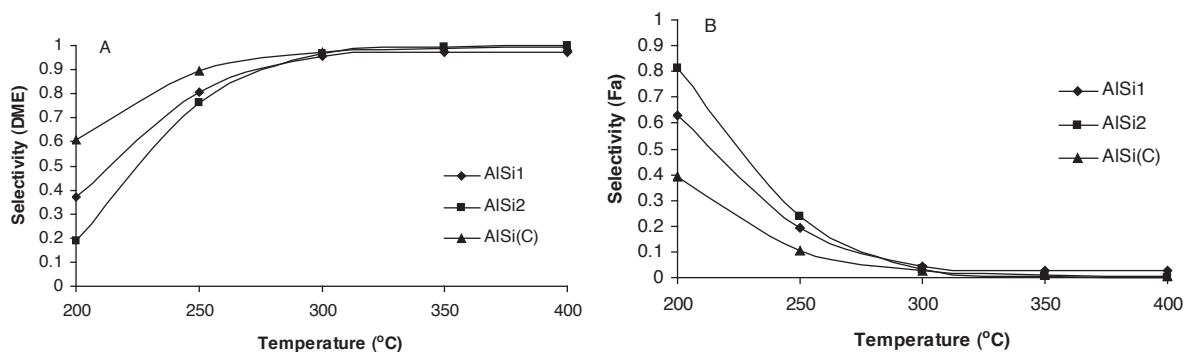


Figure 9. Selectivity of DME (A) and formaldehyde (B) over different aluminosilicate catalysts.

Besides dimethylether, formaldehyde was produced as a byproduct in the methanol dehydration reaction (Figure 9B). Formaldehyde formation took place especially at low reaction temperatures, below 300 °C. Formation of formaldehyde became negligible at temperatures higher than 300 °C.

The results showed that aluminosilicate catalysts, giving DME yield values over 0.70, are good candidates for the methanol dehydration reaction. The other types of solid acid catalysts studied in this work were pure silicotungstic acid and silicotungstic acid impregnated aluminosilicate. Experiments carried out in a temperature interval of 180-300 °C with a space time of 0.27 sg/cm³ showed that pure silicotungstic acid gave a methanol conversion of 0.3 (Figure 10) at about 250 °C. However, in the case of STA impregnated aluminosilicate (STAMAS) a conversion value of about 0.84 was obtained at the same temperature. STAMAS showed much greater activity than pure STA even at reaction temperatures as low as 180 °C. As reported in our earlier publication,¹⁶ by the impregnation of STA into aluminosilicate a high surface area solid acid catalyst was obtained. This is the main reason for having higher catalytic activity in STAMAS than STA in the alcohol dehydration reaction. Although the Bronsted acidity of pure STA is very high, its extremely low surface area mainly affected the activity in the methanol dehydration reaction. Silicotungstic acid catalysts, either in pure form or impregnated on aluminosilicate, showed quite high DME selectivity values reaching 0.90 at around 200 °C (Figure 11). Above this temperature, STA showed slightly higher DME selectivity than STAMAS. Pure STA is essentially a dehydration catalyst. However, aluminosilicate support also provides some sites for the formation of some formaldehyde. Formation of formaldehyde below 300 °C was also observed with pure aluminosilicate catalysts. If we consider the yield of DME, which is evaluated by multiplying methanol conversion by DME selectivity, very high yield values were obtained over 200 °C with the STAMAS catalyst (Figure 12). Differently from STAMAS, for pure STA methanol conversion and consequently the DME yield values (Figure 12) decreased with an increase in temperature over 250 °C. This can be explained by the coke formation and deactivation of STA above this temperature. However, for the high surface area STA impregnated catalyst no deactivation was observed even over 250 °C. This result indicated that by the impregnation of STA into aluminosilicate a more stable catalyst was produced. Impregnation of STA on a mesoporous support greatly increased the activity and stability of this catalyst in the methanol dehydration reaction, giving much higher DME yields (Figure 12).

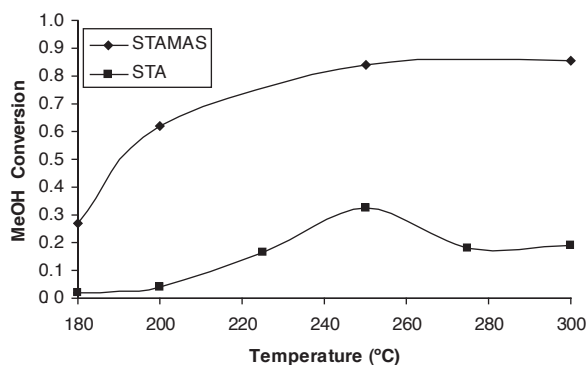


Figure 10. Conversion of methanol over STA and STAMAS.

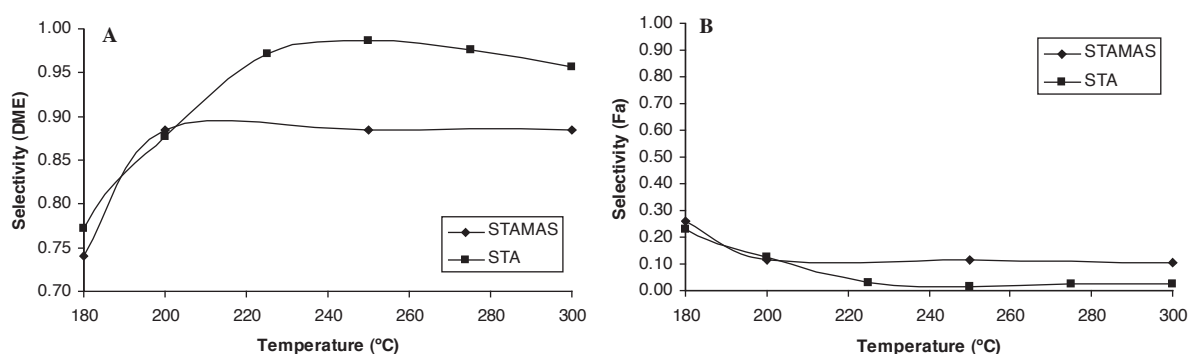


Figure 11. Selectivity of DME (A) and formaldehyde, Fa, (B) over STA and STAMAS.

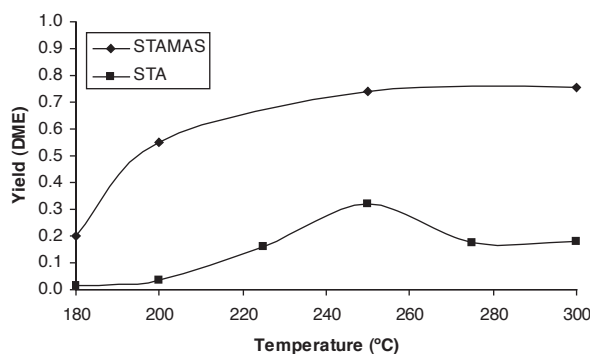


Figure 12. Yield of DME over STA and STAMAS.

Conclusion

Aluminosilicate catalysts showed quite high activity in the methanol dehydration reaction at temperatures higher than 200 °C. It was concluded that due to the effects of acid strength and surface area values there is an optimum Al/Si ratio (about 0.09) that gave the highest methanol conversion and DME yield. It was also shown that aluminosilicate catalysts having high surface area and mesoporous structure could be successfully synthesized following a hydrothermal synthesis route. STAMAS catalyst, which was prepared by impregnating

silicotungstic acid into aluminosilicate, showed higher activity than aluminosilicates and pure STA in the methanol dehydration reaction, with a conversion value of around 0.8 and very high DME selectivity even at temperatures as low as 250 °C. Both aluminosilicate and silicotungstic acid impregnated aluminosilicate catalysts are highly selective to DME formation.

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