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## Original Research Paper

## Development of surface modified mordenite catalysts and their stability in hot liquid water

Umer Khalil<sup>a</sup>, Oki Muraza<sup>a,b,\*</sup>, Adnan Al-Amer<sup>a</sup><sup>a</sup> Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia<sup>b</sup> Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

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## ABSTRACT

Stable zeolites are demanded in heterogeneous catalytic upgrading of water-containing feedstocks such as biomass and heavy oil. Herein, we report hydrophobic mordenite (MOR) via chemical liquid deposition (CLD). Prior to the surface treatment, pure MOR was synthesized with a Si/Al ratio of 15. The Si/Al ratio plays a crucial role in the synthesis of pure MOR phase. Surfaces of MOR crystals were treated with two different silane reagents and multiple-cycle treatments. Improved hydrophobic surface properties were observed for tetraethyl orthosilicate (TEOS) as compared with 3-aminopropyl triethoxysilane (3-APTS). The amount of silane compound deposited on the zeolite surface increased with an increase in the number of cycles. These findings are expected to stimulate the applications of hydrophobic zeolites in biomass and heavy oil conversion.

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## 1. Introduction

The need to process biomass and heavy oil in the presence of water has stimulated numerous research activities in hydrophobic zeolites to develop highly stable catalyst in an aqueous environment [1–3]. Different approaches have been explored to stabilize zeolites in water [3]. One way to increase the hydrophobicity is by increasing the Si/Al ratio or by dealumination of zeolite. However, this approach resulted in the loss of Brønsted acid sites and as a consequence a reduced catalytic activity [4,5]. Surface modification of zeolites with sodium fluoride, lanthanum, phosphorus, and organo-silane may also increase the hydrophobicity of zeolites without significant loss of the acid site density [6–10]. Cerqueira et al. [11] studied the effect of the phosphorus addition on the hydrothermal stability of H-MFI in steam environment. Impregnation of different Si/Al ratios ZSM-5 with phosphorus in H<sub>3</sub>PO<sub>4</sub> form was reported by Corma et al. [6]. Hydrophobic siliceous ferrierite was reported, for instance, by the introduction of pyridine and sodium fluoride [8].

The objective of this work was to develop hydrophobic MOR catalysts using organosilane groups as surface modifier reagents. Previously, various catalysts have been modified using organo-

silane compounds to achieve desired properties such as competitive adsorption of water and toluene [12], biofuel upgrading, selective skeletal isomerization of *n*-butene to isobutene in addition to improved thermal stability. Silane modification of zeolite H-Y, H-USY, and H-ZSM-5 to enhance their hydrophobicity reported recently [13]. MOR has chemical formula Na<sub>8</sub>(H<sub>2</sub>O)<sub>24</sub>[Si<sub>40</sub>Al<sub>8</sub>O<sub>96</sub>] with parallel 12-ring channels (0.67 × 0.70 nm) along the *c*-axis direction and these channels are interconnected by 8-ring (0.34 × 0.48 nm) channels along *b*-axis [14,15]. All 12-rings are interconnected with suppressed 8 rings and due to the small size of 8 rings, MOR is practically considered as a one-dimensional zeolite, especially in adsorption and catalytic applications [16].

In this work, post-synthesis modification of MOR was applied using chemical liquid deposition (CLD) of reagents such as tetraethylorthosilicate (TEOS) and 3-aminopropyl triethoxy silane (3-APTS) to enhance its hydrophobicity. The reason of the selection of these organosilanes was that their kinetic diameters are too large to enter into pores of MOR and they can modify only external surface [17]. MOR with different Si/Al ratios was prepared with fixed Na/Si ratio. MOR with Si/Al ratio of 15 showed pure phase and selected for surface modification.

CLD was chosen because of its better practical applicability for large industrial scale than chemical Vapor deposition (CVD) although both CLD and CVD could be used for surface modification of MOR [18].

\* Corresponding author at: Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.

E-mail address: [omuraza@kfupm.edu.sa](mailto:omuraza@kfupm.edu.sa) (O. Muraza).

## 2. Experimental

### 2.1. Synthesis and surface modification of mordenite

All zeolites were synthesized hydrothermally using PTFE-lined stainless steel autoclave with a volume of 100 ml. We followed the procedure described by Hincapie et al. [14]. Gel composition of final mixture was 7.8 Na<sub>2</sub>O:1 Al<sub>2</sub>O<sub>3</sub>:30 SiO<sub>2</sub>:780 H<sub>2</sub>O prepared by adding sodium hydroxide (NaOH pellets, PRS-CODEX 98%) in double deionized water (DDW) followed by sodium aluminate (NaAlO<sub>2</sub>, Sigma-Aldrich) as aluminum source. Silica gel (Sigma-Aldrich, pore size 60 Å, 70–230 mesh), as silica source, was added in the mixture under stirring. After the stirring for 1 h at 25 °C, the mixture was transferred to 100 ml autoclave and crystallization was carried out at 180 °C for 48 h in a conventional oven. The product was washed several times with deionized water until its pH was reduced to neutral. The sample was dried at room temperature for 12 h.

The catalyst was then calcined at 550 °C for 12 h. The protonated form, H-MOR, was obtained by ion-exchange. Typically, 1 g of catalyst was suspended in 20 g of 2 M ammonium nitrate (NH<sub>4</sub> (NO<sub>3</sub>)) and the solution was heated under stirring for 3 h. The catalyst was dried and washed three times with deionized water. After washing step, the ion-exchange procedure was repeated followed by the calcination of the final product. The Si/Al ratios (15, 20, 25, and 50) were synthesized through the same procedure as described above.

### 2.2. Silylation of mordenite

Protonated MOR was silylated using procedure previously reported by Lercher group [17] using chemical liquid deposition (CLD) technique, which involves liquid phase reaction and calcination. In a typical run, 1 g of catalyst was suspended in 25 ml of cyclohexane and the solution was heated under reflux condition. Two organosilane reagents, namely tetraethyl orthosilicate (TEOS) and 3-Aminopropyl triethoxysilane (3-APTS) were used for silylation treatment. TEOS with an amount of corresponding to 4% of SiO<sub>2</sub> was added to the mixture and the solution was stirred for 1 h under reflux. Cyclohexane was separated from the catalyst and dried, then calcined for 5 h at 500 °C. The Same methodology was adopted when 3-APTS was used as a modifier. Multiple cycles were employed to enhance the deposition hence procedure was repeated thrice including calcination of catalyst. Samples prepared using TEOS with one, two and three cycles referred as TEOS-1, TEOS-2 and TEOS-3 respectively. Similarly, 3-APTS modified samples were named as APTS-1, APTS-2, and APTS-3.

Parent and modified MOR were tested in hot water. Zeolite (0.2 g) was suspended in 30 g of distilled water. Each mixture was transferred to PTFE lined autoclave and heated at 200 °C for 72 h. The water/catalyst ratio was set in accordance to volume of autoclave.

### 2.3. Characterization of parent and surface modified mordenite catalysts

XRD analysis of parent and modified samples were performed using a diffractometer (Rigaku MiniFlex) to confirm the phase purity of MOR. The XRD was performed using CuK $\alpha$  radiation with 2 $\theta$  from 5° to 50° with a scanning step of 0.02 and a scanning speed of 3 degree per min. Morphology and crystal size were studied using scanning electron microscope (SEM-FIB, TESCAN, LYRA 3). FTIR spectrometer (Nicolet 6700) was used to study surface groups of modified samples and IR spectra for the Si–O–Si band was reported. The sample was prepared by mixing 2 mg of catalyst in

200 mg KBr then characterized using an FTIR spectrometer at wavenumber 1500–600 cm<sup>−1</sup>. Physisorption was studied by using a porosimeter. Prior to N<sub>2</sub> adsorption–desorption studies, a quantity of zeolite powder was degassed at 300 °C for 12 h at ambient atmosphere. The BET specific surface area, micropore volume, and external surface area were reported. All solid-state <sup>27</sup>Al MAS-NMR spectra were recorded by using a Bruker MSL300 spectrometer.

## 3. Results and discussion

### 3.1. Effect of Si/Al ratio on the purity of mordenite

Our previous studies show that pure zeolite catalysts at different Si/Al ratios can be prepared by optimizing synthesis parameters such as crystallization temperature and time, aging time and Na/Si ratio [19,20]. The effect of different Si/Al ratios (15, 20, 25 and 50) on the phase purity of MOR was studied at fixed temperature, crystallization time, aging time and Na/Si ratio. XRD patterns of MOR samples for different Si/Al ratios in Fig. 1 showed that the increase in Si/Al ratio produced a co-crystallized phase, which was referred as analcime [14].

Morphology and crystal size of samples with Si/Al ratios of 15, 20, 25 and 50 are presented in Fig. 2. Rod-like hexagonal crystals were obtained for all four Si/Al ratios. This morphology was previously reported by Mao et al. for large MOR crystals (75  $\mu$ m) synthesized using different Al sources [21]. The smallest crystal size of 5  $\mu$ m was obtained at Si/Al of 15 while impure phase appeared at higher Si/Al ratios (Fig. 2). Very large size crystals of up to 20  $\mu$ m were produced at higher Si/Al ratio 20  $\mu$ m.

Fig. 1 shows that the peak intensity of co-crystallized phase (analcime) was increased with the increase of Si/Al ratio, while all other parameters were kept constant. It was observed that the only pure sample was obtained at a Si/Al ratio of 15 with Na/Si ratio of 0.52. Si/Al ratio plays an important role in the purity of MOR. Pure zeolites at higher Si/Al can only be achieved by changing the Na/Si ratio, temperature and crystallization time, as has been reported by other research groups for different zeolites such as MTT, MTW, ZSM-22 and EU-1[20].

### 3.2. Effect of surface modification on mordenite

The modified MOR catalysts were characterized by N<sub>2</sub>-Adsorption to study surface properties. Table 1 presents the textural properties of parent and modified catalysts. During the modification, organic moieties were formed on the external surface, hence it was expected that zeolite pore properties such as size and pore volume remained unchanged. These assumptions were confirmed by N<sub>2</sub>-Adsorption where negligible change was observed in pore volume and texture properties. While in the case of APTS-3 as a modifier, small increase in the external surface area was observed. This indicates that silane group attached to the external surface and did not enter the pores. These modified sites on surface repel water molecules and enhance hydrophobicity of MOR. Characterization techniques such as XRD, FT-IR and XRF were performed to identify the extent of surface modification.

XRD patterns in Fig. 3 shows that the parent, TEOS-3 and APTS-3 modified MOR samples retained their crystallinity after modification. The same intensity of MOR major peaks in both unmodified and modified samples shows no structural changes after the modification.

The simple physical test was performed to verify the surface modification of catalysts with organosilane groups [22,23]. Parent and TEOS-3 modified zeolite were suspended in water/oil emulsion. It was observed that parent zeolite quickly settled down in the water at the bottom of the water/toluene emulsion. While

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