Influence of Tetrahydrofuran (THF) in the Synthesis of Zeolite ZK-5

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ABSTRACT

ZK-5 (KFI) molecular sieve was synthesized in the K_2O : SrO : Al_2O_3 : SiO_2 : 160 H_2O : THF system using conventional hydrothermal heating. Effect of tetrahydrofuran (THF) was investigated. Products were characterized by XRD, TGA, FESEM, EDX and TPD-MS. THF influences the crystallinity and crystal size of ZK-5. The molar ratio of THF/ Al_2O_3 from 0.4 to 1.0 gives the best results in terms of crystallinity (measured by XRD) and purity for the prepared ZK-5. Crystal size of ZK-5 zeolite is reduced by the presence of THF.

Keywords: Molecular sieves, Tetrahydrofuran (THF), ZK-5.

1. Introduction

The use of amines as templates in the synthesis of zeolites is well known and documented [1-3]. Organic compounds containing no nitrogen are rarely used as templates. The first detailed investigation of the use of THF in the synthesis of MOR, FER, MFI and MTN-type zeolites was reported by Qian et.al [4]. In that case THF was used as a template for the synthesis of high-silica zeolites due to its strong affinity with the framework siliceous [4]. Y.C. Long, et. al reported the use of THF in the synthesis of FER type zeolite with and without glycerol as organic additive[5, 6].

Zeolite ZK-5 (KFI) is a low silica zeolite with a high free pore volume of 0.305 cm³/g [7]. Pore topology of this zeolite consists of two types of cages, alpha and gamma-cages [8]. Synthesis of methylamines has been tried with acid ZK-5 as a catalyst. [9-12]. According to previous work, the structure of ZK-5 provides a promising medium for hydrogen storage [13]. It has been indicated that it is difficult to produce pure ZK-5 in the Sr, K system [13], as opposed to the Cs, K-ZK-5 system [14], and also that few literature for this system exists [13]. In this work we report the crystallization behavior of zeolite ZK-5 under hydrothermal conditions and with THF in the reactant system K₂O: SrO: Al₂O₃: SiO₂: 160 H₂O: THF. Effects of a non-nitrogen organic additive like THF on particle size, purity and crystallinity have been investigated. Standard synthesis temperature and time for hydrothermal synthesis of ZK-5 are 150°C and 144 h with a batch composition of 2.3 K₂O: 0.1 SrO: Al₂O₃: 10 SiO₂:160 H₂O [15]. The aim of this work was to synthesize K, Sr-ZK-5 with improved crystallinity, and purity by using tetrahydrofuran, a cheaper reagent than DABCO or 18-crown-6 ether, both used previously in the synthesis of ZK-5 [16, 17] .

2. Experimental

Strontium hydroxide octahydrate was dissolved in double de-ionized water (DDW). Colloidal silica Ludox (R) was added to this solution. The solution was stirred until a gel was formed. Aluminum metal was dissolved in an aqueous solution of potassium hydroxide. This second solution was added simultaneously with THF to the gel that was first prepared. Water content was adjusted to this final mixture. Final solution was stirred at room temperature for 30 minutes. The gel was charged into a Teflon (R) lined stainless steel autoclave for conventional hydrothermal synthesis. Batch composition of crystallization mixtures is given in Tables 1 to 3. Temperature was kept at 150°C.

Solid products were recovered by centrifugation and washed with de-ionized water until pH of washing water was neutral. Products were dried at 100°C overnight. Products were characterized by XRD on a Scintag XDS-200 powder diffractometer on finely powdered samples using Cu-K α radiation. The crystal size reported is the average of the values obtained by applying Scherrer's equation to lines 2θ : 9.44, 20.12, 21.22, 29.41, and 31.70. The instrumental line broadening was measured using a LaB6 standard. Crystallinity of samples was calculated by XRD using the method reported by Szostak [18]. The sample with the most intense ZK-5 diffraction peaks was selected as a standard (Run 4) and 100% crystallinity was assigned to it. The crystallinity of the others samples was relative to this standard. The sum of the intensities of the peaks at 2θ 9.44, 20.12, 21.22, 29.41 and 31.70 [13] for each sample was divided by the sum of the intensity of the same peaks for the standard and multiplied by 100.

Morphology was determined on a Zeiss DSM 982 Gemini field emission scanning electron microscope (FESEM) with a Schottky emitter at an accelerating voltage of 2 kV with a beam current of about 1 μ A. An ECON IV energy dispersive X-ray (EDX) analyzer model 9800 was used for EDX studies. An average of three analyses was done to calculate average concentrations and chemical compositions.

Thermogravimetric analysis (TGA) was done on a DuPont 951 Thermogravimetric Analyzer. Temperature programmed desorption-mass spectrometry (TPD-MS) was used to determine THF. Approximately 20 mg of sample 6 (See Table 1 for description of sample) was packed in a quartz tube and loaded to a tubular furnace equipped with an Omega temperature controller. Samples were purged with helium for 4 h at room temperature followed by heating to 700°C at 15°C/min. Helium carrier gas at the exhaust was analyzed with a MKS-UTI PPT quadrupole residual gas analyzer. Evolution of water (m/z 18), oxygen (m/z 32), carbon dioxide (m/z 44), and tetrahydrofuran (m/z 42, m/z 72) were monitored.

3. Results

XRD patterns of samples prepared with different THF/ Al_2O_3 ratio, described in Table 1, are shown in Figure 1. XRD results show that the position of the peaks of samples prepared with different THF/ Al_2O_3 ratio (Fig. 1 b to 1d) is similar to that for ZK-5 (Fig. 1a) with a difference only in the intensities [16, 19]. The molar ratio of THF/ Al_2O_3 from 0 to 0.5 was used in the case of samples shown in Figure 1a to 1 d. An increase in crystallinity of ZK-5 was observed when a THF/ Al_2O_3 of 0.5 was used. Increasing the THF/ Al_2O_3 ratio from 2 to 3 (Fig. 1f and Fig. 1g) produced ERI (ERI is the three letter code of the International Zeolite Association for zeolite with the erionite

framework) impurities in the X-ray pattern [13, 20]. THF/ Al_2O_3 ratio of 1 (Fig. 1e) shows X-ray pattern that corresponds to ZK-5. These results suggest that when the THF/ Al_2O_3 ratio is kept between 0.4 and 1 the best results in terms of crystallinity of ZK-5 are obtained. Further increase in THF/ Al_2O_3 favors the formation of ERI type zeolite. The crystal size of ZK-5 measured by XRD decreased with the use of THF. From SEM micrographs (Fig 2), the particle size of ZK-5 prepared with THF is similar to that of ZK-5 prepared without THF, but the particles of ZK-5 prepared with THF have a less smooth surface.

Effects of changing the Si/Al ratio by decreasing aluminum in the initial gel can be seen in Tables 2 and 3. X-ray patterns can be seen in Figure 3. Table 2 and Fig. 3a to 3d show the effect of increasing the Si/Al ratio in the synthesis of ZK-5 without THF and Table 3 and Fig. 3e to 3h show the change in Si/Al ratio using a constant ratio of THF/ Al_2O_3 of 0.5. From Fig. 3b (Si/Al=2.7) the position of peaks is similar to those of the prepared ZK-5 (Fig. 3a). When the Si/Al ratio is increased to 2.80 by decreasing the aluminum content in the initial batch composition by 20 mol% (Fig. 3c) the crystalline structure of ZK-5 is preserved and an ERI co-crystallization phase is present in the X-ray pattern. A further increase in Si/Al ratio to 3.6 by decreasing the aluminum content of the initial reacting gel by a 30 mol% leads to an amorphous material (Fig. 3d).

A similar trend is shown in Fig. 3e to 3h when Si/Al is changed from 2.7 to 3.5 keeping a constant THF/ Al_2O_3 ratio of 0.5. A decrease of 30 mol% in the aluminum content of the initial reacting gel with THF/ Al_2O_3 ratio equal to zero and 0.5 resulted in both cases in amorphous material as shown in Fig. 3d and 3h.

The addition of THF to the reacting gel with increased Si/Al ratio favors the formation of a higher ERI type zeolite to ZK-5 ratio. Comparing experiments from Tables 2 and 3, the addition of THF in a molar ratio of THF/Al₂O₃ of 0.5 to a reacting gel of ZK-5 whose Si/Al ratio has been increased up to 10 mol% by a decrease in the aluminum content of the initial reacting gel, improves the crystallinity of the product. Further increases in this Si/Al ratio (See runs 12 and 13. Table 3) favor the production of ERI type zeolite in the first case, and amorphous material in the second case. Fig. 4 shows the SEM micrographs of ZK-5 prepared with different Si/Al ratio with and without THF. The particle size of ZK-5 does not seem to be greatly affected by the addition of THF, but the surfaces of the particles seem to have more defects than the ZK-5 prepared without THF.

TGA and TPD-MS analyses for sample labeled 6 with a THF/Al₂O₃ molar ratio of 2 (see Table 1 for description of sample) can be seen in Figs. 5 and 6 where evidence of THF is observed. The weight loss at around 100 °C corresponds to the loss of physisorbed water in the sample [21]. A weight loss peak due to THF escaping from ZK-5 occurs at 250-400°C as shown in TG analysis (Fig 5). TPD-MS results for ZK-5 with a molar ratio THF/Al₂O₃ of 2 (entry 6 Table 1) is in agreement with this result. Evolution of THF (m/z 42 and 41) from ZK-5 is shown in Fig 6. Mass peaks at m/z 42 and 41 were selected because they are the most abundant fragments in the THF mass spectrum [22]. Evolution of THF starts at 200°C reaching a maximum at around 300°C and is totally gone at 400°C. The m/z value is mainly 42, which indicated that THF comes off the sample mostly as THF not as a decomposition product.

4. Discussion

THF, $(\text{CH}_2)_4\text{O}$, plays an important role in the crystallization of ZK-5. THF is a polar cyclic ether; the oxygen has two lone electron pairs, which can form hydrogen bonds with HO-groups from water or silanol, and complexes with cations. At low temperature THF forms hydrogen bonds with water [23] as the temperature increases, the association between THF and water decreases, there is more THF available to interact with other species [24]. In the reacting gel the oxygen of THF could interact with K^+ , Sr^{2+} , Al^{3+} , water, and Si-OH. Atwood, et. al [25] were able to crystallize a complex between THF and aluminum chloride, they reported that there is a strong interaction between the free electrons of THF's oxygen and the positive charges of aluminum.

ZK-5 with the highest crystallinity and purity among the synthesized products was obtained in the range of THF/ Al_2O_3 from 0.4 to 1. At a higher molar ratio of THF/ Al_2O_3 , ERI zeolite co-crystallized with ZK-5. Increasing the Si/Al ratio of the reacting gel, without THF, ERI type zeolite co-crystallized with ZK-5. Amorphous material was formed when the Si/Al ratio was further increased. These results are consistent with those reported, for the synthesis of ZK-5 under similar conditions, by Russell, et.al [13]. Zeolites are metastable phases and ERI type zeolite is in the crystallization field of ZK-5.

The reacting gel with a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 10 produced ZK-5 co-crystallized with ERI type zeolite when the ratio of THF/ Al_2O_3 increased from 1 to 3. Apparently, the effect of increasing the THF/ Al_2O_3 ratio has the same effect as increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ in absence of THF. This may indicate that THF was interacting with the

species in the starting gel, increasing the effective $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. THF could interact with Al^{3+} forming complexes [25].

When the molar ratio $\text{THF}/\text{Al}_2\text{O}_3$ was kept in the range 0.4 to 1.0, and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 10, the crystallinity of ZK-5 was improved (85 to 100 %) compared to the material synthesized without THF. Apparently, THF contributes to the transformation of amorphous gel to crystalline zeolite. The mechanism of such transformation is very complex due to the heterogeneity of the mixture and it is more difficult to study than the crystallization from clear suspensions [1].

Results of thermogravimetric analysis for the zeolites synthesized with THF (results not shown here) were similar to those presented in figure 5. A weight loss at around 100 °C related to the loss of physisorbed water, and a weight loss at temperature higher than 200 °C, which corresponds to the loss of THF was detected. The temperature at which THF was release from the solid was higher than its boiling point maybe due to a) strong interaction between the organic molecule and the inorganic framework [26-28], b) the process of adsorption/desorption in the pores of a zeolite could be studied as capillary condensation, in this process the boiling point of liquids is higher than the boiling point in free state at normal pressure [28], and c) the aperture of the channel is a eight membered ring that difficult the desorption process [16].

Adsorption of THF after ZK-5 crystal formation should be very difficult. The size of the THF molecule is $0.52 \times 0.52 \times 0.49 \text{ nm}$ [4], larger than the pore size of ZK-5 (0.39 nm) and ERI ($0.36 \times 0.51 \text{ nm}$) [29]. The aluminosilicate framework must grow around the THF molecule [15].

The crystal size of ZK-5 synthesized with THF, calculated using Scherrer's equation from the XRD pattern, was smaller (Run 4, 66 nm) compared to ZK-5 synthesized under similar conditions but without THF (Run 1, 87 nm). These samples have similar particle size from SEM micrographs (Figures 2a and 2d). The surface of the cubic particles, typical of ZK-5, becomes less smooth when the content of THF in the reacting gel was increased (Figure 2).

The effect in size and shape of zeolites synthesized in presence of organic molecules that can form complexes with aluminum was studied by T. Ban et. al. [30]. In some cases the crystal size of one type of zeolite increased and the crystal surface was smooth, with other organic ligands the opposite effect was observed.

M. W. Anderson et. al [31] studied crystal growth of zeolites and according to them, it is a layer growth process. The density of defect sites increases when the nucleation rate increases; they also mentioned that the structure directing agents lock into the growing surface and help attaching the new layer.

The surface roughness of the crystals increased when the THF/ Al_2O_3 ratio increased. The presence of THF in the gel could increase the nucleation rate, and reduce the rate of crystal growth, decreasing the crystal size of the zeolite. THF in excess increases surface roughness maybe because the polar part of THF interacts with one layer of the framework and the apolar (-CH-) part of the THF attached to the surface of a growing crystal may repel a new layer, reducing crystal size and increasing density of defects.

5. Conclusions

THF influences the crystallinity and crystal size of ZK-5. The molar ratio of THF/ Al_2O_3 from 0.4 to 1.0 gives the best result in terms of crystallinity and purity for the prepared ZK-5. Crystal size of ZK-5 zeolite is reduced by the presence of THF. As the Si/Al ratio increases with a decrease in aluminum content in the initial batch composition, the ERI co-crystallization phase appeared along with ZK-5 zeolite.

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References

1. M. E. Davis, R. F. Lobo, Chem Mater. 4 (1992) 756.
2. R. F. Lobo, S. I. Zones, M. E. Davis, J. Inclusion Phenom. Mol. Recognit. Chem. 1 (1991) 47.
3. G. -Q. Guo, Y.-C. Long, Advances in Chemical Industry. 19 (2000) 16.
4. B. Qian, G. Guo, X. Wang, Y. Zeng, Y. Sun, Y. Long, Phys. Chem. Chem. Phys. 3 (2001) 4164.
5. G. Q. Guo, Y.J. Sun, Y.C. Long, Studies in Surface Science and Catalysis 135 (2001) (Zeolites and Mesoporous Materials at the Dawn of the 21 st Century) 527.
6. X.-W. Cheng, J.Wang, J. Guo, H.Y. He, Y.. C. Long. Micropor. Mesopor. Mater. 119 (2009) 60-67.
7. J. Jänchen, J. H. M. C. van Wolput, W. J. M. van Well, H. Stach, Thermochemica Acta. 379 (2001) 213.
8. W.J.M. Van Well, J. Jaenchen, J.W. De Haan, R.A. Van Santen, Journal of Physical Chemistry B 103 (1999) 1841.
9. S. Schwarz, D.R. Corbin, G.C. Sonnichsen, Microporous and Mesoporous Materials. 22 (1998) 409.
10. D.R. Corbin, S. Schwarz, U.S. Patent No. 5 344 989 (1994).
11. L. Abrams, D.R. Corbin, R.D. Shannon, U.S. Patent No. 4 814 503 (1989).
12. R. D. Shannon, M. Keane, L. Abrams, R. H. Staley, T. E. Gier, G. C. Sonnichsen, Journal of Catalysis. 115 (1989) 79.
13. P.C. Russell, S.L. Stuhler, A.L. Kouli, J. Warzywoda, A. Sacco, Jr, Studies in Surface Science and Catalysis. 135 (2001) 295.

14. H.E. Robson, U.S. Patent No. 3 720 753 (1973).
15. J.P. Verduijn, U.S. Patent No. 4 994 249 (1991).
16. T.Chatelain, J. Patarin, R. Farré, O. Pétigny, P. Schulz. *Zeolites*. 17 (1996) 328.
17. G.T. Kerr. *Inorganic Chemistry*. 5 (1966) 1539.
18. R. Szostak, *Molecular Sieves Principles of Synthesis and Identification*, 2nd edition, Thomson Science, London, 1998.
19. J.F. Yang, R. Krishna, J.M. Li, J.P. Li. *Microporous and Mesoporous Materials* 184 (2014) 21-27.
20. M.M.J. Treacy, J.B. Higgins. *Collection of Simulated XRD Powder Patterns for Zeolites*. 4 ed. Elsevier, Amsterdam, 2001.
21. G. Pál-Borbély, in: H.G. Karge, J. Weitkamp (Eds.), *Characterization II. Molecular Sieves. Science and Technology*, Springer-Verlag, Berlin, 2007, pp. 67-102.
22. M. Dampc, E. Szymanska, B. Mielewska, M. Zubek. *J. Phys. B: Atomic, Molecular and Optical Phys.* 44, 5(2011) 55206.
23. Sh.I. Mamatkulov, O.B. Ismailova, A.A. Saidov, P.K. Khabibullaev *Doklady Physical Chemistry* 430 (2010) 5-9.
24. R.P.W Scott. *J. Liq. Chrom and Rel. Technol.* 23 (2000) 3083-3093
25. N.C. Means, C.M. Means, S.G. Bott, J. L. Atwood. *Inorg. Chem* 26 (1987) 1466-1468
26. Y.C. Long, H.W.Jiang, H. Zong, *Langmuir*. 13 (1997) 4094.
27. B. Qian, H.W.Jiang, Y.J. Sun, Y.C. Long, *Langmuir*. 17 (2001) 1119.
28. H. Yang, Z.H. Ping, G.X. Niu, H.W. Jiang, Y.C. Long, *Langmuir*. 15 (1999) 5382.

29. W.M. Meier, D.H. Olson, Ch. Baerlocher, Atlas of Zeolite Structure Types, 4th edition, Elsevier, London, 1996.
30. T. Ban, M. Takamura, M. Morikawa, Y. Ohya. Materials Chemistry and Physics 137 (2013) 1067-1072.
31. M.W. Anderson, J. R. Agger, N. Hanif, O. Terasaki. Microporous and Mesoporous Materials 48 (2001) 1-9.

Table 1

Influence of THF/Al₂O₃ ratio on the crystallization of ZK-5.

Run	THF (x)	Average Crystal Size	% Crystallinity
No.		ZK-5 (nm)	
1	0	87	86
2	0.2	42	52
3	0.4	72	85
4	0.5	66	100
5	1	65	89
6	2	43	57
7	3	53	36

Conventional hydrothermal synthesis. Time 144 h, Temp=150°C.
Batch Composition 2.3K₂O:0.1SrO:Al₂O₃:10SiO₂:160H₂O:x THF

Table 2

Influence of different Si/Al ratio on the crystallization of ZK-5.

Run	Al₂O₃	Si/Al	Average Crystal	% Crystallinity
No	(y)	product	Size ZK5(nm)	
1	1	2.7	87	86
8	0.9	2.7	60	56
9	0.8	2.8	52	43
10	0.7	3.6	-	-

Conventional hydrothermal synthesis. Time 144 h, Temp=150°C.

Batch Composition 2.3K₂O:0.1SrO:yAl₂O₃:10SiO₂:160H₂O:xTHF, x=0.

-Amorphous

Table 3

Influence of different Si/Al ratio on the crystallization of ZK-5 with a constant THF/Al₂O₃ ratio of 0.5

Run	Gel composition		Si/Al	Average Crystal	% Crystallinity
No	Al ₂ O ₃	THF	product	Size ZK-5 (nm)	
	(y)	(x)			
4	1.0	0.5	2.7	66	100
11	0.9	0.45	2.7	54	78
12	0.8	0.40	2.9	41	40
13	0.7	0.35	3.5	-	-

Conventional hydrothermal synthesis. Time 144 h, Temp=150°C. Batch Composition
 2.3K₂O:0.1SrO:yAl₂O₃:10SiO₂:160H₂O:xTHF
 -Amorphous

Figure Captions

Figure 1. XRD patterns of ZK-5 zeolites obtained by hydrothermal synthesis at 150°C, 144h in the reacting system: 2.3 K₂O:0.1 SrO:Al₂O₃:10 SiO₂:160 H₂O:x THF. (a) Run 1, x=0, (b) Run 2, x=0.2, (c) Run 3, x=0.4, (d) Run 4, x=0.5, (e) Run 5, x=1.0, (f) Run 6, x=2.0, (g) Run 7, x=3.0

Figure 2. FESEM micrographs of ZK-5 zeolites obtained by hydrothermal synthesis at 150°C, 144h in the reacting system: 2.3 K₂O:0.1 SrO:Al₂O₃:10 SiO₂:160 H₂O: x THF. (a) Run 1, x=0, (b) Run 2, x=0.2, (c) Run 3, x=0.4, (d) Run 4, x=0.5, (e) Run 5, x=1.0, (f) Run 6, x=2.0, (g) Run 7, x=3.0

Figure 3. XRD patterns of ZK-5 zeolites obtained by hydrothermal synthesis at 150°C, 144h in the reacting system: 2.3 K₂O:0.1 SrO: y Al₂O₃:10 SiO₂:160 H₂O: x THF. Molar ratio THF/Al₂O₃=0 for samples from (a) to (d) and THF/Al₂O₃= 0.5 for samples from (e) to (h). (a) Run 1, y=1.0, (b) Run 8, y=0.9 (c) Run 9, y=0.8 (d) Run 10, y=0.7, (e) Run 4, y=1.0 (f) Run 11, y=0.9 (g) Run 12, y=0.8 (h) Run 13, y=0.7.

Figure 4. FESEM micrographs of ZK-5 zeolites obtained by hydrothermal synthesis at 150°C, 144h in the reacting system: 2.3 K₂O:0.1 SrO: yAl₂O₃:10 SiO₂:160 H₂O: x THF. Molar ratio THF/Al₂O₃=0 for samples from (a) to (d) and THF/Al₂O₃= 0.5 for samples from (e) to (h). (a) Run 1, y=1.0, (b) Run 8, y=0.9 (c) Run 9, y=0.8 (d) Run 10, y=0.7, (e) Run 4, y=1.0 (f) Run 11, y=0.9 (g) Run 12, y=0.8 (h) Run 13, y=0.7.

Figure 5. TGA result of ZK-5 zeolite obtained by hydrothermal synthesis at 150°C, 144h in the reacting system: 2.3 K₂O:0.1 SrO:Al₂O₃:10 SiO₂:160 H₂O: 2 THF (Run 6).

Figure 6. TPD-MS results for ZK-5 sample (Run 6 Table 1) obtained by hydrothermal treatment at 150°C, 144h in the reacting system: 2.3 K₂O:0.1 SrO:Al₂O₃:10 SiO₂:160 H₂O: 2 THF.

Figure 1.

Figure 2.

Figure 3

Figure 4

Figure 5

Figure 6

ZK-5