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Methanol dehydration to dimethyl ether using modified clinoptilolite

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Clinoptilolite, a natural zeolite from the Semnan region in the West of Iran, has been converted to a catalyst for the methanol dehydration to dimethyl ether process. To produce such a catalyst and to create acidic sites on the latter, the ion-exchange process has been used. In addition, to investigate and optimize the effective factors of the catalyst synthesis process, a L9 Taguchi experimental design method has been implemented. The effects of four factors have been considered: the type of ion-exchange solution (2 levels); ion-exchange solution concentration; calcination temperature and calcination time (the last three factors have been studied in 3 levels). The yield of catalyst (conversion×selectivity) has been chosen as the response of the system. The catalytic behaviour of the produced samples was investigated using a fixed bed reactor (T = 350 ºC, P = 1 atm and WHSV = 4.78 h^{-1}). The results of the statistical design showed that the optimum conditions were: calcination time – 3 h, calcination temperature – 500 ºC, ion-exchange solution concentration – 2M, and ion-exchange solution – ammonium chloride. The optimum catalyst was tested using a fixed bed reactor at 330 ºC, 1 atm and WHSV= 3.8 h^{-1} resulting in 98.1% conversion and 96.5% selectivity. In order to investigate the catalyst behaviour under industrial operating conditions, the catalyst was tested in a fixed bed reactor at 300 ºC, 16 atm pressure, and WHSV = 52.5 h^{-1}. The results were 67.02% conversion and 99.74% selectivity.

Key words: *clinoptilolite; dimethyl ether; catalyst; zeolite; Taguchi experimental design*

1. Introduction

Dimethyl ether (DME), as a multi-source, multi-purpose product, has received growing attention due to the present global environmental pollution and energy supply problems. DME can be produced from syngas, which in turn is formed from natural gas, coal or biomass. DME has a wide range of applications such as LPG substitute,

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propellant, chemical feedstock and transportation fuel, and in fuel cells [1, 2]. Catalytic dehydration of methanol over an acidic catalyst offers a potential method for the production of DME, a new spray propellant. Being identified as a potential diesel and cooking fuel, DME has many excellent characteristics. It has the oxygen content of 34.78% and can be burned without soot emission, whereas for traditional diesel fuels, simultaneous NO_x and soot emission control target cannot be expected. It has a boiling point of –25 ºC, which is 20 ºC higher than LPG and can be liquefied at 0.54 MPa (20 ºC). Therefore, based on the matured technology of LPG application, as far as storage, transportation, and usage, no remarkable problem for the use of DME exists [2, 3]. The reaction occurs in zeolite and pure γ-alumina and on γ-alumina slightly modified with phosphates or titanates, in a temperature range of 250–400 ºC and pressures up to 16 bar [4–7].

The aim of this research was to investigate the potential of the clinoptilolite-rich tuff of the Semnan region of Iran to achieve catalytic properties, especially for the MTD (methanol to dimethyl ether) reaction. Adsorptive characteristics of this material in various forms have been recently reported by Falamaki et al. [8]. The size of the channels (0.72×0.44, 0.47×0.41, 0.55×0.4 and 0.72×0.44 nm^2) as reported by Ackley and Yang [9] are of the same order of the pentasil family (0.53×0.56 and 0.51×0.55 nm^2) [10], thus making it eligible to catalyze important petrochemical reactions like methanol to dimethyl ether (MTD), methanol to olefins (MTO) and syngas to dimethyl ether (STD).

2. Experimental

Catalyst synthesis. An Iranian commercial natural clinoptilolite zeolite (Afrand Tuska Company) with less than 10 wt. % crystalline SiO_2 (quartz and cristobalite), the Si/Al ratio of 5.78, and the approximate formula $(Ca_{1.41}Mg_{0.96}Na_{1.66}K_{1.01})(Al_{7.4}Si_{42.78}O_{72.00})\cdot 23H_2O$ [8] has been used. In order to perform the ion-exchange process, the zeolite was first crushed into 100 μ granules and then thoroughly washed with distilled water. In the next step, 2 dm^3 of the solution of ammonium chloride or sulphuric acid with specific concentration was used per 30 g of raw zeolite for the ion-exchange process. The mixture was mixed for 24 h at room temperature using a propellant mixer with a mixing velocity of 1000 rpm. Then the solid product was filtered out and washed with hot deionized water until pH of the water leaving the filter was about 7. Then wet solid product was again subject to the process described above. Finally, the washed and filtered solid product was dried for 12 h at 100 °C. The ion-exchanged samples were calcined for a certain period of time.

Fabrication of acidic sites on the raw zeolite was achieved through the following methods:

1. Ion-exchange with H_2SO_4:

$$Na^+ [^-O\text{-}Z] + H^+ \rightarrow [^+H^-O\text{-}Z] + Na^+$$

2. Ion-exchange with ammonium chloride and further transformation of NH_4^+ cations into protons via thermal treatment:

$$Na^+ [^-O\text{-}Z] + NH_4^+ \rightarrow NH_4^+ [^-O\text{-}Z] + Na^+$$

$$NH_4^+ [^-O\text{-}Z] \rightarrow [^+H^-O\text{-}Z] + NH_3$$

2.1. Fixed bed reactor tests

Fixed bed reactor system. A catatest system (Fig. 1), equipped with a fixed bed reactor with the inner diameter of 1.5 cm was used to examine the catalyst activity and selectivity.

Fig. 1. The catatest system

The pressure of the system was adjusted by imparting back pressure. The reactor and the pre-heater temperatures were set by an electric jacket equipped with a PID controller to the predetermined temperature with the accuracy of ±0.5 °C. Nitrogen was used as a carrier gas to provide the required pressure and for creating the desired methanol partial pressure. The flow rate of nitrogen gas was controlled by a mass flow controller (l5850E, Brooks). Liquid methanol, which consequently evaporated in the pre-heater and was mixed in gaseous state with nitrogen, was injected into the system by a dozing pump (H94X, Milton Roy). The reactor output stream, after passing through a shell and tube heat exchanger, entered a two-phase separator. The output gas from the reactor was analyzed every 10 min by an on-line gas chromatograph (Agilent model 6890N) using a TCD detector, a 0.53 mm×30 m HP-Plot Q capillary column and helium as the carrier gas.

Reactor operating conditions. In order to better investigate the catalyst selectivity, median conditions of methanol conversion to DME and to light linear olefins were chosen as the operating conditions of the reactor. For this reason, 3 g of synthesized catalyst samples were loaded into the reactor. At first, the catalyst was activated in the presence of nitrogen with a 50 $cm^3 \cdot min^{-1}$ flow rate, at the temperature of 350 °C. Then, the nitrogen flow was increased to 180 $cm^3 \cdot min^{-1}$. After stabilization of temperature, liquid methanol at a flow rate of 0.3 $cm^3 \cdot min^{-1}$ was injected into the reactor. The methanol partial pressure and WHSV in the reactor were 0.5 atm and 4.78 h^{-1}, espectively. Reaction temperature was fixed at 350 °C under atmospheric pressure.

3. Results and discussion

3.1. Taguchi experimental design catalyst

Among the most influential synthesis parameters affecting the catalytic behaviour of the modified zeolites, the following were considered based on our previous experience:

- ion-exchange solution type,
- ion-exchange solution concentration,
- calcination temperature,
- calcination time.

The method of L9 Taguchi experimental design was used to optimize the above factors in order to obtain a high active and selective catalyst for the production of DME. Two levels were selected for the first factor (ammonium chloride solution and sulphuric acid). For the remaining factors, three levels were considered.

In this study, the yield of the catalyst (conversion×selectivity) was chosen as the main target function (response). In addition, the effects of the parameters on the crystallinity (area under XRD curve in the range of 2θ from 5° to 35°) of the catalyst samples were also examined as target functions. The conditions for catalyst preparation according to the proposed Taguchi experimental design are summarized in Table 1.

Table 1. Design for optimization of catalysts preparation

No.	Sample	Calcination temperature [°C]	Ion-exchange solution concentration [M]	Calcination time [h]	Ion-exchange solution type
1	8	500	2	1	NH_4Cl
2	4	425	1	3	NH_4Cl
3	9	500	3	3	NH_4Cl
4	7	500	0.5	5	H_2SO_4
5	2	350	1	3	H_2SO_4
6	1	350	1	1	NH_4Cl
7	3	350	1.5	5	H_2SO_4
8	6	425	1.5	1	H_2SO_4
9	5	425	2	5	NH_4Cl

The catalyst samples were analyzed and tested in a fixed bed differential reactor. Moreover, the samples were also chemically analyzed.

3.2. ICP and XRD analysis

ICP and XRD analyses were performed on the catalyst samples produced according to the conditions given in Table 1. Table 2 shows the ICP analysis of the samples.

Table 2. ICP analysis results

Ions	Sulphuric acid solution concentration [M]			Ammonium chloride solution concentration [M]			Raw zeolite
	0.5	1	1.5	1	2	3	
Mg^{2+}	0.409	0.392	0.393	0.446	0.449	0.431	0.670
Ca^{2+}	0.867	0.848	0.799	0.551	0.511	0.296	1.620
Na^{+}	0.299	0.283	0.257	0.319	0.293	0.278	1.100
K^{+}	0.365	0.386	0.419	0.374	0.365	0.266	1.140
Sample No.	7	2	6	4	5	9	

For both ion-exchange solutions, the extent of Ca^{2+} and Na^{+} exchange increased with the increase of the concentration of the ion-exchange solution. The extent of Mg^{2+} exchange is higher for the samples treated with sulphuric acid (compared with the samples treated with ammonium chloride). The opposite holds in the case of Ca^{2+}. The extent of K^{+} exchange with ammonium ion increased with the increase of the solution concentration, while treating it with sulphuric acid cause the K^{+} exchange to decrease.

The degree of substitution of alkaline and alkaline earth metals with proton (DS) is defined as:

$$D.S = \frac{\sum m_{\text{eq (cations, raw zeolite)}} - \sum m_{\text{eq (cations, ion-exchange zeolite)}}}{\sum m_{\text{eq (cations, raw zeolite)}}}$$

The degree of proton substitution for samples is summarized in Table 3. The results presented in Table 3 show that proton substitution increases with the increase of the concentration of the ion-exchange solution.

XRD analysis of the samples (Table 4) showed that the area under the curves for samples which were ion-exchanged with sulphuric acid was considerably smaller than for those ion-exchanged with ammonium chloride. In other words, the samples that were ion-exchanged with sulphuric acid were subject to significant de-alumination and amorphization. The increase in acid concentration was accompanied with the loss of crystallinity and destruction of zeolite structure.

Table 3. Degree of proton substitution

Ions	Sulphuric acid solution concentration [M]			Ammonium chloride solution concentration [M]		
	0.5	1	1.5	1	2	3
Mg^{2+}	33.91	33.34	34.37	41.88	43.71	51.30
Ca^{2+}	43.59	43.73	42.37	31.38	30.17	21.37
Na^{+}	13.10	12.72	11.87	15.83	15.07	17.48
K^{+}	9.40	10.20	11.39	10.92	11.04	9.84
Sum of equivalent	0.0993	0.0967	0.0941	0.0876	0.0845	0.0961
D.S.	53.60	54.77	56.01	59.03	60.48	67.68
Sample No.	7	2	6	4	5	9

XRD of ion-exchanged samples with ammonium chloride showed that the peaks at 9.71° and 22.27° were significantly higher than those in the samples treated with sulphuric acid. This may be attributed to a higher degree of K^+ and Ca^{2+} substitution for the samples treated with ammonium chloride[*].

Table 4. The area under XRD curve

No.	Sample No.	Area under XRD curve 2θ (5°–35°)
1	8	481.44
2	4	558.94
3	9	589.5
4	7	529.14
5	2	537.2
6	1	427.61
7	3	431.65
8	6	422.39
9	5	529.55

3.3. Evaluation of the target functions

Steady state conditions (constant reactor output stream concentration) were established after about 2.5 h from the start of the experiments while the catalyst bed temperature was constant (350 ºC). Table 5 shows the selectivity, conversion percent, and yield of the samples. These results reveal major differences in the behaviour of various catalyst samples:

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[*] XRD diffraction patterns of the samples have been published in the electronic version of the present issue (Attachments, pp. I–IV).

- The average conversion for the catalysts ion-exchanged with sulphuric acid was higher than for those ion-exchanged with ammonium chloride.
- DME selectivity in the case of catalysts ion-exchanged with ammonium chloride was relatively higher than that for catalysts ion-exchanged with sulphuric acid.
- It is observed that methanol conversion on catalysts prepared from ion-exchange with sulphuric acid of low concentration was higher than that on the catalysts prepared with ammonium chloride. It should be mentioned that generally low amounts of side products like light hydrocarbons resulted in selectivity deviation from 1.

Table 5. Reaction selectivity and conversion for each catalyst sample

No.	Sample	Conversion	Selectivity	Yield
1	8	0.0698	0.9668	0.0675
2	4	0.0649	0.9528	0.0618
3	9	0.0723	0.9803	0.0709
4	7	0.0653	0.9035	0.0590
5	2	0.0792	0.8930	0.0708
6	1	0.0478	0.9826	0.0470
7	3	0.0584	0.8829	0.0516
8	6	0.0636	0.8968	0.0570
9	5	0.0664	0.9650	0.0641

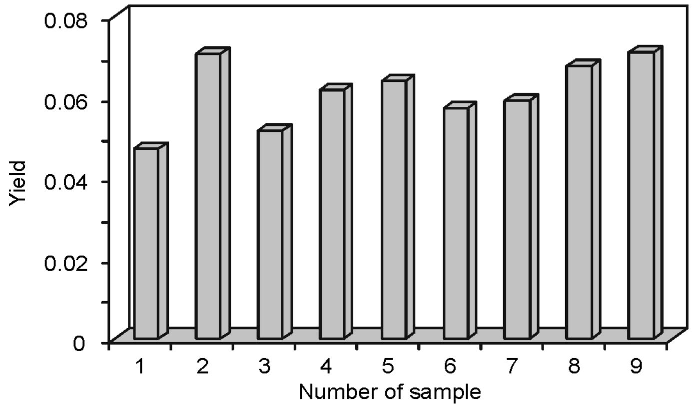

Fig. 2. The yield due to the various samples

Since, in addition to the conversion percent, the selectivity for DME is also an important factor in catalyst application, its yield, i.e. the product of conversion percent and selectivity, was considered the main response in the analysis of the variance (ANOVA) in order to evaluate the results. Figure 2 shows the changes of response for 9 samples of the Taguchi table.

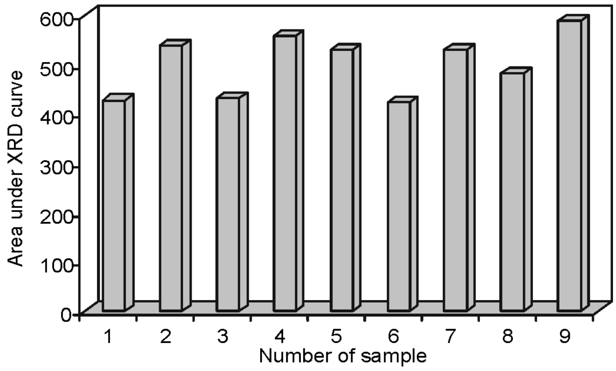

Fig. 3. The changes of crystallinity of the samples

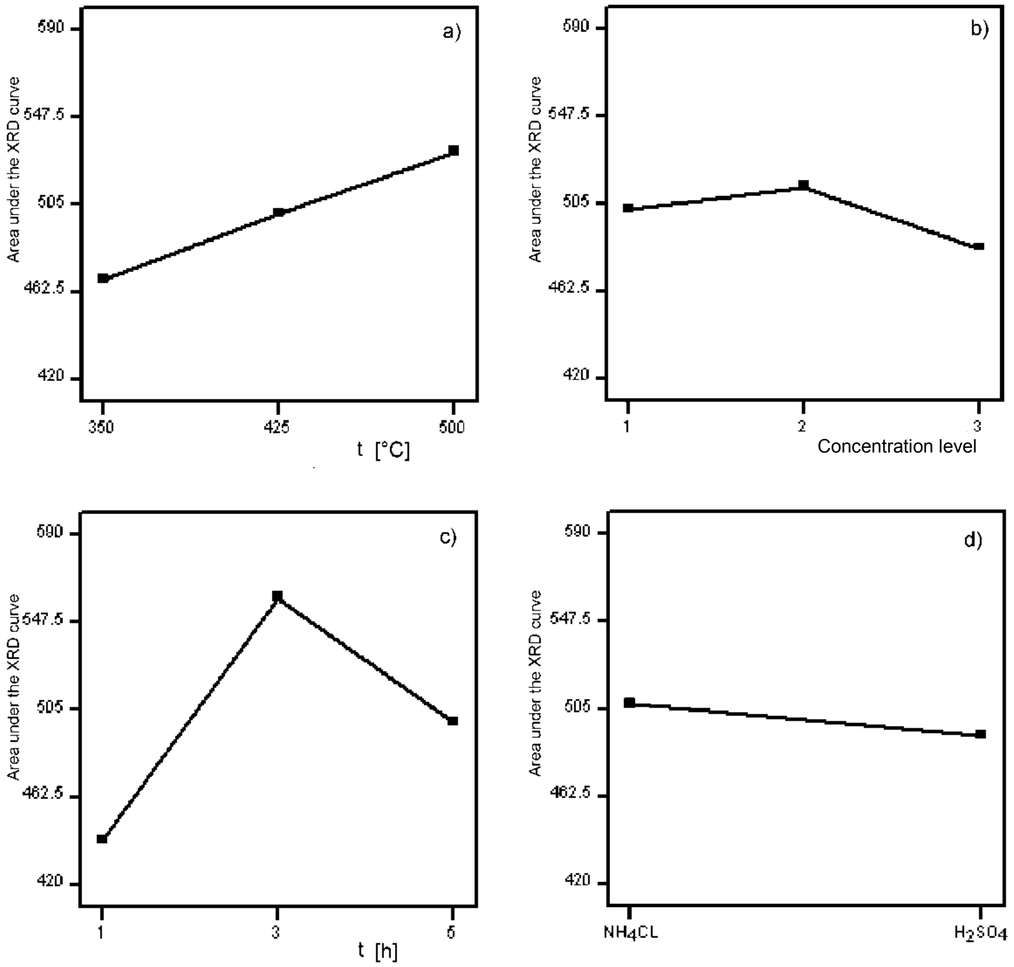

Fig. 4. The effect of the respective factors on crystallinity

Figure 3 shows the second target in this study (crystallinity, the area of the XRD curve in the range of $2\theta = 5°–35°$) for 9 samples. The effect of factor levels on crystallinity degree is shown in Fig. 4. A comparison between Figs. 2 and 3 shows that the trend of response changes versus experiment number is the same except for experiment No. 8. Generally, high concentration of acid solution results in loss of crystallinity. Calcination temperature has a positive effect on crystallinity while a long calcination causes destruction of the crystal structure.

Based on ANOVA, the following relation between crystallinity and the factor levels has been obtained:

$$\begin{aligned}&\text{Area under XRD Curve} \equiv \text{crystallinity}\\&= 499.97\\&+ 31.38A[1] - 0.55A[2]\\&-9.47\,B[1] - 6.77B[2]\\&+ 29.04C[1] - 29.67C[2]\\&-7.68D\end{aligned} \tag{1}$$

Applying Eq. (1), the first three parameter configurations resulting in high crystallinity have been determined and summarized in Table 6. The order of factor influence on this target function is as follows:

1) calcination time,
2) calcination temperature,
3) ion-exchange solution type,
4) ion-exchange solution concentration.

Table 6. Synthesis conditions for obtaining high crystallinity

Arrangement	Predicted response	Calcination temperature [°C]	Ion-exchange solution concentration [M]	Calcination time [h]	Ion-exchange solution type
1	611.361	500	2	3	NH_4Cl
2	600.528	500	1	3	NH_4Cl
3	596.002	500	2	1	H_2SO_4

Based on ANOVA, the following relation between reaction yield and factor levels has been obtained:

$$\begin{aligned}&\text{Yield}\\&= 0.061\\&+ 4.985\times10^{-3}A[1] - 5.866\times10^{-5}A[2]\\&+ 1.631\times10^{-3}B[1] - 3.290\times10^{-3}B[2]\\&+ 2.260\times10^{-4}C[1] - 3.477\times10^{-3}C[2]\\&+ 9.114\times10^{-4}D\end{aligned} \tag{2}$$

The effect of each factor at different parameter levels is shown in Fig. 5.

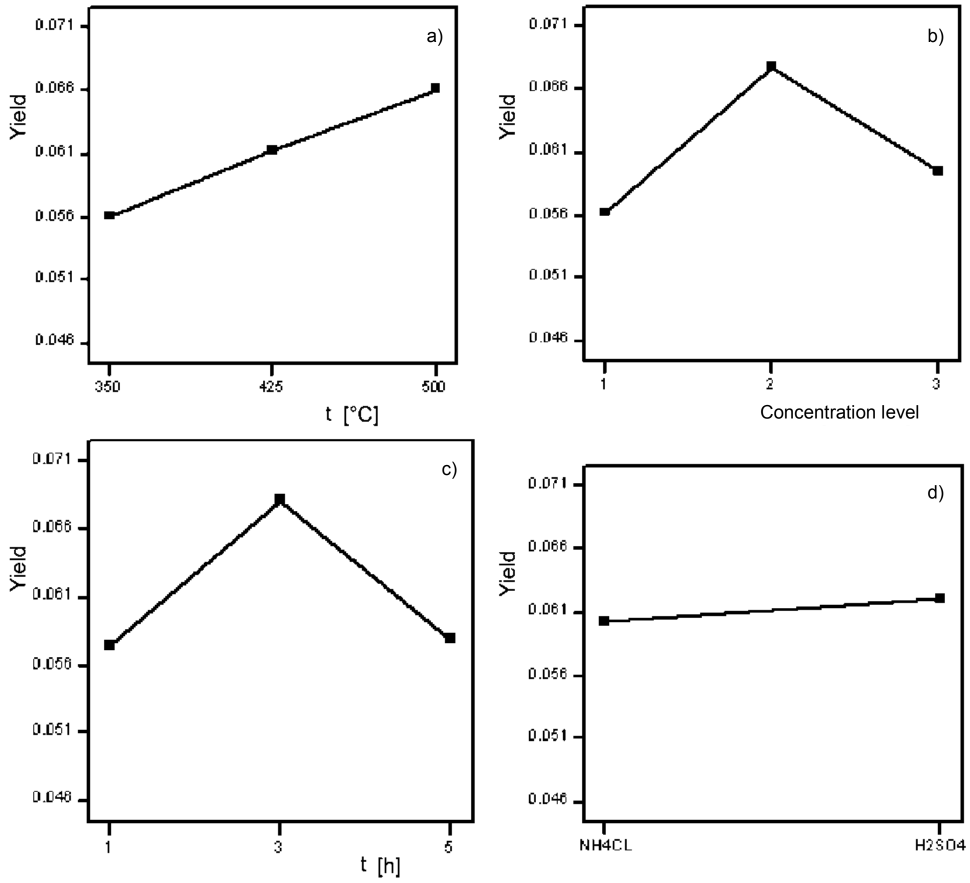

Fig. 5. The effect of factor levels on yield

The order of factor influence on the yield (main target function) is as follows:

1) ion-exchange solution concentration,
2) calcination time,
3) calcination temperature,
4) ion-exchange solution type.

Considering catalyst yield as the target function, the ion-exchange solution concentration is the most influential factor. Figure 5b indicates the 2nd concentration level as the suitable level for this factor, and increasing the solution concentration to 3rd concentration level results in the loss of catalyst yield. Based on the XRD analysis, the latter conclusion may be considered an artefact. In fact, the results of the Taguchi table for the 3M concentrations outshine the cases in which sulphuric acid was used. As previously explained, high acid concentration results in severe loss of crystallinity.

The second parameter with a positive effect on catalyst yield is the catalyst calcination time. Long calcination periods, especially at high temperatures, may cause the destruction of the zeolite structure and, consequently, the loss of catalyst yield.

Referring to Fig. 5d, the ion-exchanged sample with sulphuric acid shows more catalytic yield compared with the one ion-exchanged with ammonium chloride. However, it should be noted that although the conversion of the synthesized samples with sulphuric acid was somewhat higher than of those ion-exchanged with ammonium chloride, the selectivity of the samples treated with ammonium chloride was higher. Also, the only side products formed were trace amounts of methane and carbon dioxide. On the other hand, the application to sulphuric acid results in catalyst amorphization and faster deactivation. In conclusion, the ion-exchanged samples with ammonium chloride are practically more suitable than those treated with acid, due to the higher stability and reaction selectivity.

Based on Eq. (2), the factor configurations leading to the two highest target responses (yield) have been calculated and are summarized in Table 7. The first configuration shown in Table 7 is unacceptable as the concentration of acid equal to 1 M may indeed cause severe amorphization. Therefore, the optimum factor level configuration proposed is calcination temperature 500 ºC, ion-exchange solution concentration 2 M, calcination time 3 h, and ion-exchange solution – ammonium chloride.

Table 7. Factor configurations resulting in the two highest target functions (yield)

No.	Predicted response	Calcination temperature [°C]	Ion-exchange solution concentration [M]	Calcination time [h]	Ion-exchange solution type
1	0.081	500	1	3	H_2SO_4
2	0.079	500	2	3	NH_4Cl

To check the validity of the Taguchi experimental design in obtaining the optimum catalyst preparation procedure, a catalyst was prepared accordingly. The catalytic behaviour of the latter was investigated using a fixed bed reactor, charged with 5 g of the catalyst. The reaction conditions without nitrogen flow were: pressure – 1atm, reaction temperature – 330 °C, liquid methanol flow rate – 0.4 $cm^3\cdot min^{-1}$ (WHSV = 3.8 h^{-1}). In this test, the catalyst was activated for 1 h in the presence of nitrogen prior to methanol injection.

The steady state conditions were established within 2.5 h. Analysis of the output gas stream showed the conversion level of 98.1% and the selectivity of 96.5%. In order to investigate the catalyst deactivation, the reaction was continued for 14 h. No deactivation was observed. Methane and carbon dioxide were the only side products.

In addition, to investigate the optimum catalyst behaviour under industrial operational conditions, a fixed bed reactor test was performed using 1 g of the catalyst at the pressure of 16 atm and temperature of 300 °C, with a liquid methanol flow rate of 1.1 $cm^3\cdot min^{-1}$ and nitrogen flow rate of 50 $cm^3\cdot min^{-1}$ (WHSV = 52.5 h^{-1}) for 40 h.

The Arak petrochemical complex (Arak, Iran) facilities were applied in the latter experimental run. The corresponding results are summarized in Table 8.

Table 8. Results of the test of industrial operational conditions

At steady state		After 40 hours on stream	
Conversion [%]	Selectivity [%]	Conversion [%]	Selectivity [%]
67.02	99.74	58.42	99.8

4. Conclusions

The optimally modified clinoptilolite zeolite that is the subject of this study is a potential candidate for being used as a methanol dehydration catalyst for DME production. The Taguchi experimental design was successfully applied for obtaining the optimum ion-exchange and calcination conditions for modifying the raw zeolitic material. The optimized catalyst of this work has a high selectivity for the MTD reaction, the only analyzable side products being methane and carbon dioxide. At the same time, catalysts like H-ZSM5 and H-Mordenite result in side products like ethane, propane, ethylene, which induce deactivation.

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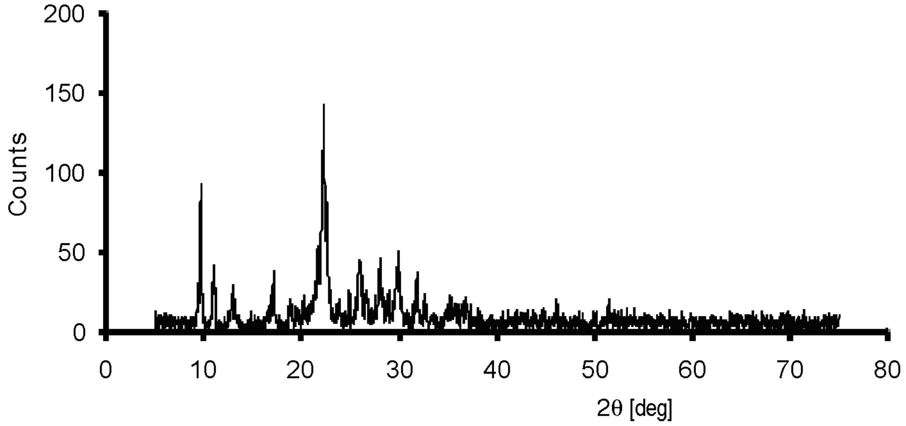
Attachments. XRD diffraction patterns of the samples



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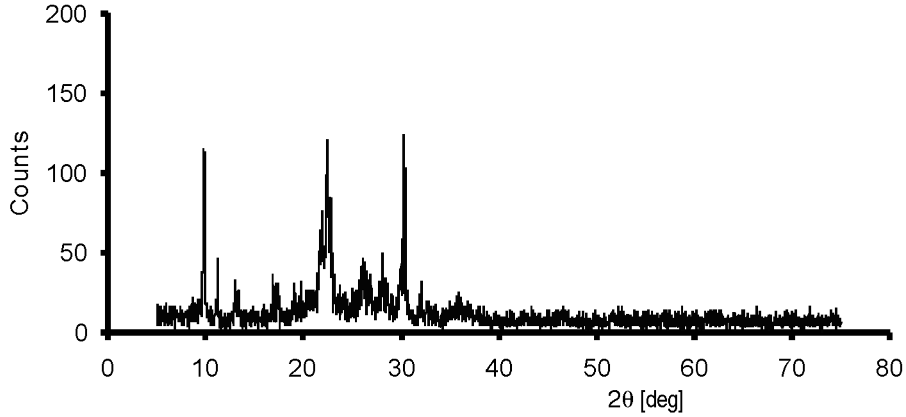

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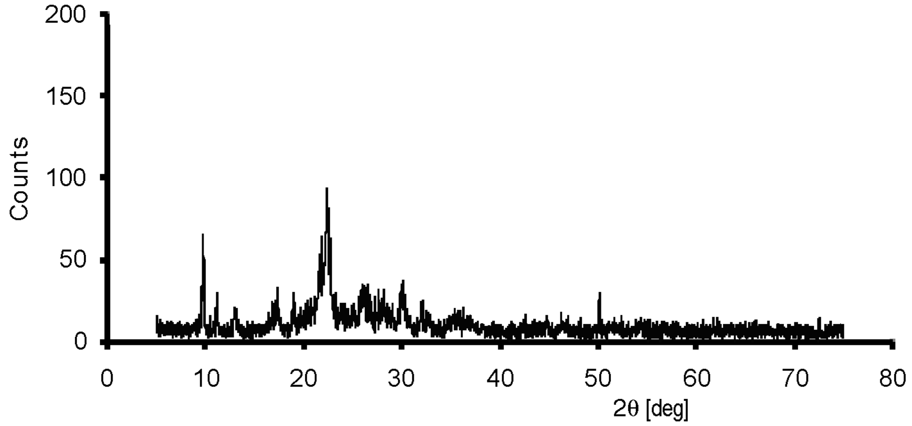

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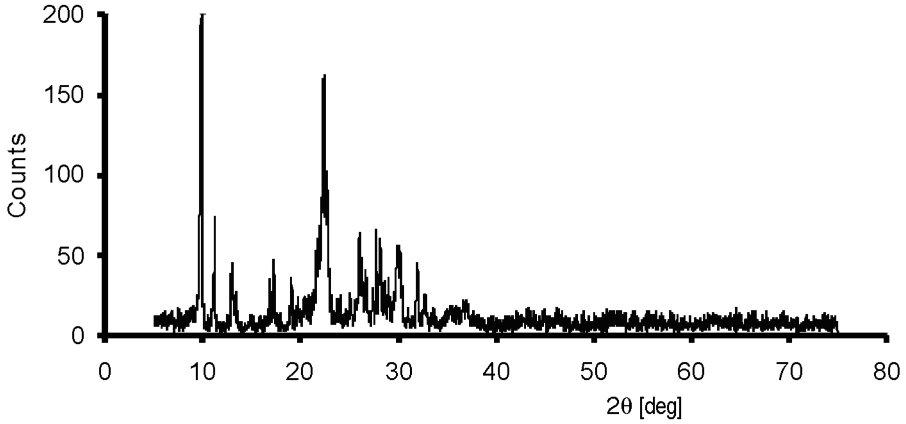

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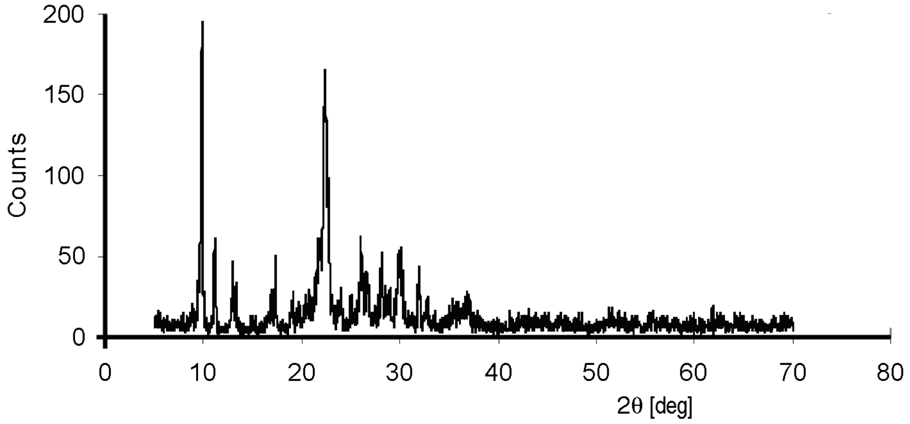

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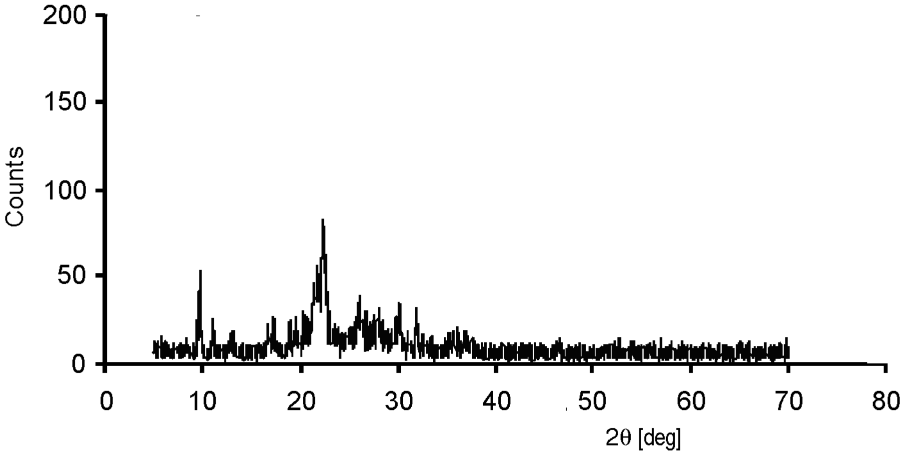

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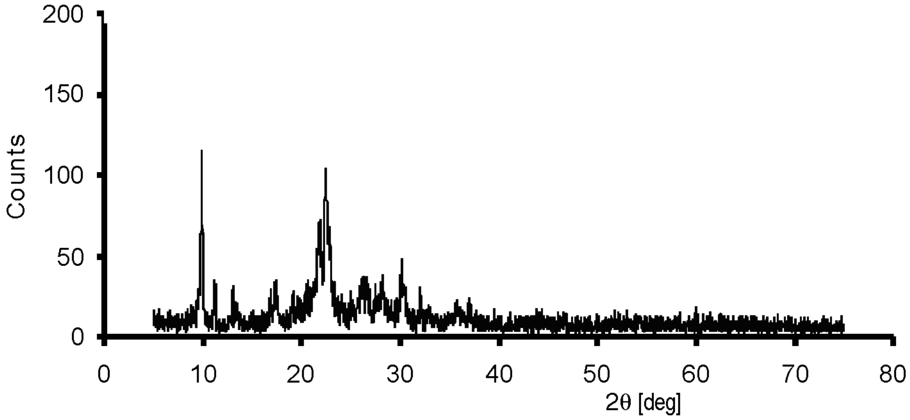

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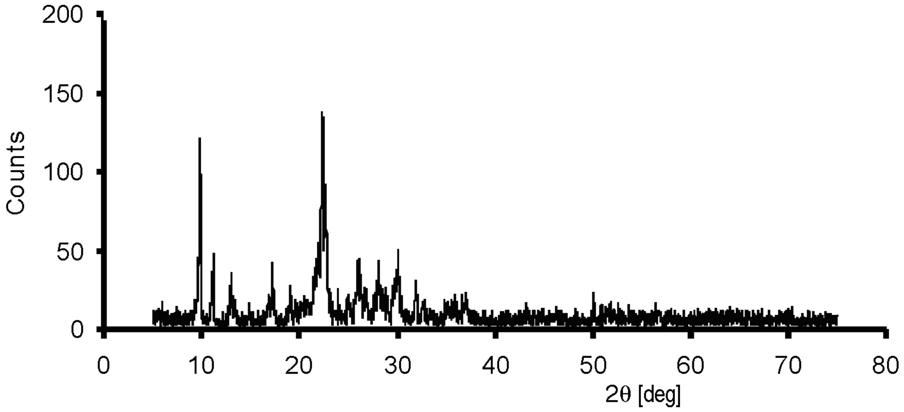

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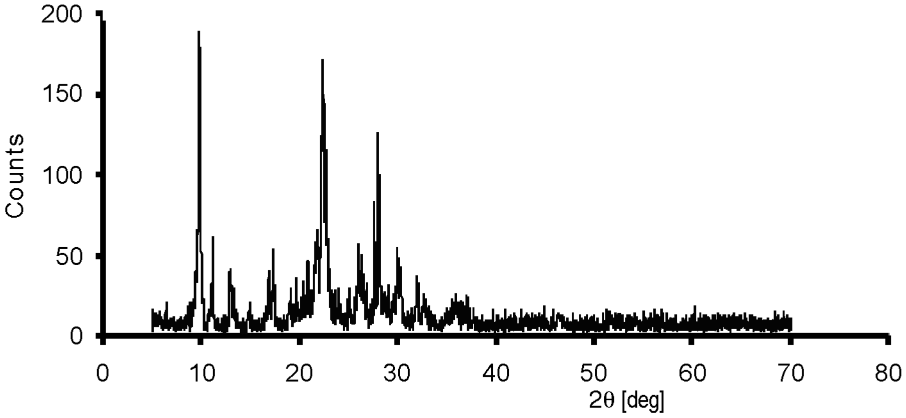

Sample 9 from table 4