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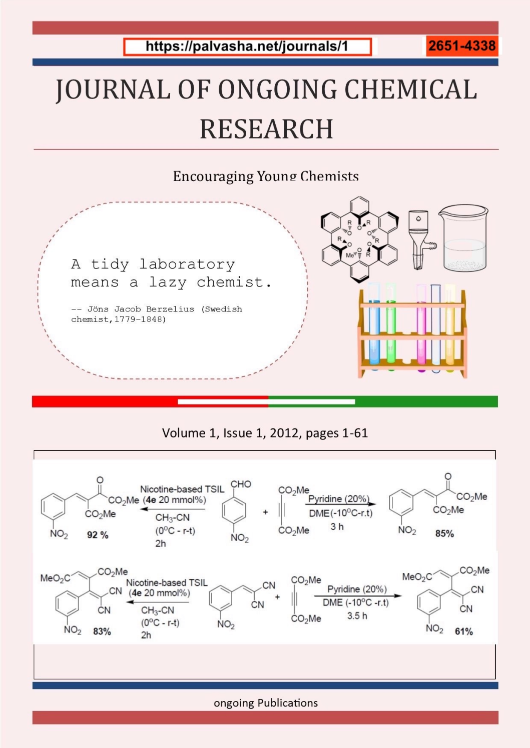

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JOURNAL OF ONGOING CHEMICAL RESEARCH

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A tidy laboratory means a lazy chemist.

-- Jöns Jacob Berzelius (Swedish chemist,1779-1848)

Volume 1, Issue 1, 2012, pages 1-61

ongoing Publications

JOURNAL OF ONGOING CHEMICAL RESEARCH

2019
Volume: 4
Issue: 1
Pages: 6-10
Document ID: 2019JOCR30
DOI: 10.5281/zenodo.3592241

J Ong Chem Res, 2019, **4**(1): 6-10, Document ID: 2019JOCR30, doi:10.5281/zenodo.3592241

Research Article

Formation and Characterization of ZnS Nanoclusters in the Pore Channels of Mordenite Zeolite

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Abstract

Mordenite zeolite was synthesized without organic structure directing agents. We used ion exchange to create the zinc sulphide nano-clusters inside the zeolite framework. The as-synthesised (Na-MOR zeolite) and exchanged samples (Zn-MOR, ZnS-MOR zeolites) were characterised by X-ray powder diffraction (XRPD), solid state magic angle spinning nuclear magnetic resonance (MAS NMR), energy-dispersive X-ray (EDX) elemental analysis, Brunauer-Emmett-Teller (BET) surface area analysis, and transmission electron microscopy (TEM). PXRD shows that exchange does not affect the zeolite framework, a a slight increase in the unit cell parameters from Na-MOR to ZnS-MOR is observed. The successful incorporation of Zn^{2+}into the MOR framework is confirmed by ^{23}Na NMR. EDX, BET, and TEM analyses also provide evidences for the formation of ZnS nano-clusters.

Keywords: Zeolite, Nanoclusters, Ion Exchange, Structure, Diffraction, Microscopy

INTRODUCTION

Zeolites are porous alumino-silicate minerals with regular, well-defined 1-, 2- or 3- dimensional channel structures [Barber, 1949; Barrer, 1949; Barrer, 1965; Breck, 1984; Cundy et al, 2003; Cundy et al, 2003]. These channels or pores can accommodate guest molecules, particles or clusters, and can act as solid support [Bellussi, 2004; Bhatia, 1989]. The attachment of particle on the internal surface of the zeolite offers many advantages for various applications due to the high thermal and mechanical stability of molecular sieve support, and access of the particles through the channel system of a zeolite. Semiconductor nano-clusters, which can be introduced in zeolites pores, can find wide applications in photo-catalysis, sensors, displays, etc. [Iacomi, 2003; Mac, 1989; Nirmal, 1996; Stucky et al, 1990].

Previous work on the formation and applications of nano-clusters in mordenite zeolite was mainly focused on binary systems (NiS, CdS, PbS, CdSe, ZnS) and ternary systems (NiCoS, ZnCdS, ZnCdSe) [Chen, 2000; Lee, 2018; Raymond, 2003; Sohrabnezhad, 2008; Garca, 2001]. Although much data were collected on some of those systems, there are still questions on the location of those clusters, whether the clusters disrupt the framework or not, and interaction of those clusters with catalytic sites within the zeolite itself. In this work, we study the formation of ZnS clusters in mordenite zeolite (MOR) which was crystallized with no organic structure directing agents. We chose this zeolite with “medium” pore size and stoichiometric formula $6Na_2O:Al_2O_3:30SiO_2:780H_2O$ as it provides a balance between a desired large number of exchangeable Na^+cations, and a desired small number of catalytic sites. The interaction between the catalytic sites and clusters in the pores is still not fully understood. Structurally, mordenite zeolite has an orthorhombic structure with twelve rings channels in the [001] and eight rings channels in [100] directions. The apertures of those channels are 6.5 by 7.0 Å and 2.6 by 5.7 Å,respectively, [Kim, 1991] as shown in figure 1.

We have previously studied the formation of reactive, such as sodium hydride and sodium amide, nanoparticles in amorphous silica, where it was shown that silica protects the nanoparticles and makes them less pyrophoric and air- and moisture-sensitive while providing a chemical structural stabilization [Ogilvie, 2013; Seel et al, 2011].

RESULTS AND DISCUSSION

Naoparticles derived from both synthetic[Sartbaeva et al, 2006] and natural products [Yildiztekin et al, 2016] are nowadays attracting the attention of scientists. This study is about the formation and characterization of ZnS nanoclusters in the pore channels of mordenite zeolite. The powder patterns of as-synthesized, zinc and sulfur exchanged mordenite zeolite are shown in figure 2. SEM images show the morphology of the modernite zeolite being boat-shape, with the length about 40 µm. Only MOR framework diffraction peaks are observed in all samples of mordenite zeolite. The unit cell parameters are calculated from the powder pattern and shown in table 1. A very slight decrease in all cell parameters Zn-MOR to ZnS-MOR as compared with Na-MOR is observed. The changes in cell parameters are more dramatic after ion exchange with sulfur compared to the ion exchange with zinc.

Table 1. Unit cell parameters and cell volume of Na-MOR, Zn-MOR andZnS-MOR

Sample	a/Å	b/Å	c/Å	V/cm^3
Na-MOR	18.288(3)	20.081(3)	7.618(1)	2797.57(5)
Zn-MOR	18.249(3)	19.953(3)	7.596(1)	2765.88(5)
ZnS-MOR	17.872(3)	19.780(3)	7.533(1)	2663.76(47).

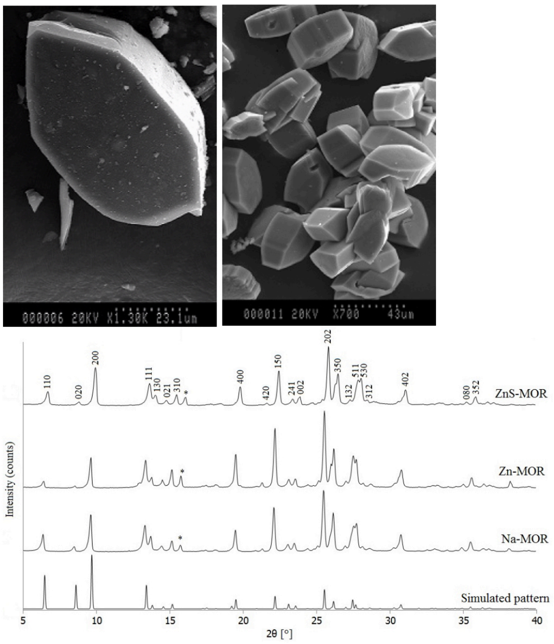

Figure 1. Powder diffraction patterns of mordenite zeolites with Miller indices corresponding to the MOR framework, an asterisk indicate the presence of a small amount of an impurity and SEM images of as-synthesised modernite zeolite

Table 2 summaries the ^{29}Si, ^{27}Al, and ^{23}Na NMR data† of the as-synthesised and ion-exchanged mordenite zeolite samples. Three ^{29}Si signals around -98.9ppm, -105.5ppm, and -112.4ppm are presents in all samples, which are attributed to Si(2Al), Si(1Al), and Si(0Al) local environments, respectively [Barras, 1994; Fyfe, 1983; Klinowski, 1988; Nearchou, 2015; Price et al, 2017; Sartbaeva, 2013]. Only one ^{27}Al NMR signal (around 52-54 ppm) is observed in all samples. This indicates that Al was tetrahedrally coordinated in the framework. No other signals, indicating octahedral, pentagonal or other possible coordination, are observed.

It is interesting to notice that two ^{23}Na NMR signals were observed after an exchange with Zn^{2+}ions, which can be explained by a simplified reaction mechanism of the ZnS nano-clusters formation as shown in figure 3. After an exchange with Zn^{2+}, the framework of Zn-MOR contained both Zn^{2+}and Na^{+}as charge balancing cations. Therefore, there are two sodium environments - a Na^{+}ion with either a Na^{+}ion or a Zn^{2+}ion as a neighbor. After an exchange with Na$_2$S solution, the framework Zn^{2+}reacted with the S^{2-}to form the ZnS nano-clusters, while the Na^{+}in the solution replaced the Zn^{2+}, and therefore only one sodium environment is observed in the ZnS-MOR sample.

Table 2. MAS NMR of as-synthesised and exchanged mordenitezeolite samples

Sample	Si/ppm	Al/ppm	Na/ppm
Na-MOR	-98.7, -105.4, -109.1, -110.9, -113.0	54.8	-11.9
Zn-MOR	-98.9, -105.9, -112.2	52.27	7.39, -21.0
ZnS-MOR	-98.8, -105.9, -112.4	54.5	-16.2

Table 3. The chemical composition of various mordenite zeolites in weight percent (wt%) calculated from EDX measurements

wt%	Na-MOR	Zn-MOR	ZnS-MOR
Si	20.9±1.2	27.2±4.82	18.0±8.9
Al	3.6±0.86	2.9±0.93	3.2±1.4
O	60.5±0.93	61.1±3.2	60.0±5.0
Na	2.8±0.54	1.0±0.61	2.5±0.68
Zn	-	3.3±0.91	3.7±0.83
S	-	-	1.2±0.23

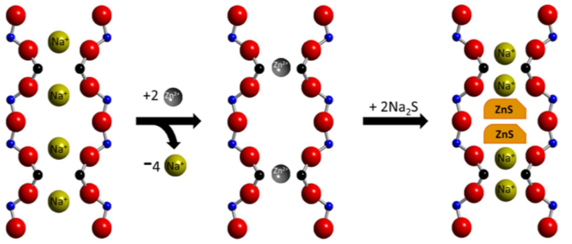

Figure 2. Proposed simplified reaction mechanism of the formation of ZnSnano-clusters inside the pores of mordenite zeolite. Blue spheres - framework Si atoms, black spheres - framework Al atoms, yellow spheres - extra framework Na ions, grey spheres - extra framework Zn ions, orange rectangles - ZnS nano-clusters

The presence of Zn and S in different stages of the ZnS formation can also be traced by EDX†. Table 3 shows the elemental analysis of the Na-MOR, Zn-MOR, and ZnS-MOR samples. The amount of framework building elements, i.e. Si, Al, and O, are similar in all samples. The amount of Na in Na-MOR dropped from 2.8 wt % to 1.0 wt %, and the presence of 3.3 wt % of Zn indicated that Zn ions were successfully incorporated into the MOR framework by the ion exchange step. The amount of Zn in the ZnS-MOR sample remains the same after exchanged with Na_2S solution, and 1.2 wt % of S is also present in the sample.

Table 4. Unit cell parameters and cell volume of Na-MOR, Zn-MOR andZnS-MOR

Sample	Total surface area/m2g−1	External surface area/m2g−1	Micropore area/m2g−1	Micropore volume/cm^{3}g−1
Na-MOR	29.41±0.10	2.9	26.5	0.0103
Zn-MOR	27.10±0.12	3.1	24.0	0.0093
ZnS-MOR	8.50±0.12	4.4	4.1	0.0017

The formation of ZnS nano-clusters can be identified by BET analysis, as shown in table 4. The as-synthesised Na-MOR sample has a much smaller total (BET) surface area and micropore volume compared to the literature values [Zendehdel, 2012]. After exchanging with Zn^{2+}to form Zn-MOR, there is a 6.9% increase in the external surface area and a 9.4% decrease in the micropore area. There is also a 9.7% decrease in micropore volume. This is because Zn^{2+}is larger than Na^{+}, and takes up more space in the micropore. The evidence of ZnS nano-cluster formation is an increase of 42% in the external surface area of the ZnS-MOR sample. It is very likely that the ZnS clusters are formed on the surface of the mordenite zeolite crystals. As the channel openings are blocked by the ZnS clusters, the access of $N_2$to the internal zeolite micropore is limited, which can explain the dramatic decrease in both micropore area (83%) and volume (82%) of ZnS-MOR. However, the formation of ZnS nanoclusters inside the MOR framework ZnS nano-clusters may have formed inside the framework channels cannot be ruled out because it can also explain the decreases in micropore area and volume. TEM images in figure 4(b) also showed that.

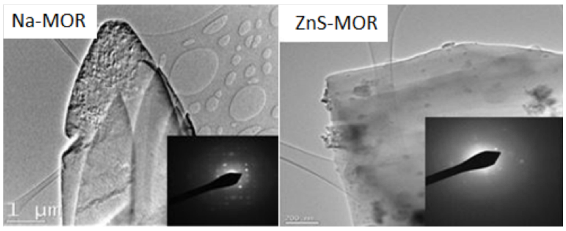

Figure 3. TEM images of a) Na-MOR and b) ZnS-MOR, scales on imagesare 1μm and 200nm respectively

EXPERIMENTAL

Synthesis of mordenite zeolite

High silica content Mordenite zeolite crystals were synthesized without organic template using a modified recipe reported by Kim et al. 3.45 g of sodium hydroxide (NaOH) was dissolved in 20 ml of distilled water. Sodium aluminate (1.56 g) was then added to the NaOH solution. This was stirred until a transparent solution was formed. Additional 80 ml of distilled water was added during the stirring process. 29 ml of Ludox HS-30 (colloidal silica 30 wt.% suspension in H_2O) was then added to the solution and, this mixture was stirred for 1hour until a uniform gel was formed. The molar composition of the above gel was $6Na_2O:Al_2O_3:20SiO_2:780H_2O$. The gel was transferred to a Teflon lined steel autoclave and heated at 170°C for 7 days. The as-synthesised zeolite was then filtered, thoroughly washed with deionized water and dried at 110°C overnight.

Ion exchange

The cation sources used for ion exchange were $NaNO_3$and Na_2S. The mass of each cation source was calculated so that the exchange solutions contained a surplus of the exchanging cation that was twice the theoretical amount of Na^{+}in the pores of 1 g of mordenite zeolite.

$NaNO_3$ was first dissolved in 50 cm^3 of deionized water. 1 g of the as-synthesised mordenite zeolite was added and the solution was stirred for 6 hours at 65 °C. This was then filtered and washed with deionized water and the exchanged zeolite left in an oven to dry overnight at 100 °C. The same procedure was repeated using Na_2S, with the exchanged mordenite zeolite contain Zn^{2+}.

Characterization

X-ray Powder Diffraction

The phase purity of the as-synthesised mordenite zeolite was determined by X-rays powder diffraction analysis using an X'pert high-resolution diffractometer operated at 45 kV and 40 mA, using CuKa radiation, in 2Qrange from 3°to 70°in steps of 0.02°, with a sampling time of one sec per step.

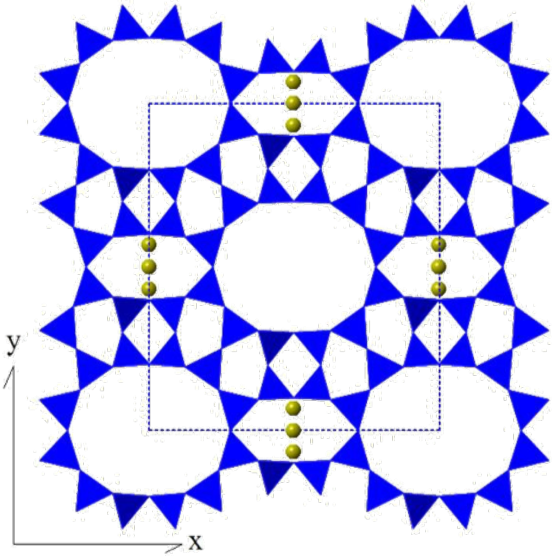

Figure 4. MOR framework with 6 member rings and 12 member ring channels along the z-axis. Na$^+$cations are shown within the channels as yellow spheres

Solid state magic angle spinning nuclear magnetic resonance

All NMR experiments were done by the EPSRC UK National solid-state MAS NMR Service at Durham. ^{29}Si and ^{27}Al spectra were recorded at 79.44 MHz using a Varian VNMRS spectrometer and a 6 mm (rotor o.d.) magic-angle spinning probe. The spectra were obtained using direct-excitation with a 5 µs 90 °pulse, 10 seconds recycle delay, at ambient probe temperature (25°C) and at a sample spin-rate of 6000 Hz. Between 200 and 500 repetitions were accumulated. Spectral referencing was with respect to an external sample of neat tetramethylsilane.

Energy-dispersive X-ray elemental analysis

The elemental analysis of Na-MOR, Zn-MOR, and ZnS-MOR was done by using the EDX spectrum of all the samples were recorded. Various scans were recorded of all the samples in order to get the accuracy of the composition of all elements.

Brunauer-Emmett-Teller (BET) surface area analysis

The BET surface analyses were run on a Micromeritics TriStar 3020 instrument. The sample was first degassed and heated to 350 °C under vacuum for 6 hours and then allowed to cool under a flow of the dry, clean stream of nitrogen.

Transmission electronic microscopy

High-resolution transmission electron microscopy experiments have been carried out on a JEOL 3000F field emission gun instrument.

CONCLUSION

From the technological, scientific and materials point of view, semiconductor ZnS clusters embedded in zeolites present very interesting advances in materials development (Iacomi, 2003; Iacomi et al., 2003; Macdougall et al., 1989; Readman et al., 2000). The zeolite matrix can be varied – possibilities include varying the pore diameter, pore size, framework geometry, internal surface and even cations (Doan et al., 2017; Fletcher et al., 2015; Gatta et al., 2009; Price et al., 2017; Sartbaeva et al., 2006; Wagner et al., 2018; Wells et al., 2015). All of those would bring changes to the cluster behavior and properties, which in term could be manipulated via chemical adjustments of the clusters. These properties make semiconductor clusters in zeolites very attractive for applications in photocatalysis, switching, signaling, displays, and other advanced applications.

Mordenite zeolite was synthesized without using any organic structure directing agents. The powder diffraction patterns show that there is no loss of framework structure after Zn and S ion exchange. A small shift to higher 2Qis observed in both Zn-MOR and ZnS-MOR samples as an indication of a decrease in unit cell parameters. ^{29}Si NMR gives three local Si environments, and all Al atoms are tetrahedrally-coordinated. ^{23}Na NMR gives two signals which indicate the successful incorporation of Zn^{2+}ions into the MOR framework. The presence of Zn and S ions in Zn-MOR and ZnS-MOR samples is proved by EDX. BET surface area analysis confirms the formation of ZnS, but it is difficult to determine whether such formation is on the surface of the mordenite zeolite crystals or within the framework channels.

Acknowledgements

PA thanks Abdul Wali Khan University, Mardan, Pakistan and AS thanks the Royal Society and University of Bath for funding. LF thanks KACST for funding a post-doc position, and PPE thanks KOPRC for funding. We would like to thank Microscopy and Analysis Suit at Bath for help with SEM and EDX work. We thank David Apperley for collecting SS NMR at the EPSRC-funded SS NMR facility at Durham University.

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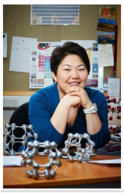

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