

A STUDY OF THE INTERACTION OF SOME KETONES WITH HZSM-5 ZEOLITE

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ABSTRACT

Interaction of several ketones with HZSM-5, NaZSM-5 and HY zeolites was studied. Acetone and methylethylketone on HZSM-5 were investigated in greater detail. IR study of surface complexes remaining in zeolites after treatment at various temperatures in vacuo was used, as well as the temperature-programmed desorption of very small amounts of preadsorbed ketones which was linked directly to the mass spectrometer. It was concluded that acetone transformation proceeds via the decomposition of surface intermediates formed by acid-catalyzed intermolecular acetone condensation. With methylethylketone (and higher ketones) intermolecular dehydration prevails and is enhanced but not conditioned by the presence of zeolitic acid centers.

INTRODUCTION

HZSM-5 zeolite catalyzes the transformation of oxygenated organic compounds such as alcohols, ethers, aldehydes, acids and esters into aliphatic and aromatic hydrocarbons (1). Particular attention has been paid to the conversion of alcohols, especially methanol and numerous theories have been advanced for the reaction mechanism (2). Of the ketones, only acetone has been studied and the reactions on ZSM-5 and faujasites were compared (3). Condensation of acetone to oxygenated products at low temperatures (in some cases up to mesitylene) was assumed to be the first reaction step, followed by cracking to isobutene or -ane and acetic acid. While C_4H_{8-10} hydrocarbons were actually observed on ZSM-5 and rare-earth Y, acetic acid appeared only on the latter zeolite. At higher temperatures, aromatics dominated in the products, with a composition dependent on the zeolite type according to its shape selectivity (1,3).

In order to obtain a deeper insight into the processes occurring during the transformation of carbonyl-group-containing compounds over zeolites, we have focused our study on the comparison of the reaction

of several ketones, mainly acetone and methylethylketone, on HZSM-5. Two experimental methods were used: i) Infrared spectroscopy (IR) of surface compounds which were formed during the adsorption of ketones at room temperature and after their desorption at elevated temperatures. The gaseous products were collected and analyzed mass spectrometrically. ii) Mass spectrometric detection of the products of very small amounts of ketones preadsorbed at room temperature and released during temperature programmed desorption (TPD). In some cases, the catalytic reaction at low-pressure flow conditions was also investigated and the activity of HZSM-5 was compared with that of NaZSM-5 and HNaY.

EXPERIMENTAL

ZSM-5 zeolite with an Si/Al ratio equal to 19 was synthesized in the usual way (4); organic cations were decomposed in an oxygen stream at 870 K. NaZSM-5 was converted to the NH_4 form by ion exchange. The sorption capacity measured with Ar was 5.4 mmol g^{-1} (related to the dry sample). The Si/Al ratio of $(\text{NH}_4)_{70}\text{Na}_{30}\text{Y}$ was 2.5 and the sorption capacity equalled 10.6 mmol g^{-1} . Before the measurements, all the samples were dehydrated and deammoniated in vacuo at 670 K for 18 hrs. Ketones (p.a. purity, Lachema) were predistilled in vacuo and degassed by repeated freezing and thawing. Acetone- d_6 (enrichment 99.5 %, Institute of Nuclear Research, Poland) was pretreated in the same way.

The infrared spectra of selfsupporting pellets of zeolites were measured at ambient temperature using a Nicolet MX-1E Fourier transform infrared spectrometer. The spectra presented here correspond to a sample thickness of 7 mg cm^{-2} . Ketones were adsorbed in successive doses up to 5 mmol g^{-1} at room temperature. The zeolite was then heated (rate, 6 K min^{-1}) and the evolved vapours were collected in the temperature ranges 430 - 530, 530 - 630, and 630 - 730 K by freezing-out into separate bulbs. Up to 430 K, the desorbed gases were pumped off. The collected desorbate was analyzed by a mass spectrometer (MI 1302, USSR). The IR spectra of the zeolites were recorded both during the adsorption and after reaching the temperatures 430, 530, 630 and 730 K, when the samples were rapidly cooled to the ambient temperature.

The TPD was measured on the same mass spectrometer using 0.1 g of the zeolite. After 30 min. adsorption of $5 \times 10^{-2} \text{ mmol g}^{-1}$ at room temperature, the zeolite was heated (6 K min^{-1}) with direct pumping of the gaseous products through the spectrometer. A by-pass evacua-

tion was used to ensure that the maximum pressure of the evolved vapours did not exceed 1×10^{-3} Pa. When measuring the catalytic reaction, the zeolite (0.05 g) was placed in a reactor in front of the ionization chamber of the spectrometer and allowed to react with the ketone at inlet and outlet pressures of 10^{-2} and 4×10^{-4} Pa, respectively. The flow under these conditions was about $3 \times 10^{-4} \text{ l h}^{-1}$.

RESULTS

Acetone. Fig. 1a shows the TPD of acetone from HZSM-5: a small amount of acetone is released above 370 K, followed by desorption of butene which exhibits two maxima, at about 570 and 670 K. Between these two maxima, C_{6-7} dienes or most probably cyclohexenes are evolved. Above 570 K aromatics appear with the maximum of toluene. The last observed product above 620 K has the composition C_3H_4 , corresponding to allene or methylacetylene. The catalytic reaction under low-pressure flow conditions yields products of very similar composition at the relevant temperatures, as can be seen in Fig. 1b. The TPD of fully deuterated acetone demonstrates that hydrogen from the zeolitic OH groups is incorporated into the products from the very beginning of the reaction. With increasing temperature, the isotopic exchange increases.

In contrast to HZSM-5 almost no conversion of acetone is observed over NaZSM-5; the desorption of physisorbed acetone starts above 520 K and reaches its highest value at about 600 K.

The IR spectra depicted in Fig. 2 show deep changes in the composition of the surface complexes during the desorption of acetone from HZSM-5 between 295 - 530 K. At room temperature, acetone is preferentially adsorbed on the framework OH groups, forming H-bonded complexes with them. This is reflected in the disappearance of the OH band at 3610 cm^{-1} (a, curve 1,2), the appearance of broad OH bands below 3000 cm^{-1} and shifts of the position of bands of adsorbed acetone (b, curve 2) related to the vibrations of molecules in the gas phase. The most pronounced change is that in the $C=O$ vibration adsorbing at 1740 cm^{-1} (gaseous acetone) and at 1670 cm^{-1} (H-bonded acetone) which indicates a partial loss of double bond character. Acetone molecules of further doses are considerably less perturbed as follows from the position of the $C=O$ band at 1720 cm^{-1} . This band is dominant in the spectrum at high pore filling (not shown in Fig. 2). The removal of the adsorbed acetone between 295 - 430 K is accompanied by the formation of new surface species characterized by the bands at 1618 cm^{-1} which can be attributed to

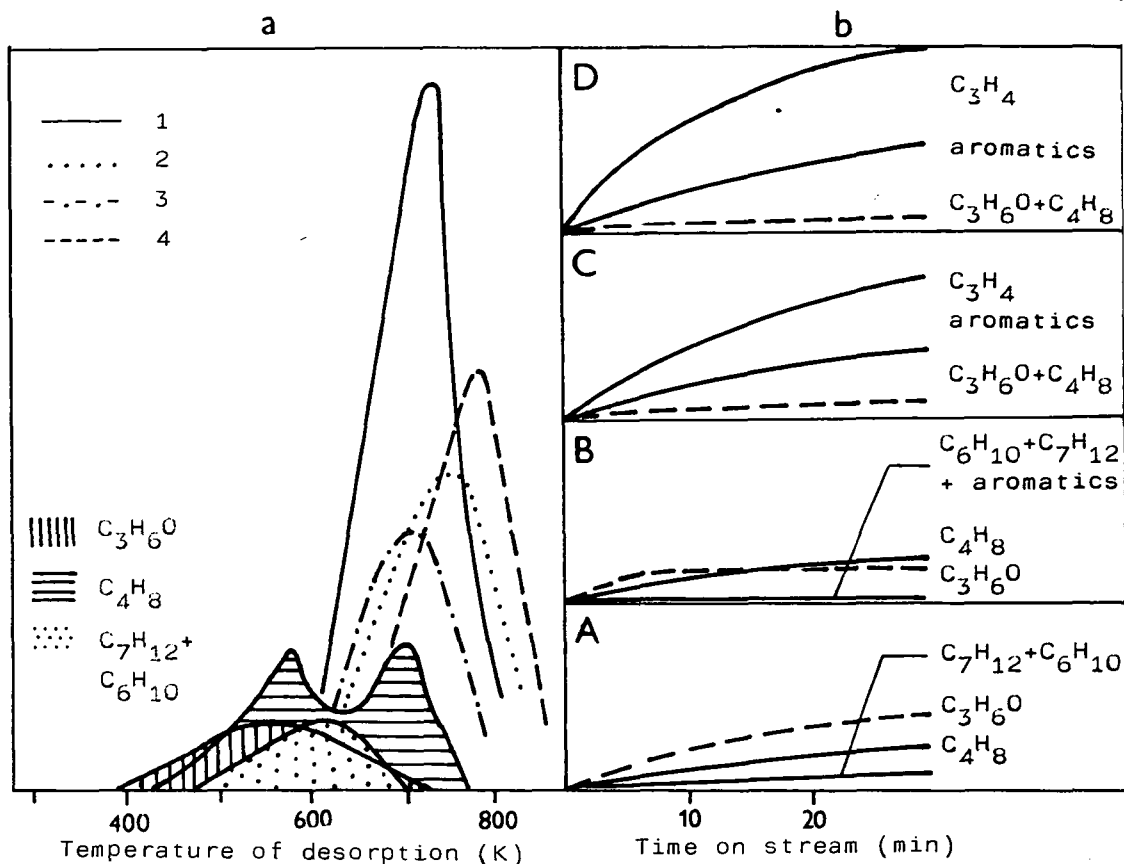


Fig. 1. Acetone (C_3H_6O) reaction with HZSM-5, a) TPD of gas products, b) low-pressure flow conversion at 370, 450, 710 and 790 K, A,B,C,D, respectively

1- C_7 aromatics, 2-benzene, 3- C_{8-9} aromatics, 4- C_3H_4

the C=O and C=C vibrations, respectively, in the products of acetone condensation (b, curve 3). The spectrum of the OH groups (a, curve 3) shows that these products also interact with the framework hydroxyls. Further heating to 530 K leads to a new rearrangement of surface species with simultaneous removal of adsorbed acetone molecules (b, curve 4) and the appearance of isobutene in the gas phase. As this new compound exhibits high thermal stability and the zeolitic OH groups can be restored in the original amount only after complete decomposition during 2 h evacuation at 770 K, it can be assumed that it is bonded directly to the lattice. This together with the prominent bands at 1644, 1543 and 1511 cm^{-1} assigned to the C=O and C=C vibrations support the idea of lattice oxygen bonding with the ketene, e.g.:

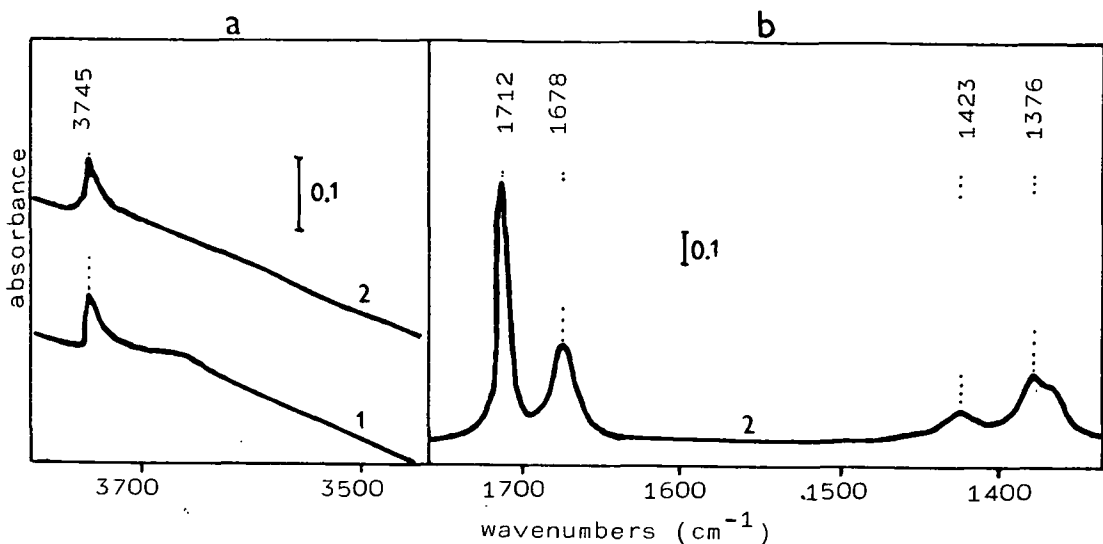


Fig. 3. IR spectra of acetone on NaZSM-5, a) OH groups, b) surface complexes

1-original zeolite, 2-after adsorption of excess acetone and desorption up to 530 K

bient temperature as well as during thermal desorption without any catalytically conditioned changes.

Methylethylketone. The TPD of this ketone is depicted in Fig. 4a,b for HZSM-5 and NaZSM-5, respectively. The conversion is substantially higher with the acid form, where only a very small amount of unreacted ketone appears, preceded by the evolution of propene and C₄₋₇ olefins and cycloalkenes. The amount of these substances is relatively low and is followed above 570 K by a much greater release of propene, C₅H₆ (probably cyclopentadienes) and especially butadiene (dimethylacetylene) and C_{6,7} aromatics. The small maximum of products below 500 K is missing with NaZSM-5 while a large amount of unreacted ketone starts to desorb. This is followed by the release of C₅H₈ (less unsaturated product than with the acid zeolite form), propene and butadiene in almost the same amounts as with HZSM-5. The release of C₆₋₈ aromatics is much lower with NaZSM-5 than with HZSM-5.

The IR spectra of adsorbed species on HZSM-5 (Fig. 5b, curve 2) together with spectral changes in the region of OH vibrations (Fig. 5a, curves 1,2) show that, at room temperature, H-bonded complexes of methylethylketone are preferentially formed with framework hydroxyls. The C=O vibration band at 1650 cm⁻¹ again indicates an

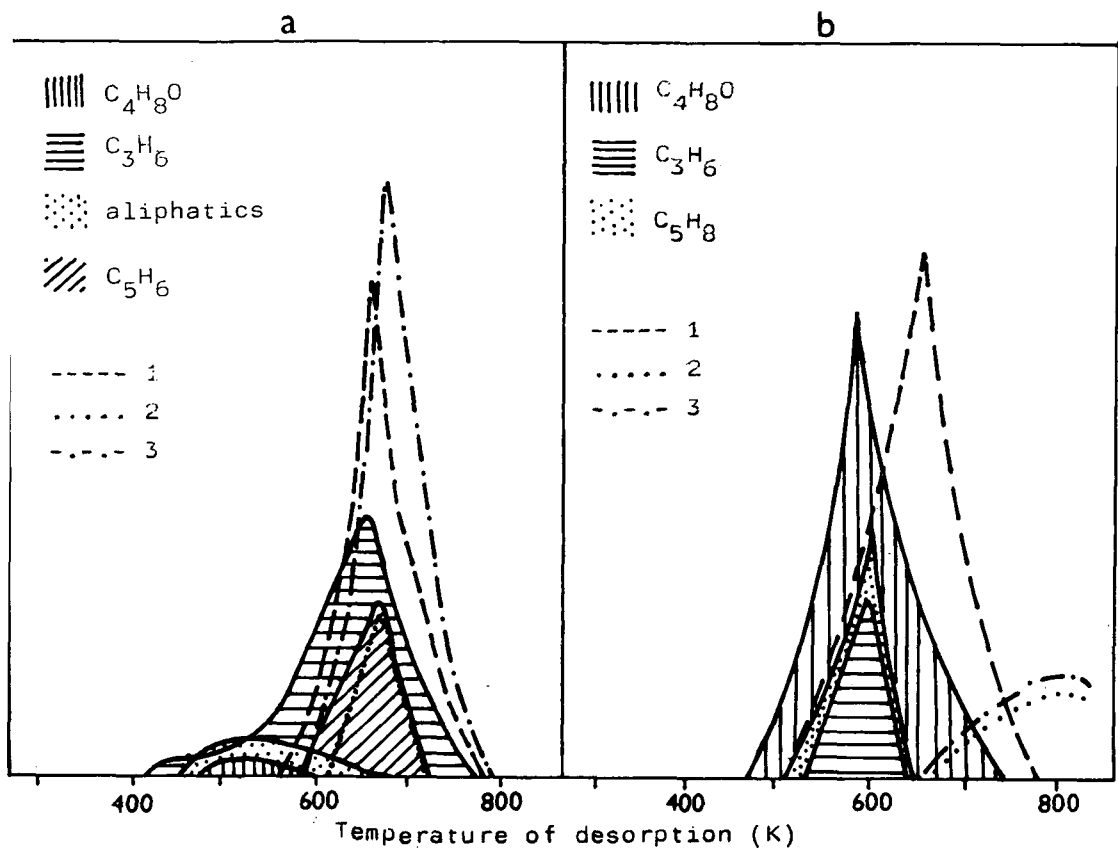


Fig. 4. TPD of methylethylketone, a) from HZSM-5, b) from NaZSM-5

1- C_4H_6 , 2-benzene, 3- $C_{7,8}$ aromatics

appreciable weakening of the double bond in comparison with the gas molecule ($\nu_{C=O} = 1740 \text{ cm}^{-1}$). Thermal desorption leads to the progressive removal of surface species without such pronounced transformations as those observed for the acetone. Only several new weak bands are found in the region $1510 - 1580 \text{ cm}^{-1}$; however, their intensity is changed without any special interrelations. The evolved gas always contains unreacted ketone. Similarly as in TPD, the products of catalytic reaction appear in considerable amounts above 570 K with predominant aromatics. These data support the assumption that the weak band at $1510 - 1570 \text{ cm}^{-1}$ which remains in the spectrum of the surface at the relevant temperatures (Fig. 5b, curves 4,5) most probably corresponds to adsorbed aromatics.

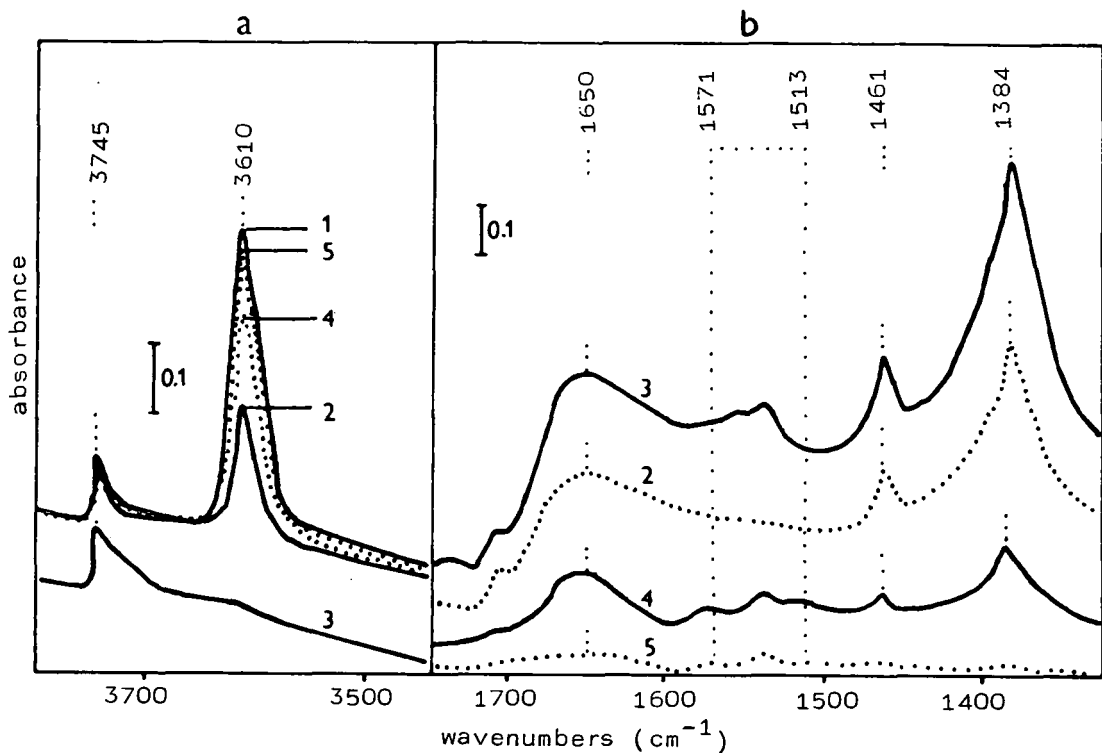


Fig. 5. IR spectra of methylethylketone on HZSM-5, a) OH groups
 b) surface complexes
 1-original zeolite, 2-after adsorption of 0.4 mmol g⁻¹ ketone,
 3-5- after addition of excess ketone and thermal desorption up
 to 430, 530 and 630 K, respectively

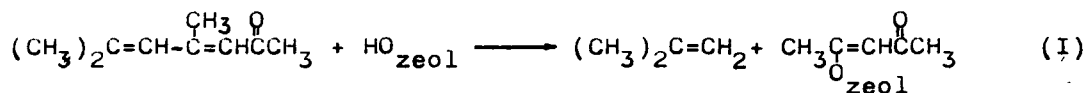
DISCUSSION

Before discussing the results, it should be mentioned that the interaction of small amounts of reactants with zeolites exhibits special features. This results from the fact that, under these conditions, molecules are preferentially influenced by the most active sites on the surface and mutual interactions among the reactant, intermediates and products are appreciably reduced. The product composition is thus more intimately connected with the first reaction steps and with the presence of various types of surface complexes than for reactions proceeding at higher pressure. Increasing pressure (amount of adsorbed species) naturally changes the product distribution; however, the most characteristic compounds almost always appear (5).

Acetone and methylethylketone are the two simplest compounds in the broad family of ketones. Nevertheless, they can serve as an

example of the substantially changed reaction path in catalytic transformation on the same zeolites. The condensation of ketones in acid media, leading to a series of dehydrated products is well known from organic chemistry. This type of reaction apparently occurs with acetone on HZSM-5 which contains framework hydroxyls of high acid strength, while NaZSM-5 with only Na ions and electron-accepting sites is inactive. The formation of H-bonded complexes, demonstrated by the IR spectra, is probably responsible for the enhanced reactivity of adsorbed acetone because of facilitated splitting off of hydrogens from the methyl groups. The mobility of H⁺ between acetone and zeolite follows also from the easy isotopic exchange of deuterated acetone with the hydroxyl hydrogens.

In contrast to (3), oxygen-containing products of acetone condensation were not observed in the gaseous phase, but they were found in the zeolites even below 430 K. As the temperature increased up to 530 K, these condensates were transformed to isobutene, which was released into the gas phase, and to a new carbonyl compound firmly bound to the zeolite lattice. The framework hydroxyls could aid in the cracking of the acetone condensate, e.g. as follows:



The new surface species (I) is thermally stable but it can take part in a further reaction when interacting with a compound able to donate a proton for the re-formation of the framework hydroxyls. This most probably occurs at higher temperatures along with cyclization to aromatics which are the prevailing gaseous products. The thermal decomposition of surface ketene (I) might be responsible for the release of C₃H₄ observed in TPD as the last product; however, this compound can also be formed via an intramolecular dehydration.

The interaction of methylethylketone with zeolites is clearly of different character than that of acetone: i) both the acid and the Na form of ZSM-5 catalyzed the transformation, ii) C₄H₆ was formed in an appreciable amount over both zeolites and iii) no firmly bound surface ketene similar to (I) was observed. It can thus be assumed that a simple intramolecular dehydration of methylethylketone to C₄H₆ plays an important role here. This reaction is not apparently conditioned by the formation of H-bonded complexes, as the influence of Al electron accepting sites, Na ions and electrostatic field of zeolites sufficiently activates the ketone molecules.

Butadiene most probably takes part in the formation of aromatics, as follows from their release from NaZSM-5. However, HZSM-5 exhibits much higher activity, reflected in the total conversion and the product composition. This is apparently caused by the participation of the OH groups influencing the transformation and by the contribution of some condensation reactions of ketone, though not as pronounced as with acetone.

Some higher ketones (diethylketone, cyclopentanone and cyclohexanone) were also studied. They released products of intramolecular dehydration which preceded the evolution of aromatics. 2,4-pentadione behaved in a very similar way to acetone, supporting the conclusion on the dominant role of acetone condensates in its transformation. *

The TPD of all these ketones was also investigated with the HY zeolite. The comparison of products released from HZSM-5 and HY reflected the higher acid strength and shape-selective properties of HZSM-5 (6).

REFERENCES

1. Chang, C.D., Silvestri, A.J., J. Catal. 47, 249 (1977).
2. Chang, C.D., Catal. Rev. 25, 1 (1984).
3. Chang, C.D., Lang, W.H., Bell, W.K., Catalysis in Organic Reactions. W.R. Moser, Ed., M. Dekker, N.Y., p. 84-93 (and refs. therein).
4. U.S. Patent 3,702,886.
5. Nováková, J., Kubelková, L., Habersberger, K., Dolejšek, Z., J. Chem. Soc., Faraday Trans. I, 80, 1457 (1984).
6. Nováková, J., Kubelková, L., Jírů, P., to be published.