

PAPER • OPEN ACCESS

Catalytic Activity of Mordenite from Natural Source in the Dimerization of α -methylstyrene

To cite this article: K R Ahmed *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **454** 012029

View the [article online](#) for updates and enhancements.

You may also like

- [Synthesis and characterization of mordenite-type zeolites with varying Si/Al ratio](#)
Mon Bryan Z Gili and Marlon T Conato
- [Preparation and Characterization of mordenite Zeolite from Iraqi Sand](#)
H M Hussain and A A K Mohammed
- [Comparative study using different external sources of aluminum on the zeolites synthesis from rice husk ash](#)
Marcos Antonio Klunk, Mohuli Das, Sudipta Dasgupta et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Catalytic Activity of Mordenite from Natural Source in the Dimerization of α -methylstyrene

K R Ahmed¹, O S Travkina², N G Grigor'eva², and B I Kutepov²

¹The Department of Chemistry, Faculty of Science, University of Zakho, Zakho International Road, Duhok 42001, Kurdistan Region-Iraq

²Federal State Budget Institution of Science, Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 prosp. Oktyabrya, 450075 Ufa, Russian Federation

Abstract. Studying the activity of any catalyst and selectivity toward special products is easy by selecting a module reaction, and choosing appropriate condition. In our case the reaction of α -methylstyrene dimerization was a choice to study the activity of mordenite type zeolite crystallized from natural clay mineral (kaolin P-2), and also the selectivity toward dimers. The prepared catalyst in the form of hydrogen showed that the acceptable activity and selectivity to linear dimers were (72.5%), at 80 °C, and atmospheric pressure. Different products from the dimerization of α -methylstyrene over prepared catalyst was investigated, and the conversion rate reached to 73%wt.

1. Introduction

For decades chemicals manufacturing, petrochemicals, and oil industry are depended on the implementation of solid acid catalysts (heterogeneous), dominating commercial catalysis. [1]

Mordenite (MOR) zeolite, establishes private position among the other kinds of zeolite due to its special properties, and thus MOR-zeolite has been applied as catalyst for significant reaction, such as isomerization, alkylation, cracking, etc... [2, 3, 4].

Generally powdered MOR-zeolite in their Na-form prepared using aqueous solution of Na-silicates and Na-aluminates [5].

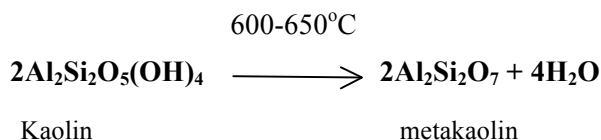
MOR-zeolite exists naturally and it can be synthesized. In the development of the industrial process for the production of particular products, it is almost necessary to solve the problems of reducing its cost and simplifying technology for the synthesis, as well as taking into account the environmental consideration. In the production of zeolites, these mentioned problems are tried to solve, including the partial or complete replacement of synthetic sources of Al and Si, into natural aluminosilicates. One of the most suitable raw materials is kaolin [6, 7].

Recently many synthesis procedures of powdered MOR-zeolite have been published. The synthesis is depending on raw materials as source of Al and Si from natural and synthetic sources [8-12].

Using natural clay minerals as an alternative source of raw materials (Si and Al) in the zeolite synthesis documented in [13].

Prior to use kaolin as source for Si and Al in the synthesis of MOR-zeolite, it requires applying high temperature (calcination at 600 °C for 4h) to convert kaolin into amorphous metakaolin [14].





Dimers produced from alpha-MS (α -methylstyrene) dimerization reaction can be well manufactured over solid acid catalyst crystallized from zeolites. N. G. Grigor'eva et al. and V. P. Talzi et al. showed that the selectivity of linear dimers over Y-zeolite is 90-92% [15, 16].

The products of alpha-MS dimerization resulting in the formation of linear, cyclic dimers, and trimers, are described in [17].

It is familiar that using clay minerals as a source material of crystallization of zeolite in the alpha-MS dimerization reaction differ from other kinds of catalysts. Therefore we excited to study the activity of MOR-zeolite obtained from Prosyansky kaolin P-2 in the dimerization of alpha-MS as module reaction.

2. Experimental

2.1 Chemicals

Commercial clay mineral Prosyansky kaolin abbreviated as P-2 used as source of Si and Al to prepare MOR type zeolite. The chemical composition of P-2 is given in table 1. Ufaorgsyntes Ufa, Russia was provided the alpha-MS (α -methylstyrene), and prior to use alpha-MS subjected to distillation.

Table 1. Chemical composition of P-2 clay [14]

Material	Content % wt.					
	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	TiO ₂	CaO
Prosyansky kaolin P-2	56.1	41.5	0.2	0.6	0.8	0.8

2.2 Synthesis of MOR type zeolite

MOR type zeolite from kaolin P-2 (P-2 converted to metakaolin prior to synthesis MOR) and MOR from aqueous solution of Na-aluminate and Na-silicate were prepared in their Na-forms as described in [18].

2.3 Synthesis of Solid Acid Catalysts

The both samples; MOR-zeolite from kaolin P-2 and from aqueous solution of silicate and aluminate, converted to NH₄-form of zeolite using ion exchange of Na⁺ ion by NH₄⁺ ion in aqueous solution of NH₄NO₃. Following the exchange of Na⁺ ion by NH₄⁺ ion, samples were thermally treated at 540 °C for four hours to synthesis of the solid acid catalysts 0.96 HNaMOR from kaolin P-2, and 0.94 HNaMOR from aqueous solution of aluminate and silicate.

2.4 Evaluation of Solid Acid Catalysts Activity

The activity of 0.96 HNaMOR, and 0.94 HNaMOR catalysts in the dimerization reaction of alpha-MS was performed. Before testing catalysts, both samples were thermally treated at 300-350 °C for three hours under inert atmosphere using argon.

Three-neck flask used as reactor provided with mechanical stirrer. Chlorobenzene used as solvent. 0.96 HNaMOR, and 0.94 HNaMOR catalysts activity was determined as a function of alpha-MS conversion(K), and the dimerization products selectivity.

2.5 Solid Acid Catalysts and Products Characterization

Different techniques were applied to characterize the zeolite samples and dimerization products. Zeolites and 0.96 HNaMOR, and 0.94 HNaMOR catalysts well characterized by x-ray diffraction technique, and classic temperature programmed desorption of NH₃ system (TPD- NH₃). The

adsorption capacity of the solid catalysts was measured by the vapours of C_7H_{16} , C_6H_6 , and H_2O at 20 °C and P/Ps = 0.7 - 0.8 using the desiccator method which described in [19].

The analysis of products from alpha-MS dimerization reaction were performed by (Tsvet) chromatograph with a flame-ionization detector, a (2mx2mm) column packed with 5% SE-30-coated Chromaton HMDS, in the style of temperature programming from 50 to 280 °C at a rate of (8 K/min), and detectors and evaporator temperatures of 250 and 300 °C, respectively, using He as a carrier gas at a flow rate of 30 ml/min.

Collected data on catalytic activity in dimerization reaction and physicochemical properties of zeolite samples and catalyst from kaolin P-2 were compared with conventional MOR zeolite catalyst which crystallized from aqueous solution of Na-silicate and Na-aluminate.

3. Results and discussion

3.1 Characterizations of the Catalysts

Acidic properties obtained by TPD- NH_3 and thermal stability distinguish MOR zeolite from other types of zeolite. The catalysts used in this work were 0.96 HNaMOR zeolite and 0.94 HNaMOR zeolite, and the acidity for both samples is high enough to serve as acid catalyst as shown in table 2. Solid acid catalyst 0.96 HNaMOR contains less (strong) acidic sites than 0.94 HNaMOR.

Table 2. Equilibrium adsorption capacities and acidic properties of zeolite samples and catalysts

No	Sample	Equilibrium adsorption capacities (cm^3/g) for:			Na ₂ O cont. α - Na ₂ O %		Amount of desorbed NH ₃ $\mu mol/g$ sample		
		H ₂ O	C ₆ H ₆	n-C ₇ H ₁₆			100-350 °C	350-550 °C	100-550 °C
1	MOR from kaolin(P-2)	0.14	0.12	0.14	6	-	377	44	421
2	Sample 1 after 4 ion exchange	0.16	0.185	0.22	0.24	0.96	624	476	1100
3	large pores MOR	0.17	0.16	-	6.4	-	349	37	386
4	Sample 3 after 4 ion exchange	0.19	0.18	0.20	0.40	0.94	719	597	1316

It is clear from the data listed in table 2 of adsorption capacity by water, benzene, and n-heptane vapours that the 0.96 HNaMOR catalyst has higher adsorption capacity of benzene, and n-heptane vapours than the 0.94 HNaMOR catalyst. We suppose that, during crystallization process of mordenite type zeolite from kaolin two or more crystalline particles are joined together to form a structure in addition to surface of zeolite that use the internal space between these particles to uptake more molecules of heptane and benzene.

The condition of crystallization and chemical composition of prepared zeolite from the reaction mixture ($3Na_2O \cdot Al_2O_3 \cdot 12SiO_2 \cdot 300H_2O$) are given in table 3.

Table 3. Crystallization conditions and chemical composition of the prepared zeolites

The reaction mixture composition	Zeolite sample	SiO ₂ /Al ₂ O ₃ mol. ratio	τ , h	T, °C	Chemical composition % mass		
					Na ₂ O	Al ₂ O ₃	SiO ₂

$3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{SiO}_2 \cdot 300\text{H}_2\text{O}$	Mordenite from kaolin P-2	10.1	13	145-150	6	13.5	80.5
$3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{SiO}_2 \cdot 300\text{H}_2\text{O}^a$	large pores mordenite	9.8	10	145-150	6.4	13.9	79.7

^a Specific Surface Area 278 m²/g

3.2 Evaluation the Catalytic Activity of Catalysts

The results that we have in this study of the activity of zeolite samples and prepared catalysts in the dimerization reaction of alpha-MS are illustrated in table 4. This Table shows that, there are no β -linear dimers in the products of dimerization in the presence of Na-form zeolite from aqueous solution and 0.94 HNaMOR catalyst, but the selectivity of MOR zeolite from kaolin toward β -linear dimers is 0.6%. This allows us to suppose that, the low amount of TiO_2 , Fe_2O_3 and CaO in raw kaolin used in crystallization is promoting the forming β -linear dimers. The amount of linear dimers increased over catalysts from kaolin P-2 and aqueous solution as a source of Al and Si by 69.6% and 16.4% respectively. Thus, under the condition of dimerization reaction that we used, linear dimers dominate the portion. For both samples used in this study products of trimer species were investigated.

It is evidence that, from the results of dimerization reaction the selectivity of linear dimers rely on the type of material used for the zeolite crystallization. In addition the selectivity towards linear dimers increased after ion exchange of Na^+ ion by NH_4^+ ion followed by heat treatment to get H-form of zeolite.

As stated by the adsorption capacity measured by water, benzene, and n-heptane vapours, and XRD-data as shown in figure 1, all zeolite samples prepared and used in this study have the crystallization degree close to 100%.

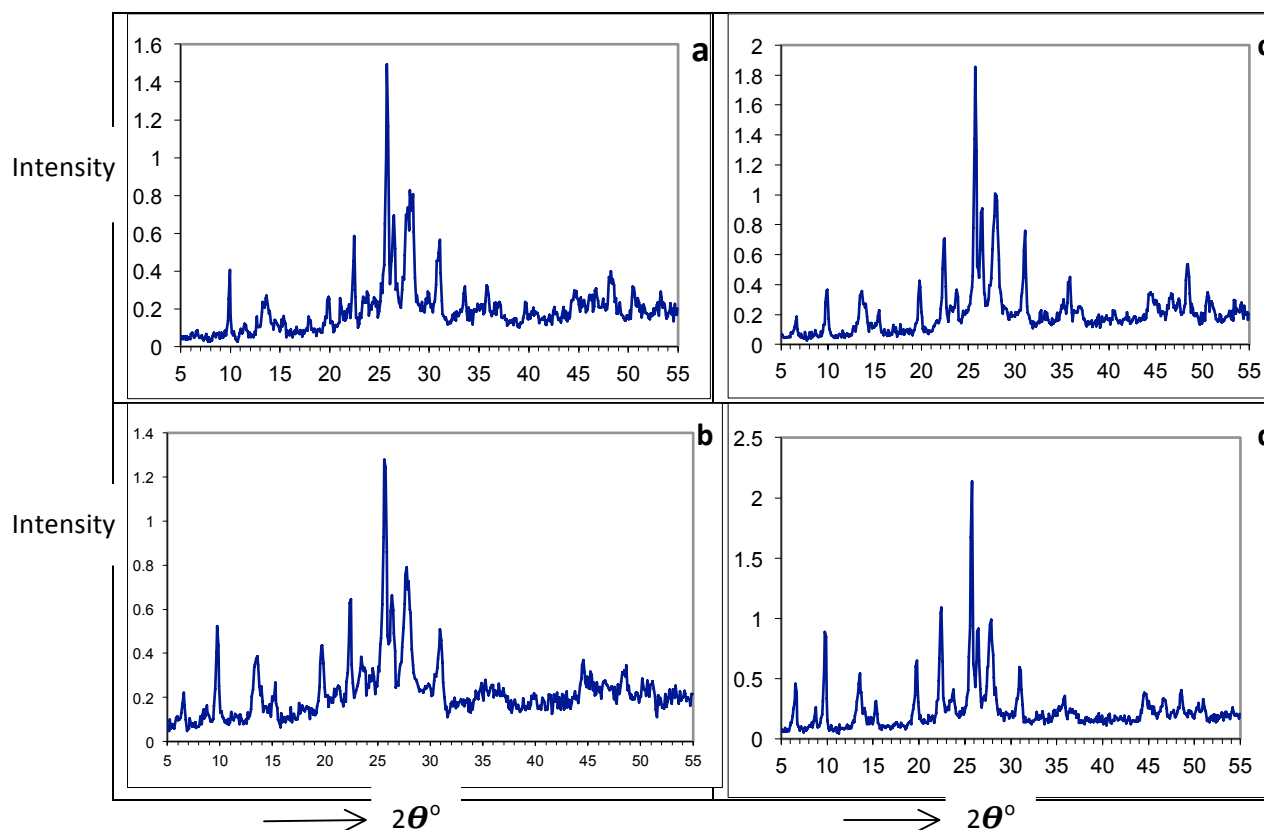


Figure 1. X-ray diffraction patterns of the catalysts and MOR-zeolite samples:

- a) MOR from kaolin (P-2).
- b) 0.96 HNaMOR catalysts.
- c) MOR zeolite from aqueous solution of aluminate and silicate.
- d) 0.94 HNaMOR catalysts.

Table 4. α -Methylstyrene dimerization on MOR zeolite samples and catalysts
Conditions: Chlorobenzene solvent, 10% cat., 80 °C, 3h, Ar-atmosphere

catalyst	SiO ₂ /Al ₂ O ₃ mol. ratio	α -MS conversion, %wt	Selectivity, %				
			Oxidation products	linear dimer		cyclic dimer	trimers
				α	β		
MOR from kaolin(P-2)	10.1	8.40	75.2	2.4	0.6	0	21.8
0.96 HNaMOR	10.1	73.0	3.8	72.5	-	11.8	11.9
large pores MOR	9.8	14.74	20.4	59.8	-	13.4	6.4
0.94 HNaMOR ^a	9.8	59.2	10	76.2	-	5.4	8.4

^a Specific Surface Area 393 m²/g

It is clear from the results listed in table 4 that, the catalyst 0.96 HNaMOR exhibits good catalytic activity in the dimerization reaction of α -MS, and the activity for 0.96 HNaMOR is higher than 0.94 HNaMOR activity.

The α -MS conversion over 0.96 HNaMOR catalyst is increased by 64.6 wt% after ion exchange process, and by 44.5 wt. % over 0.94 HNaMOR catalyst. Thus, the conversion percentage of prepared catalyst from kaolin P-2 is better than conventional catalyst crystallized from aqueous solution of silicates and aluminates.

Since the purpose of this study was to observe the activity of MOR catalyst crystallized from kaolin, it was fixed that the catalyst prepared from kaolin P-2 is active in the dimerization reaction of α -MS.

This high activity registered, could be due to the concept of almost acidic sites of 0.96 HNaMOR catalyst are reachable by α -MS molecules and the products of dimerization can desorbed out easily from porous and the channels of prepared catalyst.

It is important to point out that, without using of solvent in the dimerization reaction of α -MS led to fast deactivation of 0.96 HNaMOR and 0.94 HNaMOR catalysts as mentioned in [18]. Therefore, the conversion of α -MS in dimerization reaction is preferred in the presence of solvent, in our case chlorobenzene. Besides to the dimerization reaction of α -MS over tested samples in chlorobenzene solvent, formation of oxidation products was also examined. Table 4.

Note. *The results on large pores MOR and 0.94 HNaMOR were published in [18], and provided in this work as reference for the comparison with MOR from kaolin and prepared catalysts.*

4. Conclusion

Mordenite type zeolite exhibit unique properties with respect to both activity and selectivity. The dimerization reaction of α -MS over zeolite catalysts allowed us to investigate the activity and selectivity of 0.96 HNaMOR catalyst crystallized from kaolin followed by ion exchange process. In this study 0.96 HNaMOR catalyst converts α -MS to the products of dimerization more effectively than 0.94 HNaMOR which associated with the SiO₂/Al₂O₃ molar ratio and with the different content of acid sites.

A comparison of the catalytic activity, acidic characteristics, and adsorption capacity of the tested zeolite catalysts showed that, synthesized a promising catalyst for dimerization of α -MS based on the crystallization of clay mineral (kaolin P-2) in sodium silicate solution with the reaction mixture (3Na₂O.Al₂O₃.12.SiO₂.300H₂O) and SiO₂/Al₂O₃ molar ratio equal to 10.1.

5. References

- [1] Krijn P de Jong 2009 Synthesis of Solid Catalysts ©2009 WILEY-VCH Verlag GmbH & Co. KGaA Weinheim 3-6
- [2] Tsai T C, Chang SY, and Wang I 2003 On the Study of Operating Conditions of Cumene Disproportionation over a Commercial Mordenite. *Ind. Eng. Chem. Res.* **42**, 6053–6058
- [3] Dimitrova R, Gündüz G, and Spassova M 2006 A comparative study on the structural and catalytic properties of zeolites type ZSM-5, mordenite, Beta and MCM-41. *J. Mol. Catal. A Chem.* **243** (1) 17–23
- [4] Agabekov V E and Sen'kov GM 2006 Catalytic isomerization of light paraffin hydrocarbons *Catalysis in industry* **No.5** 31–41
- [5] Breck D W 1974 Zeolite Molecular Sieves: Structure, Chemistry and Uses (N. Y. Wiley) 788
- [6] Pavlov M L, Travkina O S, and Kutepov B I 2008 Development of Synthesis of Powdery A Type Zeolite from Kaolin *Neftepererabotka i neftekhimiya* **Issue 4 - 5** 59 - 61
- [7] Pavlov ML, Travkina OS, Kutepov BI, and Veklov V A 2008 Development of Synthesis of Powdery X Type Zeolite from Kaolin *Neftepererabotka i neftekhimiya* **Issue 4 - 5** 61 - 63
- [8] Giudici R 1999 Synthesis, Dealumination, and Adsorption Behavior of Mordenite Extrudates: diss. submitted for the degree of doctor of technical science Zurich 143
- [9] Patent 5215736 US1992IPC C01B33/34. Philippe C, Jean-Louis G, Anne-Catherine F, Jean-Francous J, Christine T, and Francis R Mordenite Type Zeolite and its Preparation Process Institut Francais de Petrole. Filing date: 30.03.; Publ. Date: 01.06.1993
- [10] Patent 4935217 USDale P SIPC C01B33/28. Mordenite and Mordenite Aggregate Syntheses Lehigh University Filing date: 10.11.1988; Publ. Date: 19.01.1990
- [11] Patent 4525466 US. IPC B01J 29/18 Enrico M, Valentino Z, Raymond L, Mario P, and Marcello S M Process for Synthetizing Zeolites having a Mordenite Structure and having High Catalytic Activity Filing date: 24.11.1982; Publ. date: 25.01.1985
- [12] Patent 5219547 US. Stuart D. Hell ring, Randy F. StriebelIPC C01B33/34, B01J29/28 Synthesis of Crystalline Mordenite Type Material Mobil Oil Corp Filing date: 04.10.1991; Issue date: 15.06.1993. 10
- [13] Marcelo L. M et al. 2008 Synthesis of Mordenite Using Kaolin as Si and Al Source *Applied Clay Science journal* **41** 99–104
- [14] Pavlov ML, Basimova R A, Travkina O S, and Kanaan R A 2012., Improvement of Synthesis Methods of Powdery Mordenite Type Zeolite © *Oil and gas business journal* **No2** 459-469
- [15] Grigor'eva N G, Paukshtis E A, and Kutepov B I et al. 2005 Type Y zeolites in the dimerization reaction of α -methylstyrene *Pet. Chem.* **45**, 419-425
- [16] Talzi V P, Doronin V P, and Sorokina T P 2000 On some methods of oligomerization of α -methylstyrene *Journal of Applied Chemistry* (St. Petersburg) **73**, 787
- [17] Grigor'eva N G, Galyautdinova R R, Paukshtis E A, et al. 2006 Dimerization of α -methylstyrene on high-silica zeolites *Petroleum Chemistry* **46** 332-337
- [18] Kanaan R A 2013 Isomerization of n-hexane over Granular Mordenite Zeolite Catalyst without Binders Ph. D. dissertation (Ufa, Russia) 73 -82
- [19] Kel'tsev N V 1984 The Fundamentals of the Adsorption Engineering Trod.Mosc.Chemistry Tech. Inst. ImMendeleeva592