

NOVEL METHOD FOR THE ETHYLATION OF TOLUENE BY NANO-MODIFIED CLINOPTILOLITE

Nora Elizondo-Villarreal¹, Ricardo Obregón-Guerra¹, Manuel García-Méndez¹, Ana Patricia Sánchez-Espinoza¹, Arquímedes Cruz-López², Víctor Coello³, F. Vengoechea⁴ and Víctor M. Castaño⁵

¹Department of Physics, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N. L., CP 66451, México

²Civil Engineering Faculty, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N. L., CP 66451, México

³CICESE, Monterrey, Km 9.5 Nva. Carretera Aeropuerto, PIIT, Apodaca, N. L., México, C.P. 66600, México

⁴Laboratorios Avimex, Maíz 18, Cd. de México 09810, México

⁵Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Boulevard Juriquilla 3001, Querétaro 76230, México

Received: January 11, 2017

Abstract. The alkylation of toluene reaction on natural clinoptilolite was carried out in a differential fixed-bed reactor. The natural zeolite was treated under the strictly defined conditions of thermal and acidic treatments of parent rocks. Hydrothermal reaction was conducted with HCl-treated clinoptilolite at 50 °C. The acidic-clinoptilolites zeolites (AC) were modified chemically by adding silicon layers on its surface at nanometric scale. Catalytic reactions using acidic modified clinoptilolites (AMC) as catalysts were carried out at 350 to 500 °C. The ratio of reactants (toluene/ethanol) was kept 3:1 with a flow WHSV of 2 h⁻¹. The organic products of the reactions were analyzed by gas chromatography. High-resolution electron microscopy (HRTEM) was used to observe the modified surfaces of catalysts. The effect of chemical modification of natural clinoptilolite in the alkylation of toluene was carrying out by ethanol media. The AC showed activity to the formation of ethyltoluene. The added silicon on acidic clinoptilolite samples favored the conversion of toluene to 23 mass%. Added silicon contributed to increase the formation of ethyltoluene at 75 mass%. Catalyst test results indicated the possibility of using clinoptilolite as a raw material in the preparation of catalysts for alkylation of toluene with ethanol reaction.

1. INTRODUCTION

Alkylation of aromatic hydrocarbon compounds are the most important and useful reactions of hydrocarbons. Lewis and Brønsted acids including a variety of natural and synthetic zeolites have been used as catalysts. Amongst them, the formation of alkylaromatic compounds as byproducts of the alkylation or disproportion is a reaction of great value in which these shape-selective zeolites can be applied as catalysts [1-13].

The Ethyltoluene (ET) is a volatile organic compound employed for the production of methylstyrene, which is a chemical intermediate used in the manufacture of plasticizers, resins and polymers. Moreover, for the production of polymethylstyrenes is possible to use toluene as a substitute for benzene in petrochemical synthesis [14].

The unique physical and chemical properties of natural clinoptilolite zeolites, combined with their abundance in sedimentary deposits and rocks

Corresponding author: Nora Elizondo-Villarreal, e-mail: nelizond@yahoo.com

derived from volcanic parent materials, have made them very useful in many industrial and research processes [15-18]. There are several research works where the natural zeolites with certain crystallinity have been used as catalyst. Some interesting results show the catalytic activity and selectivity of modified natural clinoptilolite for alkylation reactions like in the synthesis of ZSM-5 from modified clinoptilolite in alkylation of benzene to ethylbenzene [19-24].

The aim of our work is to explore the possibility of using natural clinoptilolite as raw material in the preparation of catalyst for alkylation of toluene with ethanol reaction.

2. MATERIALS AND METHODS

The natural clinoptilolite (*NC*) was mined in Puebla State of México. The *NC* was ion-exchanged by heating at 50 °C in an aqueous solution of HCl (0.1 N). It was placed inside a cooling bath and kept in these conditions for one week. By this method, the *NC* was converted to the acidic clinoptilolite (*AC*). Afterwards *AC* samples were chemically modified on its surface by adding the following amounts of silicon: 0.2, 0.6, 1, and 1.5 ml in presence of peroxide and heptane at 70 °C. Thus, a series of acidic modified clinoptilolites (*AMC*) were obtained: *AMC1*, *AMC2*, *AMC3* and *AMC4*, respectively.

All catalysts were analyzed by X-Ray Diffraction (XRD), Scanning Electronic Microscopy (SEM), High-Resolution Transmission Electron Microscopy (HRTEM), X-Ray Photoelectron Spectroscopy (XPS) and Inductively Coupled Plasma Spectroscopy (ICP).

A SEM Model JSM 300 was used to determine the crystallite size of catalysts, both before and after ion-exchange. The crystal structures of zeolites *NC*, *AC*, *AMC* and *H-MFI* were determined with X-ray powder diffraction by using a RIGAKU MiniFlex II diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. X-ray diffraction data were collected within the 2θ range from 5 to 90°, at a scan rate of 0.02°/sec.

HRTEM was applied to determine the subnanometer structure and homogeneity of the zeolites. For these analyses, the samples were sonicated in isopropanol and deposited on lacey carbon on copper grids. They were carried out in a JEOL 2010 F microscope equipped with a Schottky-type field emission gun, an ultra-high-resolution pole piece, operating at 200 kV.

XPS analyses were carried out on a modified laser ablation system Riber LDM-32. The pressure in the analysis chamber was approximately 10^{-10} Torr and 10^{-9} Torr at the sample-loading chamber.

The X-ray $\text{AlK}\alpha$ line at 1486.6 eV was utilized. The binding energies were calibrated with reference to $\text{Cu}2p_{3/2}$ and $\text{Ag}3d_{5/2}$ at 932.67 eV and 368.26 eV, respectively. The maximum resolution attained with this set up was 1.1 eV measured for the graphite C1s signal. The spectra were collected by acquiring the data every 0.2 eV with an energy resolution of 0.8 eV.

The catalytic experiments were carried out in a fixed-bed reactor. The amount of zeolites *AC*, *AMC* and *H-MFI* (the international zeolite association structure-code for the H-ZSM5) as reference catalyst charged was of 1.75 g of each one and its particle size was of about 4mm. Before each experiment, the catalyst was pretreated with dry-air flow at 550 °C for 5 hours. Then, a flow of dry-nitrogen (free of traces of oxygen) passed through the system at the same temperature for 2 h. Finally, the reactions were carried out in a catalytic system with a differential fixed bed reactor in a temperature range between 350 and 500 °C; the ratio of reactants (toluene/ethanol) was 3:1 with a flow WHSV of 2 h^{-1} . During the alkylation of toluene by ethanol reaction, we obtained products in three phases: gaseous, watery and organic. The products of the reactions were analyzed by gas chromatography equipped with FID detector. The organic products were studied in a column of Bentone 34 while the watery phase and the hydrocarbon gases C1-C4 were studied in a column of Porapak Q using a FID detector.

3. CALCULATION

For every sample, XPS spectra were taken in the survey mode, scanning from 1486.6 to 0 eV. After that, narrow scans were performed in the high resolution mode for the Si2p, O1s, Al2p and C1s windows. Also, narrow windows were taken for Mg2p, Na1s, Fe2p, Ca2p and S2p, which accounts for impurities within the zeolite system. Binding energies (BE) were referenced with respect to the C1s signal at 284.5 eV after taking measurements, in order to correct induced charge-effects.

Surface elemental stoichiometries were calculated from the peak area ratios. Synthetic zeolite ZSM5 (MFI) was taken as a reference (standard). It was assumed an ideal SiO_2 tetrahedral arrangement where oxygen to silicon ratio atomic concentration is $\text{C}(\text{O}1s)/\text{C}(\text{Si}2p) = 2$. From XPS O1s and Si2p transitions taken from standard and assuming the ideal ratio of 2. It was obtained that oxygen to silicon ratio sensitivity factors were about of $\text{S}(\text{O}1s)/\text{S}(\text{Si}2p) = 3.6$, which were very similar to the ones already reported [12].

Table 1. Chemical analysis data of natural clinoptilolite zeolite (NC)^a.

Components	wt. (%)	Ion contents in the elemental cell	
SiO ₂	62.36	Si	28.18
Al ₂ O ₃	13.14	Al	7.01
CaO	2.72	Ca	1.32
Na ₂ O	3.99	Na	3.50
K ₂ O	1.20	K	0.69
Fe ₂ O ₃	1.63	Fe	0.55
FeO	-	-	-
MgO	0.92	Mg	0.62
TiO ₂	0.39	Ti	0.13
H ₂ O ^b	8.32	H ₂ O	20.57
H ₂ O ^c	5.33	O	72.0

a Clinoptilolite: Na_{3.50}K_{0.69}Mg_{0.62}Ca_{1.32}[(Al_{7.01}Fe_{0.55})(Si_{28.18}Ti_{0.13})O_{72.0}].20.57-H₂O.

b Crystallization water.

c Extra water which is present in clinoptilolite mineral and does not form its crystal structure.

The core level spectra of Si2p and O1s narrow scans were performed by using a non-linear fit of Gaussian-Lorentzian functions. Gaussian-Lorentzian proportion of 0.9-0.1 was kept constant. The intensity ratio of Si2p_{3/2} and Si2p_{1/2} transitions was maintained 2:1 proportion with BE at a constant separation of 0.61 eV [25]. Besides, the full-width-half-maximum (FWHM) were allowed for fitting purposes.

4. RESULTS AND DISCUSSIONS

The chemical composition of natural clinoptilolite zeolite is included in the Table 1. This composition gave Si/Al ratio of 4.74, which is close to the ratio reported by Breck [28].

The bulk structure of AC and AMC was confirmed by XRD analysis identified as clinoptilolite in the RIGAKU MiniFlex II diffractometer program with Cu K α radiation [29]. The chemically modified AMC with silicon layers did not display changes in their crystalline structures, as can be seen from Fig. 1. After each reaction, the zeolites did not change their structures and chemical composition. The only accumulated side-product, coke, was removed by regeneration. After reactions, the zeolites could be regenerated with a flow of hot air at 550 °C for 3 hours through the catalytic system. The conducted experiments proved that the acidic framework designation defined by IZA for acidic ZSM-5(H-MFI) and clinoptilolite, which were stable with respect to coke accumulation, participated in the reaction for several hours and worked successfully as catalysts for a relatively short-time.

Fig. 2 is the SEM image corresponding to natural clinoptilolite zeolite (AC). This zeolite presented a crystal size in the range of about 2 to 15 μ m. This range of crystal size was also observed approximately for AC, AMC and H-MFI zeolites.

Fig. 3 presents the XPS spectra for Si and O windows, where their respective fitting is included for sample MFI (the framework designation defined by IZA for synthetic zeolite ZSM5). The envelope of the Si window consists of a convolution of Si2p_{3/2} and Si2p_{1/2} -oxide and a Si2p_{3/2} and Si2p_{1/2} -metallic transitions. The envelope of the O window consists

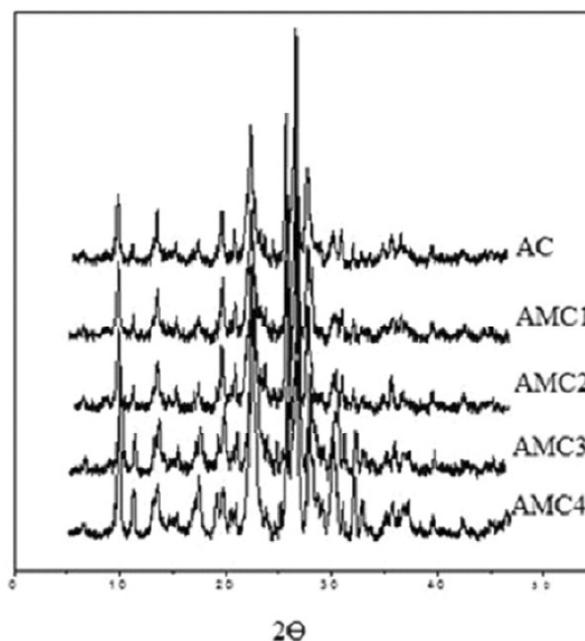


Fig. 1. X-ray diffraction patterns of acid treated (AC) and acidic modified clinoptilolites (AMC).

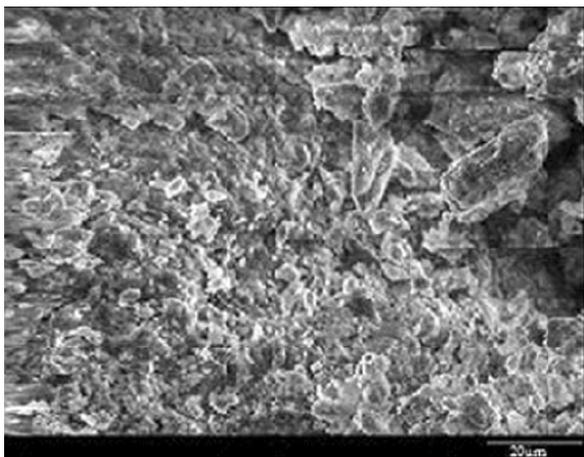


Fig. 2. SEM image displaying the morphology of natural clinoptilolite (NC).

of a convolution of O1s related with a tetrahedral bonding to Si, and an O1s related to a signal coming from contamination or impurities. Atomic concentrations were calculated from the peak areas of Si2p-oxide and O1s curve fit components and reported sensitivity factors [12]. Photoionization cross sections σ were also used as an additional method for calculation of atomic concentrations, where results were very similar. In this case, oxygen to silicon ratio was about of $\sigma(\text{O1s})/\sigma(\text{Si2p})=3.3$ (where $\sigma_{\text{O1s}}=63.54$ and $\sigma_{\text{Si2p}}=19.14$ [30], very similar to the ratio found for the case of oxygen to

silicon sensitivity factors. Table 2 includes the calculated atomic concentrations.

From Table 2 it can be observed for samples *AMC1* to *AMC4* the slight increase in the silicon atomic concentration, from 30% (sample *AMC2*) to almost 34% (sample *AMC4*) as a result of the treatment with silicon addition, compared with the 29% of the standard sample (*ZSM5*). In all samples there were not changes in the values of BE's, as long Si2p-oxide (102.8 eV) as O1s-SiO₂ (532.3 eV). The added Silicon atoms were attached to the structure of the sample with no change in the nature of the Si-O bonding in SiO₂. In this case, the nature of the Si-O bonding remains as a feature of all the samples, very close to the SiO₂ stoichiometry, which in the ideal case is the tetrahedral-type [31].

The activity and selectivity of the alkylation of toluene by ethanol on the acid clinoptilolite zeolite (AC) used as catalyst can be seen in Table 3. From it sees that there is not an important effect of temperature on the conversion of toluene in the range 350 to 500 °C. Nevertheless, at 450 °C the selectivity towards p-ethyltoluene showed an increase of 15%.

The results of the activity, the concentration of products in the organic phase and the selectivity of the alkylation of toluene by ethanol can be seen in Table 4. The distribution of the products in the organic phase and the conversion of toluene were different when we compared AC and AMC zeolites as can

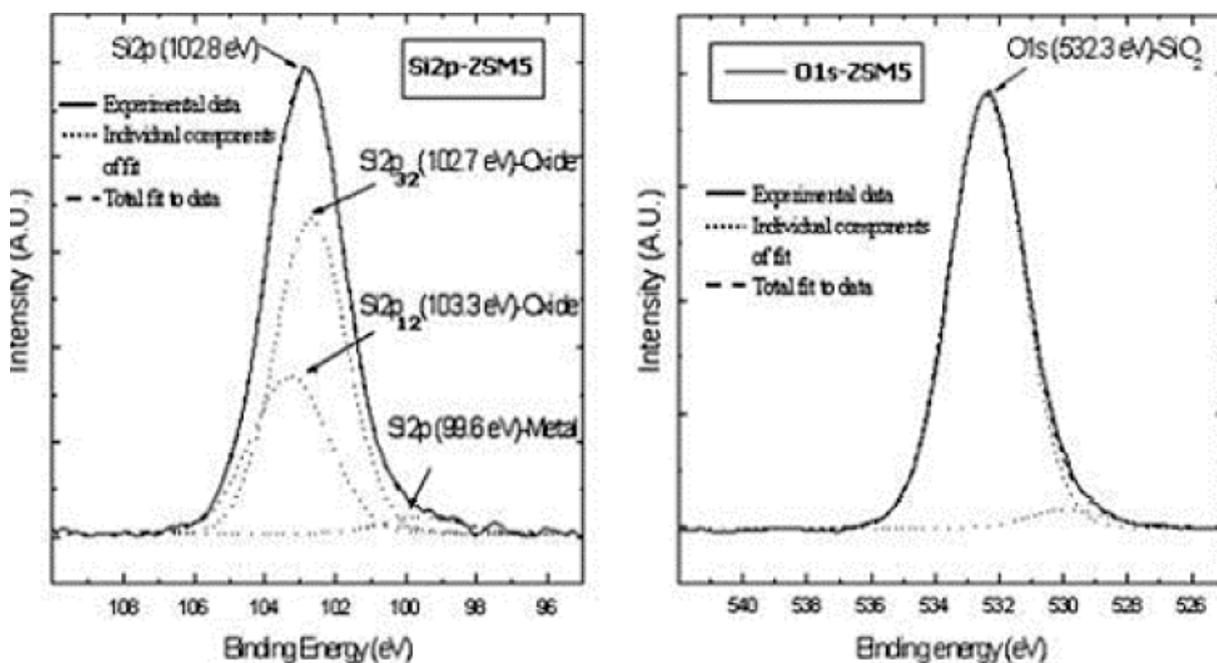


Fig. 3. High resolution XPS spectra for (a) Si and (b) O window corresponding to the synthetic zeolite ZSM-5, which was utilized as a standard for quantification. Atomic concentrations were calculated from the peak areas of the Si2p and O1s curve-fit components. The same procedure was followed for all the samples, whose calculated atomic concentrations are shown in Table 1.

Table 2. Calculated atomic concentration for samples. Atomic concentrations were calculated from the peak areas of the Si2p and O1s curve-fit components. See Fig. 1, where Si and O windows spectra for the standard sample (ZSM5) are displayed.

SAMPLE	ATOMIC CONCENTRATION (%)		
	O	Si	C (O)/C (Si)
ZSM5	71.0	29.0	2.44
NC	69.3	30.0	2.26
AC	70.0	30.0	2.33
AMC1	68.1	31.8	2.14
AMC2	69.4	30.5	2.27
AMC3	67.4	32.5	2.07
AMC4	66.1	34.0	1.94

Table 3. Results of the activity, the concentration of products in the organic phase and the selectivity of the alkylation of toluene by ethanol on the acid clinoptilolite zeolite (AC) used as catalyst at WHSV of 2 h⁻¹ and molar ratio T/E of 3.

Temperature (°C)	350	400	450	500
Xylene	—	14.3	13.4	—
Ethyltoluene	66.3	50.7	29.4	42.2
Benzene	6.2	10.3	0.7	33
C ₅ ⁺ Aliphatic hydrocarbons	27.5	24.6	53.9	24.8
Collateral Aromatic hydrocarbons	—	—	2.5	—
Conversion (mass %)	14.2	14.5	15.5	14.6
Selectivity of p-ethyltoluene	40	42	55	40
Selectivity of (m- y o-) ethyltoluene	60	58	45	60

Table 4. Results of toluene conversion and the concentration of the products in the organic phase of the alkylation of toluene by ethanol on the acidic clinoptilolite AC and the acidic modified clinoptilolite AMC1, AMC2, AMC3 and AMC4 at 450 °C, molar ratio T/E of 3 and WHSV of 2 h⁻¹.

Concentration of products in the organic phase (mass %)	AC	AMC1	AMC2	AMC3	AMC4
Xylene	13.4	—	11.9	46.3	14.3
Ethyltoluene	29.4	40.8	51.6	26.2	75
Benzene	0.7	4.1	25.1	13.2	5.2
C ₅ ⁺ aliphatic hydrocarbons	53.9	53.6	11.4	11.4	5.6
Conversion of toluene (mass %)	15.5	15.2	16.7	16.0	23.0
Selectivity of p-ethyltoluene	55	51	45	48	32
Selectivity of (m- y o-) ethyltoluene	45	49	55	52	68

be seen from Table IV. In the case of AMC zeolites the conversion of toluene reached 23 mass%, the maximum concentration of ethyltoluene was of 75 mass% whereas, in the case of AC zeolite the maximum conversion of toluene was of 15.5 mass % with a concentration of ET of 29.4 mass%, this was accompanied by the increase of the C₅⁺ aliphatic

hydrocarbons in the organic phase. The tendency of the increase in concentration of ET group in relation with the increase of the amount of added silicon chemically in the AMC zeolites was observed.

The silicon layers were deposited with certain crystallinity at nanometric scale on the surface of AC, forming AMC as can be observed in the HRTEM

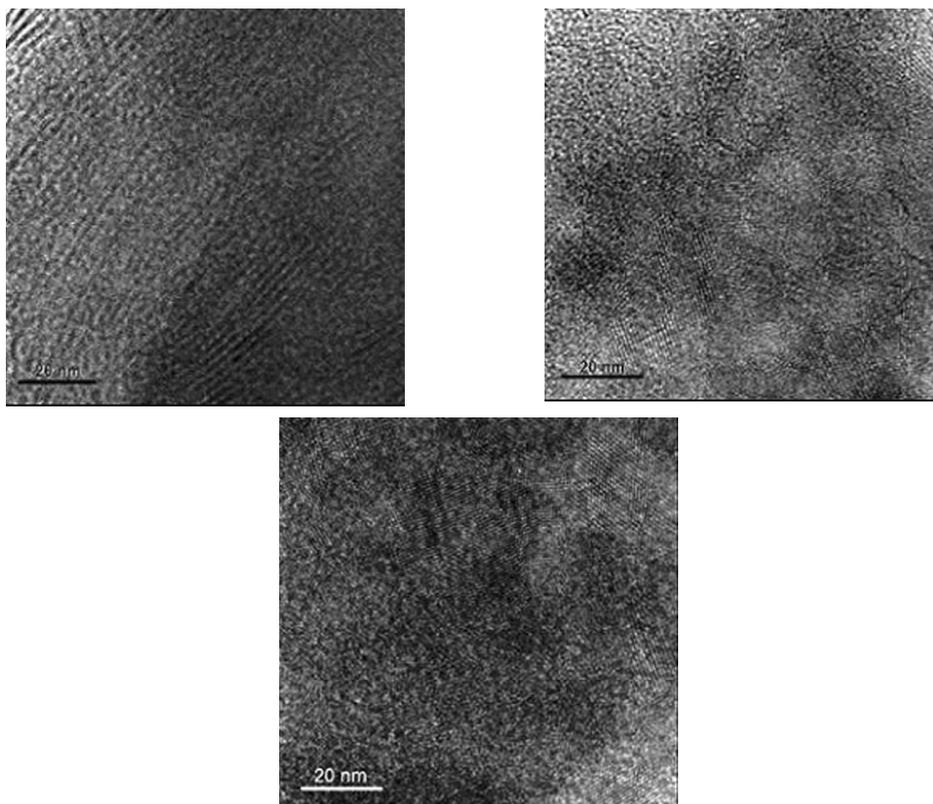


Fig. 4. Images HRTEM of clinoptilolite zeolites, show the comparison between acid clinoptilolite-zeolite AC (A) with acidic modified clinoptilolites AMC3 (B), and AMC4 (C), which have more quantity of silicon over each surface respectively. They revealed how the silicon layers were deposited with certain crystallinity at nanometric scale on the surface of AC, forming AMC respectively.

images from Fig. 4. The chemical modified catalysts turned out to be active for the alkylation of toluene with ethanol, favoring the shape- selective formation of ethyltoluene.

5. CONCLUSIONS

The conditions of alkylation of toluene by ethanol have been determined using the modified natural clinoptilolite zeolites AC y AMC that were active as alkylation catalysts. In the toluene ethylation on AC, the conversion of toluene at 450 °C was 15.5 mass% and the mass percentage of the ethyltoluene group was 29.4. In the toluene ethylation on modified AMC, the higher conversion of toluene was of 23 mass% at 450 °C, while the maximum mass percentage of the ethyltoluene group reached 75 mass%. The conditions of the alkylation of toluene by ethanol using natural zeolites: acidic clinoptilolite and acidic modified clinoptilolites were determined.

Catalysis test results indicate the possibility of using natural clinoptilolite as a raw material in the preparation of catalyst for alkylation of toluene with ethanol reaction to produce ethyltoluene.

ACKNOWLEDGEMENTS

The authors thank the technical assistance in TEM of Chemical Engineering Department at UT Austin, USA.

REFERENCES

- [1] A. Alietti // *Am. Min.* **57** (1972) 1448.
- [2] C.V. Bezouhanova, Ch. Dimitrov and V. Nenova // *Appl. Catal.* **49** (1989) 101.
- [3] E. G. Derovane // *Journal of Molecular Catalysis A: Chemical* **134** (1998) 29.
- [4] W.W. Kaeding, *Pat. U.S.* 4361713, 1981.
- [5] W.W. Kaeding, L.B. Young and C.C. Chu // *J. Catal.* **89** (1984) 267.
- [6] J. H. Kim, T. Kunieda and M. Niwa // *J. Catal.* **173** (1998) 433.
- [7] K. Koyama and Y. Takeuchi // *Z. Kristallogr.* **145** (1977) 216.
- [8] S.B. Kulkarni, H. Haftori and K. Tanabe // *Appl. Catal.* **49** (1989) 27.
- [9] D. H. Olson, G. T. Kokotailo, S. L. Lawton and W. M. Meler // *The Journal of Physical Chemistry* **85** (1981) 2238.

- [10] G. Paparato, E. Moretti, G. Leofanti and F. Gatti // *J. of Catal.* **105** (1987) 227.
- [11] J. Walendziewski and J. Trawczyński // *Ind. Eng. Chem. Res.* **35** (1996) 3356.
- [12] J. F. Moulder, W. F. Stickle, P. E. Sobol and K.D. Bomben, *Handbook of X-ray photoelectron spectroscopy. A reference book of standard spectra for identification and interpretation of XPS data*, ed. by Jill Chastian (Perkin-Elmer Corporation, Physical Electronics Division, 1992).
- [13] N. Elizondo, R. Obregón, M. García, A. Sánchez, M. Alcorta, V. Coello and V.M. Castaño // *Rev. Adv. Mater. Sci.* **47** (2016) 74.
- [14] L.F. Hatch and S. Matar, *From Hydrocarbons to Petrochemicals* (Gulf Publishing Co., Houston, USA, 1981).
- [15] J. A. Arcoya, N. Gonzalez, N. Travieso and X. L. Seoane // *Clay Minerals* **29** (1994) 123.
- [16] M. K. Doula and A. Ioannou // *Microporous and Mesoporous Materials* **58** (2003) 115.
- [17] 2001. T. Armbruster, In: *Zeolite and Mesoporous Materials at the Dawn of the 21st Century*, ed. A. Galarnau, F. Di Renzo, F. Faujula and J. Viedrine (Elsevier, 2001), p. 13.
- [18] C. N. R. Rao, A. Müller and A.K. Cheetham, *The Chemistry of Nanomaterials, Synthesis, Properties and Applications*, Vol. II (Wiley VCH Verlag GmbH and Co, 2006).
- [19] T. Christie, B. Brathwaite and B. Thompson // *Mineral Commodity Report* **23** (2002) 16.
- [20] J. Papp and É. Miklósy // *Reaction Kinetics and Catalysis Letters* **8** (1978) 87.
- [21] O. E. Kartal and I. Onal // *Chemical Engineering Communications* **195** (2008)1043.
- [22] G.T. Kerr // *Cat. Rev. Sci. Eng.* **26** (1984) 281.
- [23] G.T. Kokotailo, *Pat. U.S. 4229424*, 1980.
- [24] É. Miklósy, J. Vályon, E. Czárán and J. Papp // *React. Kinet. Catal. Lett.* **14** (1980) 475.
- [25] R. Szostak, *Handbook of molecular Sieves* (Van Nostrand Reinhold, New York, 1992).
- [26] J.J. Yeh, *Atomic calculation of Photoionization Cross-Sections and Asymmetry Parameters* (AT&T Bell Laboratories. Gordon and Breach Science Publishers, Langhorne, PE, USA, 1993).
- [27] A. Putnis, *Introduction to Mineral Sciences*, 2nd ed. (Cambridge University Press, New York, 1992).
- [28] S.J. Splinter and N.S. McIntyre // *Surface and Interface Analysis* **26** (1998) 195.
- [29] Breck, D.W., 1974. *Zeolite Molecular Sieves*, Wiley-Interscience.
- [30] S. Siffert, L. Gaillard and B.L. Su // *J. Mol. Catal. A* **153** (2000) 267.