

Adsorption of Paraoxon on High-silica Pentasils with Different Alkali Cations

Ankica Čižmek^{a,*} and Zlatko Ivančić^b

^aMOD, Croatian Military Academy, LABKZ, Ilica 256 b, 10000 Zagreb, Croatia

^bFaculty of Chemical Engineering and Technology, University of Zagreb, Department of Fire Fighting, Marulićev trg 20, 10000 Zagreb, Croatia

Received May 31, 2001; revised January 7, 2002; accepted January 9, 2002

Adsorption of paraoxon (diethyl-*p*-nitrophenyl phosphate) on high-silica pentasils with different alkali cations (Na^+ , K^+ , NH_4^+) was investigated using the method of measuring the acceleration of the rate of oxidation of benzidine, and it is discussed with regard to the influence of alkali metal ions present in the system during zeolite synthesis. The rate of adsorption of paraoxon on Na-ZSM-5 was investigated at different temperatures (20, 30, 37 and 45 °C).

Key words: adsorption, paraoxon, zeolites, alkali cations.

INTRODUCTION

Zeolite minerals were discovered and named in 1756 by the Swedish mineralogist Baron Cronstedt. It was early recognized that these minerals are able to exchange their metal cations by treatment with aqueous solutions of various salts and many naturally occurring or synthetic cation exchangers were named »zeolites« (Greek words *zeo*, burn and *lithos*, stone – burning stones).

Ionic properties of zeolites were the first to be commercially recognized, primarily as soil conditioners (by the 19th century soil scientists) and as water softeners (at the turn of the century).

The soil conditioning application remains an important one for natural zeolites in several countries, particularly those effected by radioactive fall-

* Author to whom correspondence should be addressed. (E-mail: acizmek@zvonimir.morh.tel.hr)

out from bomb tests and nuclear power accidents. The softening application now dominates the zeolite industry as a detergent additive.

Of particular significance, in view of the major problems resulting from the Chernobyl nuclear incident and the incident in Goyania (Brazil), are the extensive studies of Cs^+ and Sr^{2+} selectivities on a range of zeolites, particularly clinoptilolite.

Continuing studies try to alleviate the toxic influence of these ions on the population and agricultural land exposed to radioactive fallout.¹

Ames demonstrated the use of clinoptilolite as an ammonium scavenging agent for remediation of ammonium pollution in agricultural runoff and sewage treatment – two important current applications.²⁻⁵

Sorption and Separation

A major turning point in sorption studies was the first patent on hydrocarbon separations by Barrer,⁶ who used chabazite to separate normal from branched hydrocarbons (up to octanes and aromatics). This was twenty years ahead of major industrial applications of this process.

Air pollution and acid rains seriously affect the terrestrial and aquatic ecosystems and are therefore very important problems, which must be solved as soon as possible.

Exhaust gases from vehicles and industrial boilers contain mainly carbon oxides (CO and CO_2), nitrogen oxides (NO_x), hydrocarbons, sulfur dioxide, pesticides and soot.⁷

Use of inorganic ion exchangers is being considered for many special problems, e.g., in the treatment of liquid radioactive waste or for decontamination of various types of contaminated water. They have high selectivity for certain ions, higher thermal and radiation stability, often good chemical stability even in strongly acid media, and good compatibility with the matrices used for their immobilization.⁸

Besides pollution control, zeolites can be used as catalysts for petroleum fuels, chemicals and petrochemicals.

Zeolites ZSM-5 and ZSM-11 are the commercially most important end-members of a continuous series of intermediate structures belonging to the so-called pentasil family.

The first preparation of ZSM-5 was described in 1972 and since then a number of elaborate synthesis recipes have been reported in the patent literature.⁹

Zeolites (natural minerals) have characteristic cavities with a well-defined structure in the order of magnitude of atomic dimensions. This means

that they have a large specific surface area, and as a result, high adsorption capacities.^{11,12}

By means of synthesis, one can, however, generate many new structures with regular pores.

This paper deals with the influence of different alkali cations on the crystallization of ZSM-5,¹⁰ and the use of thus prepared ZSM-5 samples for the adsorption of paraoxon.

Alkali cations (salts) may influence the nucleation process of aluminosilicate gels (sols) in various ways, depending on their intrinsic properties. When introduced into an aqueous medium, charged alkali cations interact with the dipole water molecules and orient them into a firm hydration sphere with, as a first consequence, an increase of the (super) saturation of the solution, and thus influence the nucleation and crystal growth of zeolites.

The thus prepared zeolites were then investigated as sorption materials for paraoxon.

EXPERIMENTAL

Zeolites ZSM-5 with different alkali cations (Na^+ , K^+ , NH_4^+) were synthesized hydrothermally in static conditions.

The composition of the prepared gels was:



with: M = Na, K, NH_4 ; abbr. TPABr = tetrapropylammonium bromide.

The gels were kept in 20 cm³ PTFE Morey autoclaves at 170 (± 2) °C for 4 days. After crystallization was completed, the product was filtered, washed with distilled water until pH = 7 was obtained for the filtrates, and dried at 105 °C for 24 hours and finally ground in an agate mortar.

Qualitative phase analysis of the starting solids was performed by X-ray powder diffractometry using a Phillips PW 1710 diffractometer with Cu-K α radiation. The X-ray spectra were evaluated by the IS 86/OGC Ital Structure Computer Program.

For all samples, ultrasound treatment was used to separate the crystalline phase from the amorphous phase. This treatment was repeated for less crystalline samples.

A part of such »as-made« zeolites was heated at 500 °C for 4 hours in a nitrogen stream, and then at 350 °C for two hours in an oxygen stream in order to remove TPA molecules from the zeolite framework. The prepared »activated« zeolites were used in the experiments for adsorption.

Thermal analyses were carried out using a Netzch Model STA 429 simultaneous thermal analysis apparatus. The heating rate was 10 K min⁻¹ in nitrogen atmosphere. The flow rate of nitrogen was 15 cm³ min⁻¹. The samples were heated in a plati-

num crucible (diam. 6.8 mm, length 2.6 mm) from room temperature to 700 °C. About 30 mg of sample was used in each run. Calcined kaolin was used as a reference.

The thus prepared »activated« zeolites were then used in adsorption experiments.

To study the process of adsorption of (Na, K and NH₄)-ZSM-5, 2 g of solid were put into the reaction vessel containing 25 ml of paraoxon solution (0.02 M) in water.

The moment the solid was added to the solution was taken as the zero time of the adsorption ($t_{ad} = 0$).

At various times during the process of paraoxon adsorption, suspensions were drawn off for analysis (20 µL) and the sorption of paraoxon was measured colorimetrically (benzidine reagent, 420 nm).

The acceleration of the rate of oxidation of amine bases, such as benzidine, by various organophosphorus compounds was made the basis of a sensitive method for quantitative estimation of the phosphorus compound.

A spot test reaction, which produces a yellow colour when an aqueous alkaline peroxide solution is added to a nerve gas (or phosphono- and phosphoro-halides, phosphoroanhydrides and phosphorophenolate) in the presence of an oxydizable amine base, such as benzidine, was first described by Schönemann in 1944.^{13,14}

All the measurements were done with Na-, K- and NH₄-ZSM-5 zeolites. The tests with Na-ZSM-5 were done at 4 different temperatures (20, 30, 37 and 45 °C). For this purpose, the reaction vessel with double walls was thermostated at 20, 30, 37 and 45 °C.

RESULTS AND DISCUSSION

All as-synthesized, »as-made« samples, Na-, K- and NH₄-ZSM-5 zeolites, using as starting materials in adsorption studies, were fully crystalline powders having an MFI structure, as revealed by X-ray diffractometry.

Scanning electron micrographs of »as-made« and »activated« ZSM-5 crystals show that, in contrast to the »regular« shape of silicalite-1 crystals,¹⁵ ZSM-5 crystals have rough surfaces and the shape of the crystals considerably depends on the cation present in the reaction mixture during the synthesis. It is evident that the crystal size of silicalite-1 is controlled by the type of the cation; nucleation is enhanced in the presence of »structure-forming« Na⁺, and is depressed in the presence of »structure-breaking« K⁺ ions.

Figure 1 shows the scanning electron micrographs of starting powders of »as-made« ZSM-5 crystals synthesized from the system: 2.5 M₂O–TPABr–2 Al₂O₃–60 SiO₂–800 H₂O, with: M = Na (Figure 1a) and M = K (Figure 1b).

These cations have a strong influence on their particulate properties (particle size and shape, surface roughness, outer surface *etc.*, and the distribution of aluminium during the nucleation and crystal growth of ZSM-5).

Morphology, size, chemical composition and homogeneity of the (M) ZSM-5 crystallites depend on the competitive interaction between Pr₄N⁺ or

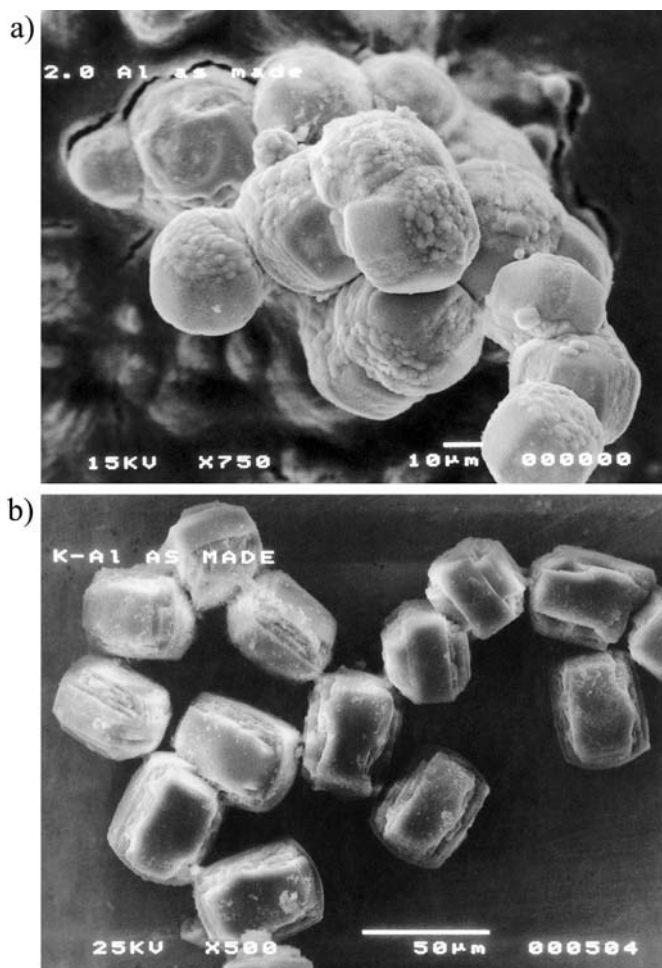


Figure 1. Scanning electron micrographs of the starting powders of »as made« Na-ZSM-5 (a) and K-ZSM-5 (b).

alkali cationic species and aluminosilicate polymeric anions at the early stages of the nucleation process. The latter, in turn, is strongly affected by the intrinsic properties of the alkali cations, such as their size, their structure-forming or structure-breaking role towards water and their salting-out power.

In the presence of structure-forming cations (Li^+ , Na^+), rapid nucleation yields Si-rich crystallites, homogeneously distributed within the 5–15 μm range. These are coated with numerous small (1 μm) Al-richer crystallites formed by a secondary nucleation process from Si-deficient gel.

Structure-breaking cations, such as K^+ , (Rb^+ , Cs^+), favour the formation of large (15–20 μm) single crystals or twins.

In the presence of NH_4^+ ions, large single crystals of ZSM-5, having an Al-deficient core and an Al-rich outer shell, as well as small Si-rich crystallites stemming from a delayed nucleation process, are formed. This particular role of NH_4^+ cations is explained in terms of its preferential interactions with aluminate rather than with silicate anions during the nucleation stage.

As a result, K- (Rb, Cs) ZSM-5 zeolites appear homogeneous in composition, while Li- and Na-polycrystalline aggregates show an apparent Al-enriched outer rim.

The DTA curve of the Na-ZSM-5 zeolite (Figure 2, curve a) shows at 388 °C a loss of 1.54% of the total mass, which corresponds to the desorption of zeolitic water, *i.e.*, dehydration of the sodium ions located in the channel/ cage system of the zeolite ZSM-5 framework.

DTA curve has the minimum at 434 °C, which corresponds to the loss of TPA (9.55% of the total mass).

DSC curve of the sample (Figure 2, curve b) has a broad endothermic minimum at 462 °C, which corresponds to the position in the DTA curve which is attributed to the loss of TPA ions.

Figure 3 shows the adsorption of paraoxon on K-, Na- and NH_4 -ZSM-5 zeolites.

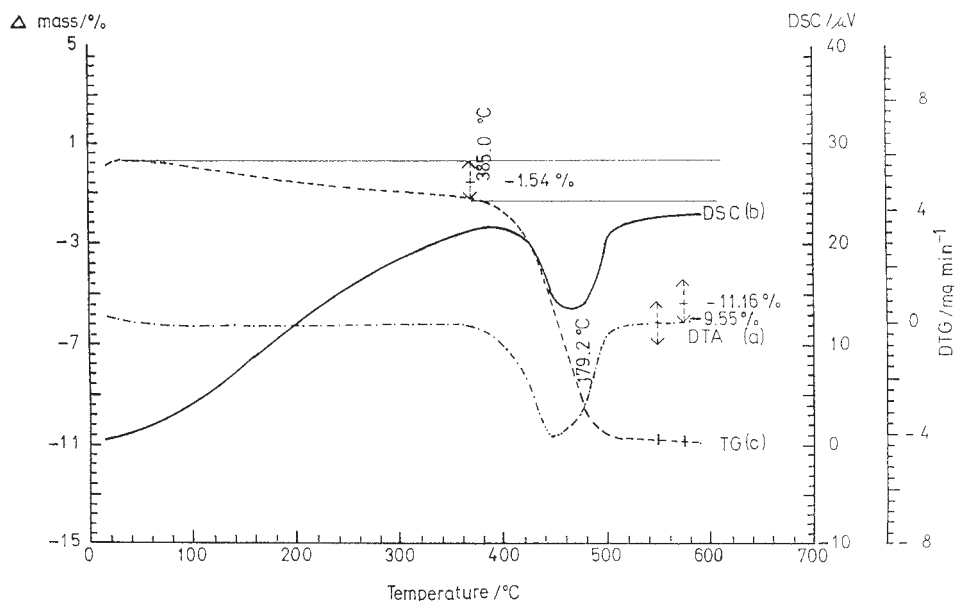


Figure 2. DTA (a), DSC (b) and TG (c) curves of «as-made» Na-ZSM-5.

There is no big difference between the adsorption of K-, Na- and NH₄-ZSM-5 zeolites, especially after the first ten minutes.

The rate of adsorption in the first ten minutes increases in the order K < Na < NH₄ (Figure 3).

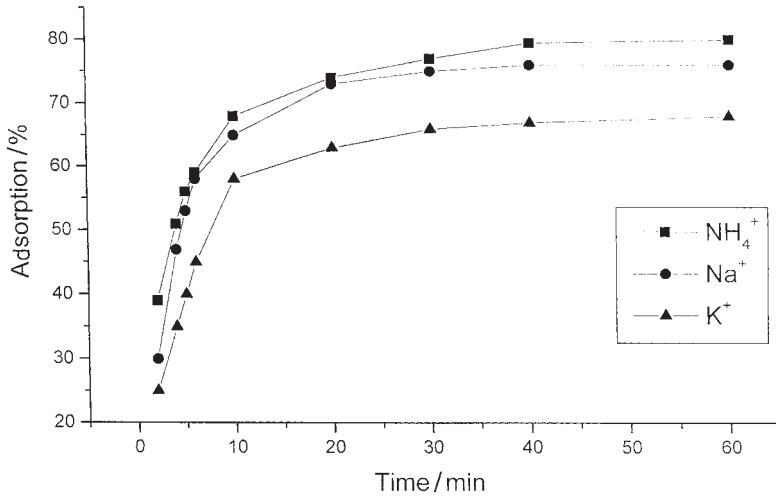


Figure 3. Adsorption of paraoxon on: K-ZSM-5 (a); Na-ZSM-5 (b); NH₄-ZSM-5 (c) at 20 °C.

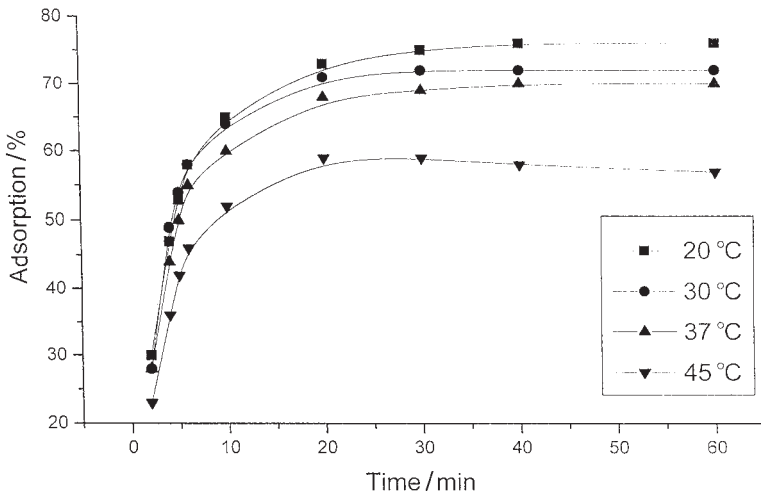


Figure 4. Adsorption of paraoxon on Na-ZSM-5 zeolite at: 20 °C (a); 30 °C (b); 37 °C (c) and 45 °C (d).

It was shown before that when these zeolites undergo dissolution in NaOH solution,¹⁵⁻¹⁸ the increase of the initial rate of dissolution, $r_{\text{diss},i}$, in the sequence $r(\text{K}) < r(\text{Na}) < r(\text{NH}_4)$ indicates that the penetration of OH^- ions from the liquid phase is faster inside smaller crystals (Na-ZSM-5) than inside larger ones (K-ZSM-5). The same reason is probably responsible for the initial increase of paraoxon adsorption.

Figure 4 shows the adsorption of paraoxon at 20, 30, 37 and 45 °C on Na-ZSM-5.

In order to analyze the relations between the equilibrium concentration (c) of paraoxon in the solution and the sorption of paraoxon on 1 g of zeolite, these concentrations (c) of paraoxon in the solution were plotted against c/x (where c is the concentration of paraoxon in equilibrium, and x is the adsorption of paraoxon per 1 g of zeolite).

In all cases (for 20, 30, 37 and 45 °C) adsorption isotherms are linear functions, indicating that:

$$c/x \text{ (20 °C)} = 1.23 \times 10^{-3} + 13.60 c \quad (1)$$

$$c/x \text{ (30 °C)} = 2.75 \times 10^{-3} + 13.89 c \quad (2)$$

$$c/x \text{ (37 °C)} = 2.74 \times 10^{-3} + 14.29 c \quad (3)$$

$$c/x \text{ (45 °C)} = 0.20 \times 10^{-3} + 17.24 c \quad (4)$$

or:

$$x \text{ (20 °C)} = 0.074 c / (c + 9.044 \times 10^{-5}) \quad (5)$$

$$x \text{ (30 °C)} = 0.072 c / (c + 1.980 \times 10^{-4}) \quad (6)$$

$$x \text{ (37 °C)} = 0.070 c / (c + 1.920 \times 10^{-4}) \quad (7)$$

$$x \text{ (45 °C)} = 0.058 c / (c + 1.160 \times 10^{-4}) \quad (8)$$

Lines are written using the method of minimum squares, and the correlation factors are 0.99 (5); 0.99 (6); 0.99 (7); 0.99 (8).

Figure 5 shows plots of $10^2 c/x$ vs. c (at 20, 30, 37 and 45 °C).

Coefficients of the lines are the reciprocal values of maximal amounts of paraoxon that can be absorbed on 1 g of zeolite.

From the Eqs. (5), (6), (7) and (8) it can be calculated that the maximal amounts of paraoxon that can be adsorbed on 1 g of zeolite Na-ZSM-5 are: 0.074 mmol (20.36 mg) at 20 °C, 0.072 mmol (19.82 mg) at 30 °C, 0.070 mmol (19.27 mg) at 37 °C, 0.058 mmol (15.69 mg) at 45 °C.

The adsorption of paraoxon on Na-ZSM-5 at these 4 different temperatures shows that adsorption decreases with the temperature.

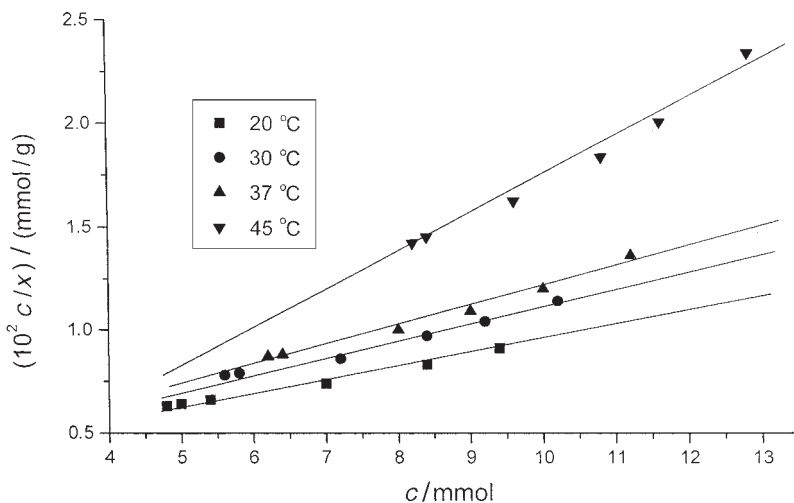


Figure 5. Plots of $10^2 c/x$ vs. c at 20, 30, 37 and 45 °C.

For NH_4 -ZSM-5 this amount is 22.0 mg of paraoxon per 1 g of zeolite, and for K-ZSM-5 the value is 18.71 mg/1 g zeolite. The measurements were performed at 20 °C.

CONCLUSIONS

The results obtained in the syntheses of K-, Na- and NH_4 -ZSM-5 confirm that inorganic cations play an important role in the synthesis of ZSM-5 zeolites.

The adsorption of paraoxon is very fast and about 80% of total adsorption is done in the first 10 minutes.

There is no big difference between the adsorption of K-, Na- and NH_4 -ZSM-5 zeolites, especially after the first ten minutes. The adsorption rate increases in the sequence $r_{\text{ads}}(\text{K}) < r_{\text{ads}}(\text{Na}) < r_{\text{ads}}(\text{NH}_4)$. This is probably a consequence of the increase of the total surface area (S) in the sequence $S(\text{K}) < S(\text{Na}) < S(\text{NH}_4)$. It should be pointed out that after the calcined treatment, the zeolite that remains is H-ZSM-5.

The adsorption of paraoxon on Na-ZSM-5 at 4 different temperatures shows that adsorption decreases with the temperature.

Maximal amounts of paraoxon adsorbed per gram of zeolite are 22.0, 20.36 and 18.71 mg for NH_4 -ZSM-5, Na-ZSM-5 and K-ZSM-5, respectively, at 20 °C.

REFERENCES

1. D. E. Vaughan, in: G. Alberti and T. Bein (Eds.), *Comprehensive Supramolecular Chemistry*, 1996, pp. 379–392.
2. L. L. Ames, *Am. Mineral.* **45** (1960) 689–700.
3. L. L. Ames, *Am. Mineral.* **46** (1961) 1120–1131.
4. L. L. Ames, *Am. Mineral.* **47** (1962) 1310–1316.
5. L. L. Ames, *Am. Mineral.* **48** (1963) 868–882.
6. R. M. Barrer, U.S. Patent 2 306 610 (1941).
7. M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine, and S. Kagawa, *J. Phys. Chem.* **95** (1991) 3727–3730.
8. F. Šebesta, J. John, and A. Motl, *IAEA Tech. Doc.* (1997) 947.
9. R. J. Argauer and G. R. Landolt, U.S. Patent 3 702 886 (1972).
10. Ž. Gabelica, E. G. Derouane, and W. Bloom, in: T. E. Whyte, R. A. Dalla Betta, E. G. Derouane, and R. T. K. Baker (Eds.), *ACS Symp. Ser.* **248**, pp. 219–251.
11. K. Meyer, P. Lorenz, B. Bökl-Kuhn, and P. Klobes, *Cryst. Res. Technol.* **29** (1994) 903–930.
12. D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, J. Wiley & Sons, New York, 1974.
13. R. B. R. Schönemann, US Department of Commerce, PB 119 887 (1944).
14. B. Gehauf, J. Epstein, G. B. Wilson, B. Witten, S. Sass, V. E. Bauer, and W. H. C. Ruggeberg, *An. Chem.* **29** (1957) 278–283.
15. A. Čižmek, Lj. Komunjer, B. Subotić, R. Aiello, F. Crea, and A. Nastro, *Zeolites* **14** (1994) 182–189.
16. A. Čižmek, B. Subotić, R. Aiello, F. Crea, A. Nastro, and C. Tuoto, *Microporous Materials* **4** (1995) 159–168.
17. A. Čižmek, B. Subotić, F. Crea, A. Nastro, and R. Aiello, in R. Aiello (Ed.), *Proc. III Convegno Nazionale Scienze e Tecnologia delle Zeoliti*, Associazione Italiana Zeoliti, Cosenza, 1995, 167–175.
18. A. Čižmek, B. Subotić, I. Šmit, A. Tonejc, R. Aiello, F. Crea, and A. Nastro, *Microporous Materials* **8** (1997) 159–169.

SAŽETAK

**Adsorpcija paraoksna na visokosilikatnim pentasilima
s različitim alkalijskim kationima**

Ankica Čižmek i Zlatko Ivančić

Proučavana je adsorpcija paraoksna (dietil-*p*-nitrofenil-fosfat) na visokosilikatnim pentasilima s različitim alkalijskim kationima (Na^+ , K^+ , NH_4^+), koristeći se metodom mjerenja povećanja brzine oksidacije benzidina. Diskutira se o utjecaju alkalijskih kationa, prisutnih u sustavu tijekom sinteze zeolita. Brzina adsorpcije paraoksna na Na-ZSM-5 određena je pri različitim temperaturama (20, 30, 37 i 45 °C).