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DRIFT study of molecular and dissociative adsorption of light paraffins by HZSM-5 zeolite modified with zinc ions: methane adsorption

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Abstract

DRIFT study of methane adsorption by ZnZSM-5 zeolites prepared by incipient wetness impregnation or by chemical reaction of the initial hydrogen form with zinc vapor at 770 K indicated an unusually broad DRIFT band with a maximum at 2805 cm^{-1}. This frequency is more than 200 cm^{-1} lower than the asymmetric ν_3 C–H stretching mode of gaseous methane and more than 100 cm^{-1} lower than the symmetric ν_1 stretching frequency. Methane adsorption by zinc cations is much stronger than that by the bridging hydroxyl groups or sodium ions. At 473 K adsorbed methane is involved in heterolytic dissociation, resulting in formation of bridging hydroxyl groups and zinc alkyls. Such dissociative adsorption blocks the sites for subsequent molecular adsorption of methane or hydrogen. In accordance with our previous results on hydrogen adsorption, we conclude that the dissociative methane adsorption occurs on acid–base pairs with distantly separated Zn^{2+} ions and basic oxygen atoms of the zeolite framework. Unusually large perturbation and dissociation of methane at the relatively low temperature are connected with only partial compensation of the positive electric charges of Zn^{2+} ions at such sites.

Keywords: ZSM-5; Methane adsorption; DRIFT; Dissociation

1. Introduction

HZSM-5 zeolites modified with Zn^{2+} ions are known as active catalysts for aromatization of light paraffins [1]. Therefore, the study of the state of zinc in these materials has been a subject of recent publications [2–5]. However, in none of those studies were zinc cations detected with any spectral technique. Zinc cations were detected only in our recent investigations [6–11] using low-temperature H_2 adsorption as a molecular probe. Perturbation of the H–H stretching frequency resulting from hydrogen interaction with zinc ions was controlled by DRIFT spectroscopy in those studies.

The results obtained indicated formation of two types of low coordinated Zn^{2+} ions in ZnZSM-5. Adsorption at 77 K of molecular hydrogen by zinc cations at the conventional ion-exchangeable sites localized at two aluminum–oxygen tetrahedra in next nearest positions results in a moderate low-frequency shift of H–H stretching vibrations. This shift is close to that we reported earlier for hydrogen adsorption by Zn^{2+} ions at S_{II} sites in ZnY zeolite [6].

The sites of much stronger perturbation of adsorbed molecular hydrogen predominate in the samples with high Si/Al ratios. Therefore, it was concluded that zinc ions at such sites are localized at the isolated aluminum-occupied oxygen tetrahedra that are distantly separated from each other due to the low aluminum density in the framework [10,11]. The excessive positive charges of Zn^{2+} ions at such sites are compensated in an indirect way by Coulomb interaction with the surrounding negatively charged aluminum-occupied oxygen tetrahedra with cationic vacancies. Adsorption of hydrogen by such sites results in a very large low-frequency shift of H–H stretching vibrations. Moreover, such acid–base pairs with the distantly separated zinc ions and basic oxygen atoms dissociatively adsorb hydrogen at temperatures only slightly above room temperature.

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Here, we report our new experimental results on methane adsorption by ZnZSM-5 prepared by incipient wetness impregnation or by chemical reaction of the bridging acidic hydroxyl groups with zinc vapor at 770 K [12,13]. As has been demonstrated in our previous work [10,11], the latter way of preparation results in more complete substitution of isolated acidic hydroxyl groups by zinc ions, creating a larger number of acid–base pairs with the distantly separated excessively positively charged zinc ions and basic aluminum-occupied oxygen tetrahedra with cationic vacancies:

$$2[\mathrm{AlO_2}]^-\mathrm{H}^+ + \mathrm{Zn}^0 \rightarrow [\mathrm{AlO_2}]^-\mathrm{Zn}^{2+} + [\mathrm{AlO_2}]^- + \mathrm{H_2}\uparrow. \qquad (1)$$

In parallel, we also studied DRIFT spectra of methane adsorbed by the hydrogen and sodium forms of the same ZSM-5 zeolite.

Broad-range DRIFT spectra of methane adsorbed by HM were reported previously [14], and transmittance IR spectra of methane adsorbed by the alkaline cationic forms of high silica zeolites were studied in Refs. [15–17]. The results obtained in those studies of hydrogen and different cationic forms of zeolites indicated that the asymmetric ν_3 stretching frequency of methane exhibits a low-frequency shift of about 20 cm^{-1} upon adsorption, whereas the symmetry-forbidden ν_1 C–H stretching frequency, which is observed in the gas phase only in Raman spectra, becomes IR active and is also moderately downshifted by 20–25 cm^{-1}. In some cases, additional splitting of both these lines due to the lowering of the symmetry of adsorbed methane was reported. The low-frequency shifts of the ν_2 and ν_4 bending frequencies are much less than those of the stretching frequencies.

2. Experimental

The preparation of ZnZSM-5 zeolite by incipient wetness impregnation from the hydrogen form (obtained from Shell) with a framework Si/Al ratio equal to 41 modified with 0.8 wt% zinc (Zn/Al = 0.5), as well as vacuum pretreatment of such samples, was described previously [8,9]. To prepare HZSM-5 and HY modified by high-temperature reaction with zinc vapor, the ammonium forms of SN-55 ZSM-5 zeolite (Alsi Penta) with Si/Al = 25 or $\mathrm{NH_4Y}$ with Si/Al = 25 (Shell), were at first decomposed under vacuum at 770 K. Then they were treated in a quartz vacuum cell for DRIFT measurements at this temperature with zinc vapor for 30 min. The molecular hydrogen released was collected in a trap with NaX zeolite that was cooled with liquid nitrogen. To remove excess metallic zinc, the modified zeolite was evacuated at the end of the hydrogen evolution for 2 h at 770 K. The zinc content in the zinc-modified ZSM-5 sample was 1.9 wt%, as detected by AAS analysis. This value is the same as that based on the volume of evolved hydrogen, which was 1.85 wt% for ZnZSM-5 and 13.25 wt% for ZnY zeolite. These values of the zinc content for both modified zeolites indicate that the Zn/Al atomic ratio in these samples was approximately 0.5.

Similar to procedures in our previous work, DRIFT spectra of the granulated zeolites with grain dimensions of 0.5–1 mm were measured at room temperature using a Nicolet "Impact 410" spectrophotometer equipped with a home-made diffuse reflectance unit. For DRIFT measurements, the zeolite grains were transferred to the side finger of a vacuum cell with a $\mathrm{CaF_2}$ window. All DRIFT spectra were transformed into Kubelka–Munk units assuming that the reflective ability of the samples at 5000 cm^{-1} was 0.9 unit. Then the background created by zeolite was subtracted.

Methane was adsorbed at room temperature at different equilibrium pressures, whereas DRIFT spectra were recorded at room temperature either in the presence of gaseous methane or after evacuation of methane at different elevated temperatures.

3. Results

Comparison of DRIFT spectra resulting from methane adsorption by the hydrogen and sodium forms of ZSM-5 is shown in Fig. 1. Both spectra correspond to superposition of the bands from gaseous or physically adsorbed methane and those from methane specifically adsorbed by protons or sodium cations.

A sharp line at 3016 cm^{-1} belongs to the vibration–rotational *Q*-branch of the ν_3 C–H asymmetric stretching vibrations of gaseous molecules. The *P* and *R* branches of the vibration–rotational structure are visible at the lower and higher frequencies. The asymmetric ν_3 stretching vibrations of adsorbed methane correspond to the maximum at 3001 cm^{-1}, while the frequencies of the weaker bands from symmetric ν_1 C–H stretching vibrations of $\mathrm{CH_4}$ perturbed by interaction with protons or sodium cations are slightly different. The maximum of the much weaker band of methane adsorbed by the hydrogen form corresponds to the frequency

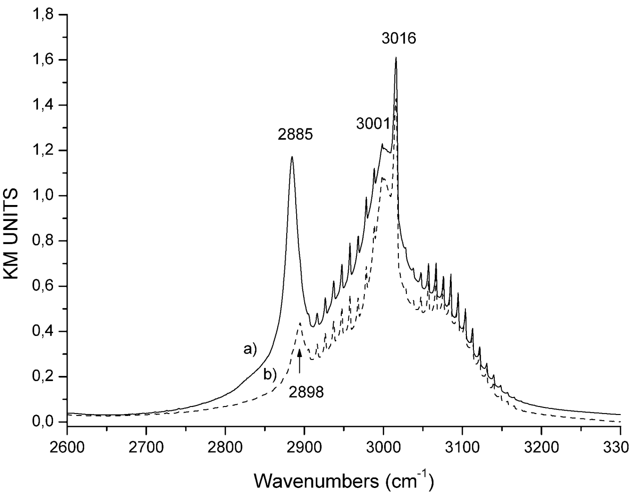

Fig. 1. Comparison of DRIFT spectra of $\mathrm{CH_4}$ adsorbed at room temperature by the sodium form (a) and the hydrogen form (b) of ZSM-5 at an equilibrium pressure of 100 Torr.

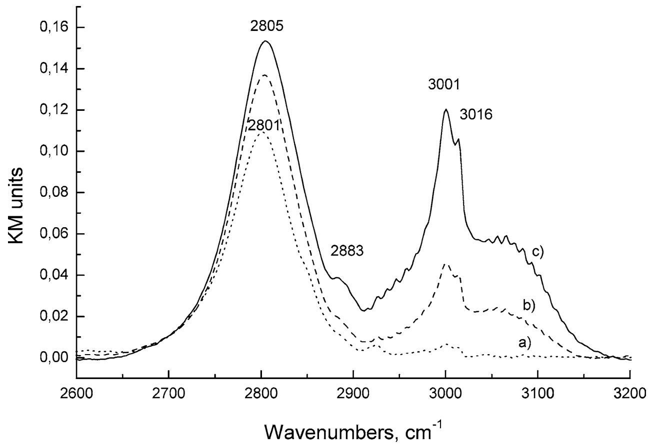

Fig. 2. DRIFT spectra of CH_4 adsorbed at room temperature and at different equilibrium pressures by ZnZSM-5 prepared by incipient wetness impregnation. (a) 1 Torr, (b) 6 Torr, (c) 15 Torr.

2898 cm^{-1}. For methane adsorption by NaZSM-5, this frequency is 2885 cm^{-1}, whereas the intensity of the corresponding band is much higher. At room temperature, adsorption of methane by both zeolites is reversible, because the corresponding IR bands are completely removed by evacuation. These and the previously published results indicate that specific adsorption of methane by sodium cations or protons develops the symmetry-forbidden ν_1 C–H stretching vibration which is more sensitive than the asymmetric ν_3 vibration to the nature of the adsorption sites. The intensities and low-frequency shifts of the former bands increase with increasing perturbation of the adsorbed methane molecules by the cations.

DRIFT spectra of methane adsorbed at different pressures on ZnZSM-5 prepared by incipient wetness impregnation are shown in Fig. 2. The bands with maxima at 3001 and 2883 cm^{-1} are similar to those observed for methane adsorption by the pure hydrogen form and consequently belong either to gaseous methane or to methane weakly adsorbed by bridging hydroxyl groups. The most exciting feature of the spectra shown in Fig. 2 is the appearance of the very broad and very intense band from adsorbed methane with a maximum at 2805 cm^{-1} after modification of HZSM-5 with zinc ions. This band is quite different from those earlier reported for methane adsorption by any cationic form of zeolite. Moreover, it does not even resemble the spectrum of gaseous methane. This band is much broader, much more intense, and much more strongly low-frequency shifted.

As follows from Fig. 2, such an unusual form of methane adsorption by zinc cations predominates at lower pressures. Therefore, it is stronger than the weaker adsorption by the bridging hydroxyl groups or sodium ions. However, at room temperature the stronger form of methane adsorption is still reversible because the corresponding broad band can be removed by very prolonged evacuation. On the other hand, as follows from Fig. 3, after ZnZSM-5 is heated in methane atmosphere at 473 K intensity of this band irreversibly decreases, indicating dissociative methane adsorption by the zinc–oxygen acid–base pairs. This effect is similar to that previously reported [9,10] for dissociative adsorption of molecular hydrogen by zinc ions and is connected with the occupation of adsorption sites by the dissociatively adsorbed species.

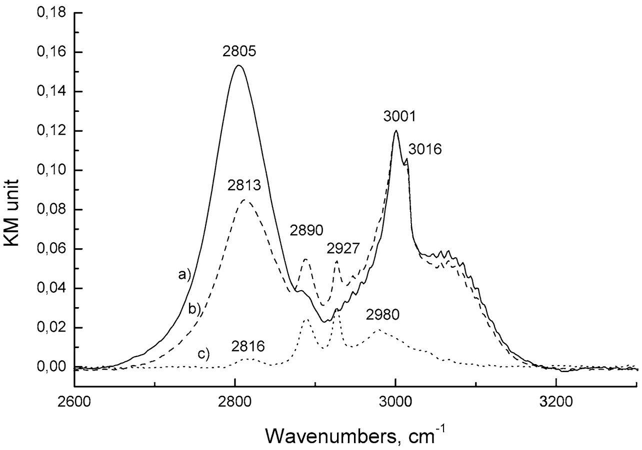

Fig. 3. Dissociative adsorption of CH_4 by ZnZSM-5 prepared by incipient wetness impregnation. DRIFT measurements at room temperature. (a) CH_4 adsorption at room temperature and at an equilibrium pressure of 15 Torr. (b) The sample was heated at 473 K in CH_4 atmosphere ($P = 15$ Torr) for 1 h. (c) Subsequent evacuation of the sample at room temperature for 1 h.

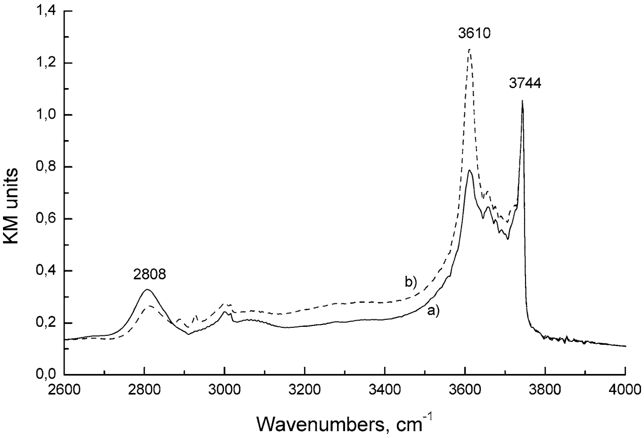

Fig. 4. Broad-range DRIFT spectra of ZnZSM-5 prepared by reaction of the hydrogen form with zinc vapor. DRIFT measurements at room temperature. (a) CH_4 adsorption at room temperature at an equilibrium pressure of 20 Torr. (b) The sample was heated at 473 K in CH_4 atmosphere ($P = 20$ Torr) for 1 h.

In addition to decreasing broad band intensity, the dissociative methane adsorption also results in the appearance of several much weaker bands in the region of the C–H stretching vibrations, with maxima at 2890, 2927, and 2980 cm^{-1}. This indicates the formation either of methyl groups which are bound to zinc cations or of methoxy groups. The choice between these alternatives is provided by the simultaneous appearance of a DRIFT band from acidic hydroxyl groups with a maximum at 3610 cm^{-1} (Fig. 4). The dissociative adsorption of methane is irreversible at relatively low temperatures, because C–H stretching bands from the chemisorbed

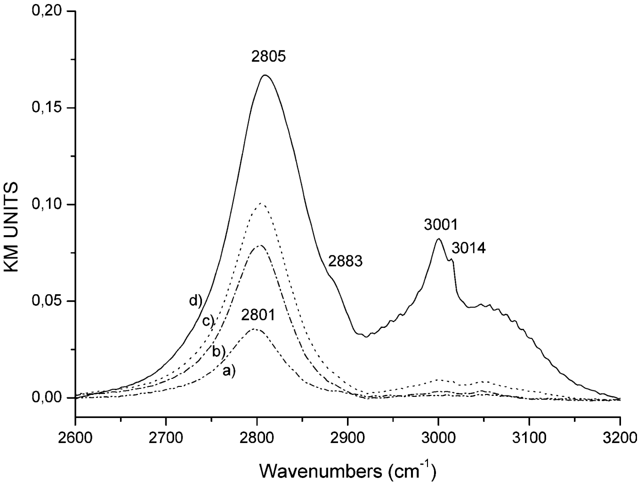

Fig. 5. DRIFT spectra of CH_4 adsorbed at different equilibrium pressures at room temperature by ZnZSM-5 prepared by high-temperature reaction of hydrogen form with zinc vapor. (a) 0.07 Torr, (b) 0.5 Torr, (c) 1 Torr, (d) 15 Torr.

species were not removed by prolonged evacuation at temperatures up to 373 K.

According to our previous studies, substitution of protons by Zn^{2+} ions via high-temperature reaction with zinc vapor is more complete than that by incipient wetness impregnation [10]. Another advantage of the high-temperature reaction with zinc vapor is the absence of small zinc oxide particles that can be formed upon incipient wetness impregnation. Therefore, we also studied methane adsorption by the sample modified by reaction with zinc vapor. The corresponding DRIFT spectra recorded at different equilibrium pressures of CH_4 are shown in Fig. 5. The intensities of the bands of gaseous methane can be used in this case as an internal standard for comparison of the amounts of strongly adsorbed methane species by the samples of different preparation. Indeed, comparison of Figs. 2 and 5 indicates that the relative intensity of the ν_1 band from methane adsorbed by zinc cations in the sample prepared via interaction with zinc vapor is about twice as high as that of the sample prepared by incipient wetness impregnation. This confirms the more complete substitution of acidic hydroxyl groups by zinc ions and makes it possible to carry out a more reliable study of methane dissociative adsorption by zinc cations.

The obtained results also demonstrate that the extent of dissociative methane adsorption increases at higher temperatures. This indicates that zinc ions are inhomogeneous. Dissociative adsorption also slightly shifts the maximum of the remaining broad band to higher frequency. This also confirms the inhomogeneity of the zinc adsorption sites that was demonstrated in our previous work by observation of two different forms of low-temperature adsorption of molecular hydrogen. On the other hand, the very large linewidth of the ν_1 DRIFT stretching band does not permit resolution via methane adsorption of different sites of localization of zinc ions.

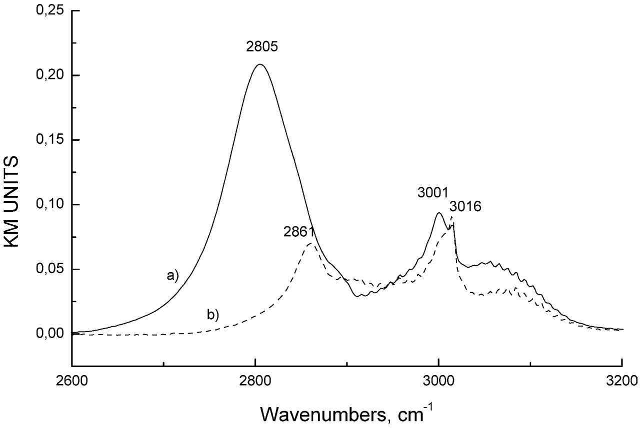

Fig. 6. DRIFT spectra of CH_4 adsorbed by ZnZSM-5 (a) and ZnY (b) at room temperature and at 20 Torr (both samples prepared by high-temperature reaction of hydrogen form with zinc vapor).

We also studied methane adsorption at room temperature by HY zeolite modified via high-temperature reaction with zinc vapor. A comparison of the obtained DRIFT spectrum with that for methane adsorption by ZnZSM-5 of similar preparation is presented in Fig. 6. As was mentioned above for ZSM-5 zeolite, the reaction of HY with zinc vapor results in complete substitution of protons by zinc ions; however, the low-frequency shift of the band from methane adsorbed by zinc cations at S_{II} sites is much less than that for ZnZSM-5.

4. Discussion

According to the present study and to papers previously published by other authors [14–17], adsorption of methane by the hydrogen or sodium forms of ZSM-5 results in the lowering of CH_4 symmetry and in the appearance of the symmetry-forbidden ν_1 DRIFT C–H stretching bands. The intensities and downshifts of those bands increase with increasing perturbations of the adsorbed molecules by interaction with different cations. Therefore, the very intense, very broad, and very strongly downshifted C–H stretching band observed in the present study most likely is the result of the ν_1 C–H stretching vibrations of adsorbed CH_4 molecules. It is also very significant that the low-frequency shift of the asymmetric ν_3 stretching vibration of methane is much weaker. Thus, adsorption of methane by modifying zinc cations results in the selective perturbation of the symmetric ν_1 C–H stretching mode and has only a minor influence on the asymmetric mode. Similarly to the previously studied hydrogen adsorption by ZnZSM-5, the low-frequency shift of this symmetric C–H stretching vibration for adsorbed methane is almost twice as larger as that for ZnY. Therefore, methane adsorption by ZnZSM-5 also most likely occurs at the distantly separated zinc ions.

In our previous studies [10,11], the main argument for this model of localization of Zn^{2+} ions at the distantly separated aluminum atoms in high silica zeolites was based on the complete substitution of isolated bridging protons via high-temperature reaction with zinc vapor. The results of the present study on the unusually strong perturbation of methane by Zn^{2+} ions localized at such sites provide further support of this model. Indeed, according to Fig. 6, the low-frequency shift of the ν_1 symmetric vibration of methane adsorbed by zinc ions in ZnZSM-5 is 55 cm^{-1} larger than that by Zn^{2+} ions at S_{II} sites in ZnY zeolite. This definitely indicates a much stronger perturbation of adsorbed methane molecules by excessively positively charged zinc ions.

It is well known that the intensities of IR stretching bands are proportional to the polarizability of chemical bonds resulting from their normal vibrations [18]. Therefore, the high relative intensity of the low-frequency-shifted broad band indicates a very strong polarizability of adsorbed CH_4 species. A very rough estimation of the extinction coefficient for this band, which was obtained from comparison of its integrated intensity with intensities of the bands from alkyl fragments appearing after dissociative methane adsorption, indicates a several times higher extinction coefficient for the molecular form. This should be explained by the interaction of adsorbed CH_4 species with the excessively positively charged zinc cations and also confirms their unusual nature.

The high polarizability of the strongly adsorbed species also explains subsequent heterolytic dissociation of methane, resulting in easy splitting of protons from adsorbed molecules. Chemical activation of adsorbed methane starts with the relatively weak interaction with the zinc Lewis sites. A much stronger activation or even dissociation of one of the C–H chemical bonds arises from the additional polarization of adsorbed species which increases the strength of their binding. This, in turn, results in an increase in the polarization and in an even stronger interaction of the CH_4 molecules with the active sites. Such self-consistent processes of polarization and stronger binding result in the heterolytic dissociation of adsorbed molecules with a low activation barrier. This results in the appearance of three new bands in the region of the C–H stretching vibrations simultaneously with the formation of the bridging hydroxyl groups. This indicates the following mechanism of dissociative adsorption:

$$[AlO_2]^-Zn^{2+} + [AlO_2]^- + CH_4 \\ \rightarrow [AlO_2]^-Zn^{2+}CH_3{}^- + [AlO_2]^-H^+. \tag{2}$$

The bridging hydroxyl groups formed upon such heterolytic dissociation are similar to those in the initial hydrogen form of HZSM-5. This should hardly be expected if heterolytic dissociation of methane involves lattice oxygen atoms adjacent to Zn^{2+} cations.

The IR spectrum of the zinc–alkyl group appearing after dissociative adsorption of methane looks somewhat unusual. Indeed, the CH_3 group with $C_3\nu$ symmetry should have only two C–H stretching vibrations: one symmetric and one asymmetric. In our case three bands were observed in the range of C–H stretching vibrations with maxima at 2888, 2927, and 2980 cm^{-1}, whereas the broader band with a maximum at 2816 cm^{-1} is most likely connected with the rest of the stronger form of molecular methane adsorption. One possible explanation for the appearance of such an additional band is the lower symmetry of the methyl fragment due to hydrogen bonding of one of the protons with a basic oxygen of the zeolite framework. Another possible reason for this phenomenon could be the formation of some secondary products upon heterolytic dissociative adsorption. We plan to discuss the first of these possibilities in our subsequent study by means of quantum chemical calculations similar to those carried out in our previous work for dissociative hydrogen adsorption [19].

Acknowledgments

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References

[1] A. Hagen, F. Roessner, Catal. Rev. 42 (2000) 403.
[2] E. Iglesia, J.E. Baumgartner, Catal. Lett. 21 (1993) 55.
[3] J.A. Biscardi, E. Iglesia, Catal. Today 31 (1996) 207.
[4] El-M. El-Malki, R.A. van Santen, W.M.H. Sachtler, J. Phys. Chem. 103 (1999) 4611.
[5] J.A. Biscardi, G.D. Meizner, E. Iglesia, J. Catal. 179 (1998) 192.
[6] V.B. Kazansky, V.Yu. Borovkov, A.I. Serykh, R.A. van Santen, P. Stobbelaar, PCCP 1 (1999) 2881.
[7] V.B. Kazansky, V.Yu. Borovkov, A.I. Serykh, R.A. van Santen, B.G. Anderson, Catal. Lett. 66 (2000) 39.
[8] V.B. Kazansky, A.I. Serykh, R.A. van Santen, B.G. Anderson, Catal. Lett. 74 (2001) 55.
[9] V.B. Kazansky, A.I. Serykh , B.G. Anderson, R.A. van Santen, Catal. Lett. 88 (2003) 192.
[10] V.B. Kazansky, J. Catal. 216 (2003) 192.
[11] V.B. Kazansky, A.I.Serykh, Micropor. Mesopor. Mater., in press.
[12] F. Roessner, A. Hagen, J. Heemsoth, E. Tegeler, Micropor. Mesopor. Mater. 46 (2001) 185.
[13] A. Seidel, B. Boddenberg, Chem. Phys. Lett. 249 (1996) 117.
[14] V.B. Kazansky, A.I. Serykh, A.T. Bell, Catal. Lett. 77 (2001) 215.
[15] E. Cohen de Lara, R. Khan, R. Seloudoux, J. Chem. Phys. 83 (1985) 2646.
[16] S. Huber, H. Knozinger, Chem. Phys. Lett. 244 (1995) 111.
[17] Can Li, Quin Xin, J. Chem. Phys. 96 (1992) 7714.
[18] G. Herzberg, Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, New York, 1947.
[19] A.A. Shubin, G.M. Zhidomirov, V.B. Kazansky, R.A. van Santen, Catal. Lett. 90 (2003) 137.