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Accessibility of Acid Sites in Hierarchical Zeolites: Quantitative IR Studies of Pivalonitrile Adsorption

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S *Supporting Information*

ABSTRACT: Accessibility studies of acid sites in zeolites involving quantitative IR measurements with hindered pivalonitrile as probe molecule were performed. The extinction coefficients of the diagnostic bands of pivalonitrile interacting with Brønsted and Lewis acid sites were determined by using several zeolites structures of different concentrations and acid strength of sites. The accessibility factor (AF) was defined as the ratio of the concentrations of acid sites accessible to pivalonitrile and sites interacting with pyridine. The AF can be applied to both Brønsted and Lewis sites, whereas the methods proposed in previous works were limited only to Brønsted sites. Moreover, this method can also be applied to the accessibility studies of transition-metal cations being active sites in redox reactions. The AF suitability for accessibility studies was investigated for desilicated zeolites HZSM-5 of medium and high Si/Al ratio treated with NaOH and NaOH/tetrabutylammonium hydroxide. The correlation between the values of mesopore surfaces and AFs for both Brønsted and Lewis sites in highly siliceous zeolites was observed. In more extensively desilicated zeolites, all of the acid sites were accessible to pivalonitrile, that is, AF = 1. Thereby, we assume that pivalonitrile can react not only with sites on external surfaces and in micropore mouths, as generally accepted, but small amounts of pivalonitrile can also migrate inside micropores. In desilicated zeolites with the extended mesopore system smaller fragments of micropores between two mesopores are preserved, which results in shorter average length of micropores. It facilitates the migration of pivalonitrile, and the sites inside micropores became accessible to bulky molecule. The accessibility of Lewis acid sites in desilicated zeolites is even more enhanced than that of Brønsted sites. Taking into consideration the fact that in desilicated zeolites the majority of Lewis sites originate from dehydroxylation of the Si—OH—Al groups, previously formed by the reinsertion of Al extracted from zeolite during alkaline treatment, their high accessibility is reasonable. Those newly formed Lewis sites are situated on mesopore surfaces, which facilitates accessibility to bulky molecules.
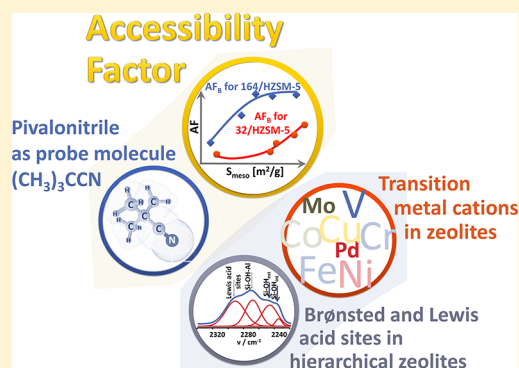
1. INTRODUCTION

Zeolites are crystalline aluminosilicates with well-defined micropore system; however, their catalytic efficiency is restricted by diffusional limitations. Diffusional limitations have a negative effect not only on zeolites activity but also occasionally on selectivity and catalyst lifetime.[1,2] Therefore, several top-down and bottom-up approaches of obtaining hierarchical zeolites with secondary mesopore system were proposed, ranging from synthesis of nanocrystalline zeolites, composites, or mesoporous crystals, through recrystallization and zeolitization of mesoporous materials, to postsynthesis treatments including dealumination and desilication with or without additional organic agents. Generated intracrystalline mesoporosity in hierarchical zeolites allows for catalytic performance enhancement by shortening the diffusion path length.[3–5]

Desilication of zeolites in alkaline solutions has emerged as the most effective and adjustable method of producing hierarchical zeolites in which an additional mesopore system improves the reactants transport to and from active sites. Since pioneering papers of Groen et al.,[6,7] much has been devoted to

the studies of desilication.[8–15] Numerous investigation have been done to optimize the desilication conditions[7] and to elucidate the desilication mechanism. The process of Al reinsertion and its role in acidity modification has been especially interesting.[7,16]

Our systematic studies of desilicated zeolites ZSM-5[17–19] allowed us to investigate the influence of different desilication conditions, for example, concentration of base, presence of TBAOH, time, and temperature of alkaline treatment, on structure, chemical composition of bulk and surface zone, and porosity of hierarchical zeolite. This work is devoted to the research on desilicated zeolites with newly elaborated method of quantitative IR studies of the accessibility both Brønsted and Lewis sites. The accessibility of acid sites to reactant molecules in desilicated zeolites is the essential problem for valuation of obtained mesoporous material. In our previous studies,[18] we followed this issue with pivalonitrile as probe molecules, and a

distinct increase in sites accessibility upon desilication was observed. This effect was more significant if desilication was done with the NaOH/TBAOH mixture. It should be mentioned that the first time pivalonitrile was used to the studies of external surfaces of zeolites was by Busca et al.[20] Both our previous IR studies of pivalonitrile adsorption and pioneering works of Busca had only qualitative or semi-quantitative character. In this study, we realized for the first time quantitative IR experiments of pivalonitrile adsorption: the extinction coefficients of the diagnostic bands of pivalonitrile interacting with protonic sites and Lewis sites were determined; subsequently, the concentration of sites accessible to pivalonitrile was calculated. In previous studies,[21,22] the semiquantitative IR investigations of the accessibility of the Si−OH−Al groups were realized by coadsorption of alkyl pyridines with CO or by the measure of the disappearance of the Si−OH−Al group band observed upon the sorption of hindered molecules. It should be underlined that these previous investigations were limited to Brønsted sites only, whereas our study concerns both Brønsted and Lewis acid sites. Our method is the tool for the studies of the accessibility of not only protonic sites but also Lewis sites independently on their nature: of both aluminum electron acceptor species as well as transition-metal cations being active sites in redox reactions.

2. EXPERIMENTAL SECTION

Parent zeolites ZSM-5 of Si/Al = 32 and 164 were supplied by Zeolyst (CBV 5524G, CBV 28014, respectively). Desilication was carried out in the 0.2 M solutions of NaOH and NaOH/TBAOH (tetrabutylammonium hydroxide) mixture (TBAOH/(NaOH+TBAOH) = 0.4) at the temperature of 338 and 353 K for 0.5 h. 100 mL of solution was added to 3.0 g of zeolite. After desilication the suspension was cooled in an ice bath, filtered, and washed until neutral pH. Next a four-fold ion-exchange with 0.5 M NH_4NO_3 was performed at 330 K for 1 h. Finally, the zeolites were again filtrated, washed, and dried overnight at room temperature. The $HY_{steamed}$ (Zeolyst, CBV500), NaHY (Linde company, LZY-62), and NaHX (Sigma-Aldrich) were used as the reference materials.

Si and Al concentrations in the parent and desilicated zeolites were determined by the ICP OES method with the Optima 2100DV (PerkinElmer) spectrometer.

The N_2 sorption processes at 77 K were studied on an ASAP 2420 Micromeritics after activation in vacuum at 670 K for 12 h. The t-plot method with the Harkins−Jura reference isotherm was used to determine the micropore volume (V_{micro}). The same model was applied for the calculation of external surface area (S_{meso}). Pore size distribution and volume of mesopores (V_{meso}) were obtained by the BJH model following the adsorption branch of the isotherm.

Prior to FTIR studies, all samples were pressed into the form of self-supporting wafers (ca. 5 mg/cm^2) and activated in situ in an IR cell at 823 K under vacuum for 1 h. Spectra were recorded with a Bruker Equinox 55 spectrometer equipped with an MCT detector. The spectral resolution was of 2 cm^{-1}. Pyridine and pivalonitrile were sorbed at 423 K and room temperature, respectively. The concentration of Brønsted and Lewis acid sites determined in quantitative IR studies of pyridine sorption was performed according to the procedure described in our previous paper.[18]

The powder X-ray diffraction (XRD) measurements were carried out using a PANalytical Cubix diffractometer, with CuK$_\alpha$ radiation, λ = 1.5418 Å, and a graphite monochromator in the 2θ angle range of 2−40°. X-ray powder patterns were used for structural identification of the relative crystallinity value (%Cryst) for all zeolites. The determination of the relative crystallinity value was based on the intensity of the characteristic peaks in the range between 22.5 and 25.0°.

3. RESULTS AND DISCUSSION

3.1. Extinction Coefficients of IR Bands of Pivalonitrile Interacting with Brønsted and Lewis Acid Sites.
The key problem in quantitative IR studies of molecules adsorbed on solid surfaces is determination of extinction coefficient of respective IR band. The simplest and most desired is the situation when each molecule introduced into the IR cell reacts selectively with only one kind of the adsorption site. In such a case, the intensity of the IR band increases linearly with the concentration of molecules adsorbed, and the slope of the line is the extinction coefficient. When on the solid surface two (or more) kinds of the adsorption sites are present, it is required to know, or to estimate, the amount of probe molecule interacting with each kind of the sites. In both cases, it is necessary to assume that each molecule introduced into the cell is adsorbed on the surface. Unfortunately this rule is not obeyed for the adsorption of hindered pivalonitrile molecule, which cannot penetrate the channels of zeolite ZSM-5. Therefore, the modified experimental procedure has been applied. According to this procedure, pivalonitrile was sorbed in both large pore zeolites (zeolites X, Y, BEA), where all acid sites were accessible to pivalonitrile molecules and in zeolite ZSM-5, in which all Si−OH−Al groups became accessible to pivalonitrile when adsorption was carried out at high (470 K) temperature. Total concentration of both Brønsted and Lewis sites in studied zeolites was independently determined by pyridine sorption. The extinction coefficient of the IR bands of pivalonitrile interacting with both Brønsted and Lewis sites was calculated from the intensities of the respective IR bands and the concentration of acid sites.

The spectrum of pivalonitrile sorbed in zeolites (Figure 1) shows three bands: 2140−2155 doublet, 2277, and 2305 cm^{-1}. Our previous study[18] verified that the 2140−2155 cm^{-1} doublet represents molecules interacting with Si−OH groups, whereas the bands at 2258−2278 and 2305 cm^{-1} are due to pivalonitrile interacting with the Si−OH−Al groups and Lewis acid sites, respectively. The extinction coefficient of 2258−2278 cm^{-1} band of pivalonitrile interacting with the Si−OH−Al groups was determined in experiments in which the excess of pivalonitrile, sufficient to saturate all the acid sites, was sorbed in zeolites NaHX, NaHY, $HY_{steamed}$, HBEA, and HZSM-5. All of the zeolites adapted for this purpose are listed in Table 1. The different structures and concentrations of protonic sites and also the presence of additional mesopore systems ($HY_{steamed}$, $HBEA_{desil(1)}$, $HBEA_{desil(2)}$) in used zeolites allowed us to establish the extinction coefficient suitable for various types of zeolites. For instance, the zeolite $HY_{steamed}$, besides typically zeolitic Si−OH−Al groups also contained other protonic sites being accessible to bulky molecules. Similarly, in zeolite NaHX and NaHY, Si−O$_1$H−Al groups characterized by IR band at 3640−3660 cm^{-1} assigned to supercages were accessible to Pn molecules. Additionally, BEA zeolites with protonic sites of different types were employed to this procedure. Besides typically zeolite HBEA, two differently desilicated zeolites ($HBEA_{desil(1)}$, $HBEA_{desil(2)}$) were adapted and Fenton detemplated zeolite BEA (HBEA-F) was also used. In all of these
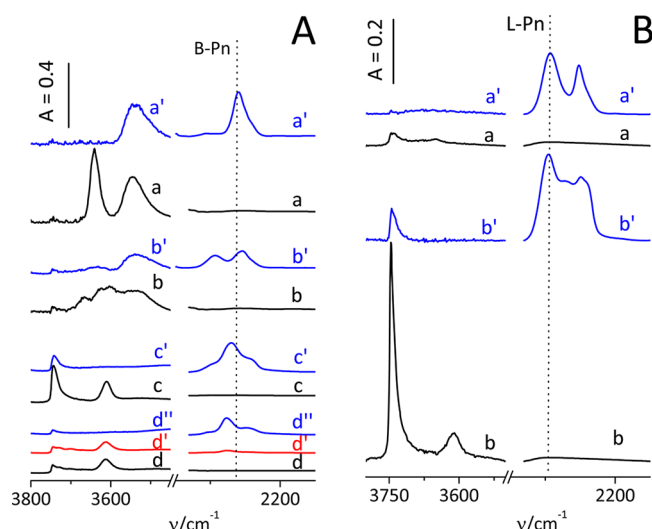
Figure 1. Spectra of OH groups and of pivalonitrile adsorbed at room temperature on zeolite NaHY (a,a′), HY$_{steamed}$ (b,b′), HBEA (c,c′), and 32/HZSM-5 (d,d′) before and after pivalonitrile adsorption. Spectrum d″ was recorded upon heating of zeolite HZSM-5 with pivalonitrile at 470 K and cooling to room temperature (A). The spectra of OH groups and of pivalonitrile adsorbed in dehydroxylated zeolite NaHY$_{dehyd}$ (a,a′) and in zeolite HBEA$_{desil(2)}$ (b,b′). The spectra a and b were recorded before and spectra a′ and b′ were recorded after pivalonitrile adsorption (B).

materials, the Si−OH−Al groups were accessible to pivalonitrile.

The adsorption of Pn led to the disappearance of the Si−O$_1$H−Al band (3660 − 3640 cm^{-1}) in zeolites X and Y as well as in BEA (3610 cm^{-1}) and gave rise to the bands at 2277 cm^{-1} corresponding to Brønsted acid sites (Figure 1A (a,a′,c,c′)). Analogous results were observed for zeolite HY$_{steamed}$; the 3600, 3620, and 3660 cm^{-1} bands vanished after Pn adsorption (Figure 1A (b,b′)). On the contrary, in the case of zeolites HZSM-5 with 10 MR pores the pivalonitrile practically did not penetrate the channel system. Therefore, the vast majority of the Si−OH−Al groups is not accessible as the representative 3610 cm^{-1} band only slightly diminished, and the intensity of pivalonitrile bands was very small (Figure 1A (d,d′)). At higher temperature, thermal vibrations of zeolite framework make the structure more flexible and the pivalonitrile molecules can penetrate even the channels of zeolite ZSM-5. It is well seen in the spectrum recorded upon heating of zeolite ZSM-5 with Pn

excess to 470 K, subsequent evacuation to remove physisorbed molecules (470 K, 20 min), and cooling to room temperature (Figure 1A, spectrum d″). The disappearance of the Si−OH−Al band was accompanied by a significant increase of 2258−2278 cm^{-1} bands, which confirms the saturation of all acid sites by pivalonitrile. In all zeolites the concentration of Pn engaged into interaction with protonic sites was assumed to be the same as the concentration of the Si−OH−Al groups (Table 1) determined in quantitative IR studies of pyridine adsorption.

The intensity of 2258−2278 cm^{-1} band was plotted as a function of the concentration of the Si−OH−Al groups in all studied zeolites (Figure 2 A), giving the linear dependence. The
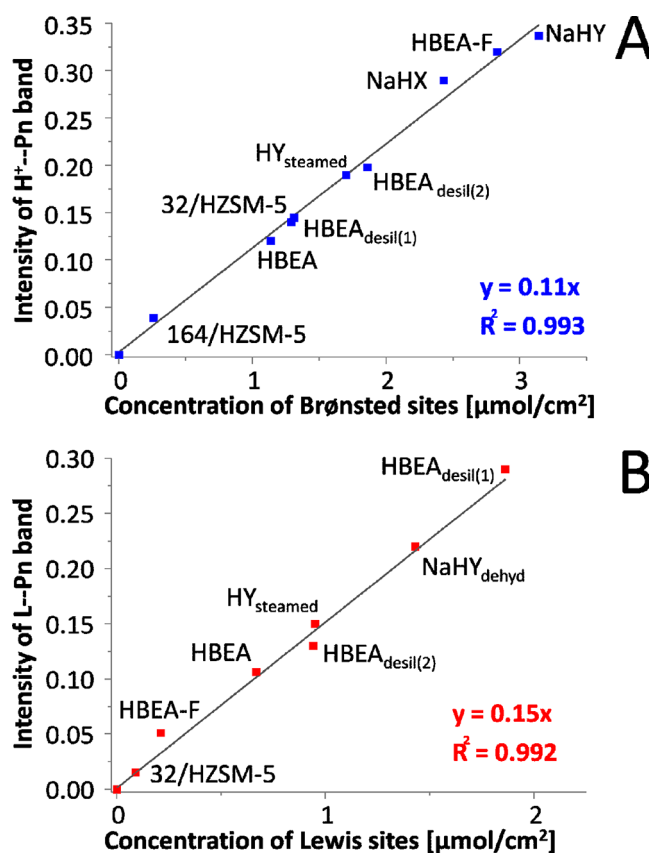

Figure 2. Plots of intensity of the bands of pivalonitrile interacting with protonic sites (A) and with Lewis acid sites (B) in different zeolites versus the concentration of sites.

Table 1. Conditions of the Zeolites Treatment and the Concentration of Brønsted and Lewis Acid Sites[a]

zeolite	treatment	Si/Al	concentration of sites [μmol/g]	
			Brønsted	Lewis
NaHY	nontreated	2.5	1070	0
NaHY$_{dehyd}$	dehydroxylated at 870 K	2.5	0	486
HY$_{steamed}$	steamed	2.6	580	323
NaHX	nontreated	1.3	826	0
HBEA-F	detemplated (Fenton method)	12	960	70
HBEA	nontreated	22	395	200
HBEA$_{desil(1)}$	desilicated with NaOH	13	440	600
HBEA$_{desil(2)}$	desilicated with NaOH/TBAOH	16	632	300
32/HZSM-5	nontreated	32	450	30
164/HZSM-5	nontreated	164	85	6

[a]Measured by quantitative experiments of pyridine sorption.

Table 2. Chemical Composition, Textural Parameters, and Acid Sites Concentration Determined with Pyridine As Well As Pivalonitrile in Desilicated Zeolites HZSM-5

zeolite	desilication temperature [K]	Si/Al	porosity data			% Cryst	Al [μmol/g]	concentration of sites [μmol/g]					accessibility factor	
			V_{micro} [cm³/g]	V_{meso} [cm³/g]	S_{meso} [m²/g]			determined with pyridine			determined with pivalonitrile			
								Brønsted	Lewis	B+L	Brønsted	Lewis	AF_B	AF_L
32/HZSM-5		32	0.17	0.06	40	100	471	450	30	480	54	7	0.12	0.24
32/NaOH	338	20	0.15	0.21	144	87	741	575	205	780	187	92	0.24	0.42
32/NaTB	338	24	0.12	0.20	175	86	622	480	160	640	218	106	0.45	0.66
32/NaOH	353	18	0.15	0.20	134	89	819	630	180	810	122	49	0.19	0.27
32/NaTB	353	22	0.09	0.23	193	88	676	545	132	687	316	130	0.58	0.98
164/HZSM-5		164	0.17	0.06	23	100	94	85	6	91	26	0	0.30	0
164/NaOH	338	123	0.15	0.15	83	88	124	96	28	124	66	11	0.69	0.40
164/NaTB	338	123	0.14	0.24	140	83	124	102	31	133	106	29	1.04	0.93
164/NaOH	353	95	0.15	0.27	108	92	149	96	60	156	98	45	1.02	0.75
164/NaTB	353	110	0.09	0.27	182	84	139	96	63	159	100	56	1.04	0.89
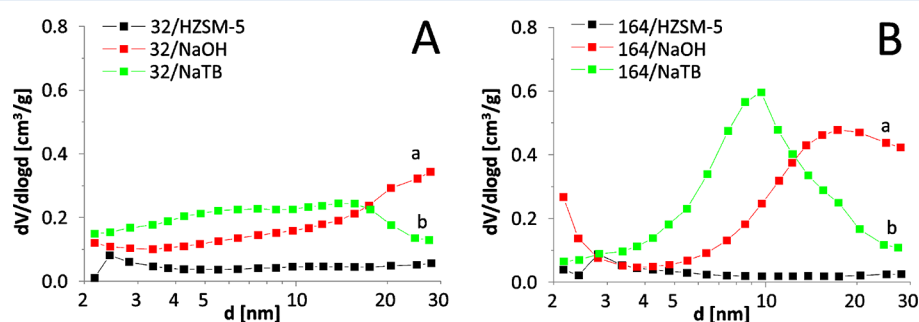
Figure 3. Distribution of pore diameter in parent zeolites and zeolites HZSM-5 of Si/Al = 32 (A) and 164 (B) desilicated at 353 K in NaOH (a) and NaOH/tetrabutylammonium hydroxide (NaTB) (b) solutions.

intensity of the 2277 cm⁻¹ band was measured upon the band fit (spectra not shown). The slope of this line was used to determine the extinction coefficient of the 2258−2278 cm⁻¹ band of pivalonitrile interacting with protonic sites. The value of 0.11 cm²/μmol was obtained. It should be underlined that for all studied zeolites independently of the structure, their acidity, and the presence of mesopores, all experimental points fit the same line. Therefore, the extinction coefficient determined in our study can be used for the investigation of accessibility of acid sites in zeolites of various structure and acidity.

Similar method was applied to determine the extinction coefficient of the 2305 cm⁻¹ band of pivalonitrile interacting with Lewis sites. In this case, the excess of pivalonitrile was sorbed in zeolites NaHY$_{dehyd}$, HY$_{steamed}$, and HBEA containing known amounts of Lewis sites (Figure 1B). For instance, the zeolite NaHY$_{dehyd}$ was dehydroxylated by activation at vacuum at 870 K, which resulted in the disappearance of the Si−OH−Al bands and the production of significant amounts of Lewis sites. Desilication of zeolites BEA (HBEA$_{desil(1)}$, HBEA$_{desil(2)}$) also resulted in production of significant amounts of Lewis acid sites. In all cases, the concentration of Lewis sites was determined in quantitative IR studies of pyridine sorption, and it is presented in Table 1.

The plot of the intensity of the 2305 cm⁻¹ band of pivalonitrile interacting with Lewis sites versus the concentration of Lewis sites was linear (Figure 2B), and the slope of this line was used to calculate the extinction coefficient of the 2305 cm⁻¹ band. The value of 0.16 cm²/μmol was obtained.

3.2. Hierarchical HZSM-5 Zeolites with Medium and High Si/Al Ratio Desilicated in the Presence of NaOH and NaOH/TBAOH. Desilication based on preferential silicon extraction from zeolite framework has proven to be the effective way for introducing the mesoporosity in different types of zeolites. That is why hierarchical zeolites HZSM-5 used in this study for accessibility investigations were prepared by alkaline treatment. Desilication was performed on zeolites HZSM-5 with different Si/Al ratio; pure NaOH and a mixture of NaOH/TBAOH were used as desilicating agents. Aluminum content in zeolite framework and the presence of TBAOH during desilication process affected not only the chemical composition of resulting materials but also the type of generated porosity, which allowed us to observe substantial differences in accessibility of acid sites to bulky molecules. Further differentiation in degrees of intracrystalline mesoporosity of hierarchical materials was obtained by varying the temperature of desilication process. (See Table 2.)

The parent materials with ratio of Si/Al = 32 and 164 were commercially available zeolites HZSM-5 denoted as 32/HZSM-5 and 164/HZSM-5, respectively. Micropore volume of 0.17 cm³/g is characteristic for the MFI structure. The textural parameters derived from low-temperature nitrogen sorption evidenced that zeolite 32/HZSM-5 has limited mesoporosity (S_{meso} = 40 m²/g), which resulted from the external surface of zeolite grains and surface roughness, which has been additionally confirmed by TEM images. (See the Supporting Information.) A similar situation was observed for high-silica parent material. The BJH pore-size distribution confirmed the purely microporous character of both parent samples (Figure 3

A). Quantitative IR experiments with pyridine as probe showed that in parent materials the total concentration of protonic sites was nearly the same as the concentration of Al, and the concentration of Lewis sites was negligible (Table 2).

The analysis of XRD patterns (see the Supporting Information) demonstrated that desilication of zeolite with medium and high Si/Al ratio practically did not disturb the crystallinity of resulting materials (Table 2); the zeolite structure was preserved.

The alkaline treatment of zeolite with medium Si/Al ratio led to the substantial increase in mesopore surface area accompanied by the loss of microporosity, which is especially well seen for materials treated with NaOH/TBAOH mixture at 353 K (S_{meso} = 193 m^2/g; V_{micro} = 0.09 cm^3/g). Similar behavior was observed for alkaline-treated high-silica zeolite. Low-temperature nitrogen physisorption evidenced that the surface of mesopores distinctly increased after desilication with NaOH/TBAOH; however, the drop in volume of micropores was observed. The formation of mesopores within the zeolite structure was also confirmed in TEM images of desilicated zeolites. (See the Supporting Information.) The BJH pore size distribution presented in Figure 3 pointed to two different effects concerning the type of desilicating agent and Si/Al ratio of zeolite. It evidenced that the presence of TBAOH resulted in the generation of narrower pores in comparison with materials treated with NaOH only, for both medium and high silica zeolites. Furthermore, for high silica zeolites, desilication even resulted in narrower pore size distribution and in the formation of pores with smaller diameter than in the case of Al-richer zeolite desilicated under the same conditions. These two different effects can be explained by considering the role of both Al extracted from zeolite framework and tetrabutylammo-nium cation (TBA$^+$) as pore directing agents (PDAs). Both of them protect zeolite against OH$^-$ attack and massive zeolite dissolution. According to Verboekened and Pérez-Ramírez,[15] narrower pores were formed when desilication was performed with tetraalkylammonium cations, whereas larger pores were produced in the presence of Al as PDAs. This is why narrower pores are produced in both zeolites (of Si/Al = 32 and 164) desilicated in the presence of TBAOH (Figure 3A,B). When desilication of highly siliceous zeolite is done with NaOH/TBAOH mixture, the concentration of extracted Al is negligible, so only TBA$^+$ cations play the role of the PDA, which results in the formation of narrow pores and narrow pore diameter distribution (Figure 3B). In zeolite of medium Al content (Si/Al = 32), both TBA$^+$ and Al can be considered as the PDAs; therefore, larger pores and more heterogeneous pore size distribution is observed (Figure 3A).

Pyridine adsorption indicated that desilication resulted in an increase in concentration of protonic sites (due to decrease of Si/Al) and in the formation of substantial amounts of Lewis acid sites. The Lewis acid sites in desilicated zeolites are supposed to be formed by the dehydroxylation of the Si−OH−Al groups, which are formed by the reinsertion of Al previously extracted from zeolite framework (together with Si) during mesopore formation and subsequently incorporated into mesopore surfaces when pH of solution decreased. The reinsertion of Al atoms was postulated by several authors.[4] Our previous study revealed[19] that such Si−OH−Al groups are prone to dehydroxylation at relatively low temperature during zeolite thermal pretreatment, producing Lewis acid sites. The dehydroxylation of zeolites usually needs temperatures higher than 870 K,[23] whereas dehydroxylation of mesoporous

aluminosilicates, despite much lower density of Brønsted acid sites, takes place at lower temperatures, and at 800 K amorphous aluminosilicates loose 35−50% of the total number of Brønsted sites. Because the formation Lewis sites at the expense of Brønsted sites during dehydroxylation requires some rearrangement of the surface' atoms, it is believed that for crystalline zeolites of very stable structure such a rearrangement is more inhibited than that on the surface of mesoporous aluminosilicates.

According to the data presented in Table 2, for the majority of desilicated zeolites the sum of concentrations of protonic and Lewis sites (B+L) was comparable to the concentration of Al, suggesting that the stoichiometry of dehydroxylation of the hydroxyls formed by Al reincorporation was 1:1. It suggests that the mechanism of the dehydroxylation of amorphous aluminosilicates is different from that of zeolites, for which the loss of two Brønsted sites results in the appearance of one Lewis sites (2:1). In hierarchical zeolites, high concentration of silanol groups occurs on the mesopores surface. The presence of a large number of silanols and a small concentration of the bridging Si−OH−Al groups (and in consequence a long distance between them) may facilitate the condensation of the Si−OH−Al and the Si−OH groups, leading to the formation of the water molecule and a Lewis acid site.[23]

3.3. Concentration of Acid Sites Accessible to Pivalonitrile − Accessibility Factor. We defined the accessibility factor (AF) as the ratio of concentration of Brønsted (AF$_B$) and Lewis (AF$_L$) acid sites able to interact with pivalonitrile and total concentration of the sites determined with pyridine. The concentration of the sites accessible to pivalonitrile was calculated by means of the IR bands extinction coefficients of pivalonitrile interacting with both protonic and Lewis sites, determined as described in Section 3.1. The AF values are presented in the Table 2. The diagrams representing the dependence of the AF$_B$ and AF$_L$ on the values mesopore surface are presented in Figure 4.

3.3.1. Accessibility of Brønsted and Lewis Sites in Hierarchical Zeolites. Both parent zeolites HZSM-5 (Si/Al =
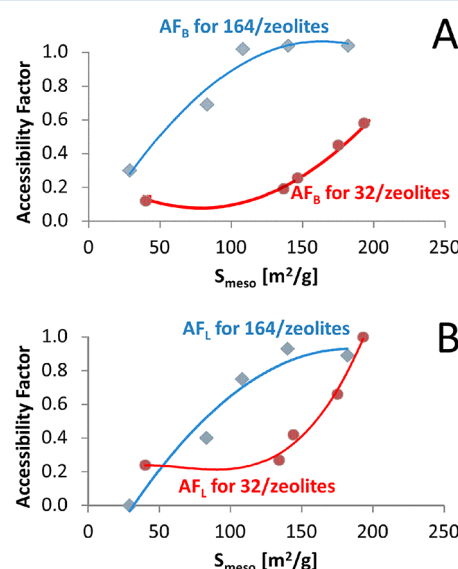

Figure 4. Plots of accessibility factor (AF) for protonic sites (AF$_B$) (A) and Lewis sites (AF$_L$) (B) versus surface of mesopores in parent zeolites and zeolites desilicated (Si/Al = 32, red line; Si/Al = 164, blue line) with NaOH and NaOH/tetrabutylammonium hydroxide.

32 and 164) contain some protonic sites accessible to hindered pivalonitrile molecules. These sites are situated on external surfaces of zeolite crystals and in pore mouths. Pivalonitrile is also supposed to interact with some sites in micropores due to thermal vibration both of zeolite framework and pivalonitrile molecules (the Si−OH−Al band at 3610 cm^{-1} only slightly diminished upon pivalonitrile sorbed at room temperature (Figure 1A (d and d′)). The desilication, producing a system of mesopores, improved the accessibility of the acid sites of both Brønsted and Lewis type. The AFs for both Brønsted and Lewis sites increased with mesopore surface (Figure 4). A similar effect was reported by Thibault-Starzyk et al.,[22] who also observed the increase in the accessibility index, for protonic sites reacting with lutidine and collidine, with enhancement of mesopore surface of desilicated zeolites.

The increase in accessibility of the acid sites to bulky molecules in desilicated zeolites can be related to the increase in contribution of the sites on external surfaces and in pore mouths in zeolites of high mesopore surfaces. Additionally, the sites inside micropores in desilicated zeolites are able to react more easily with hindered molecules, which is related to the extended mesopore system and shorter average length of micropores than in nondesilicated zeolites.

According to the data presented in the Table 2 and Figure 4, the accessibility of both Brønsted and Lewis sites in desilicated zeolite of Si/Al = 164 is distinctly better than that in zeolite of Si/Al = 32 of the same mesopore surface. It is supposed that in Al-richer zeolite, that is, of higher concentration of both types of acid sites, the bulky pivalonitrile molecules bonded with sites located near micropores mouths block the micropore entrances; therefore, sites located deeper inside micropores are not reached by pivalonitrile.

In zeolite of Si/Al = 32, in which the sites interacting with pivalonitrile are situated mostly on mesopore surfaces and in micropore mouths, the accessibility of the Lewis sites is distinctly better than the accessibility of Brønsted sites; that is, contribution of Lewis sites on mesopore surfaces and in micropore mouths is higher than contribution of Brønsted sites (Table 2 and Figure 4). These findings indicate that Lewis sites in desilicated zeolites are formed (as previously mentioned) mostly by the dehydroxylation of the Si−OH−Al groups produced by reinsertion of Al extracted from zeolite during the formation of the mesopore system. Such Lewis sites are situated on the mesopore surfaces, and they are better accessible to bulky molecules than typically zeolitic Si−OH−Al groups situated inside micropores. It should be mentioned that Holm et al.,[24] who realized IR studies of collidine and CO coadsorption, also postulated the location of Lewis sites on mesopore walls, which is in line with our interpretation.

The accessibility of both the Brønsted and Lewis sites is better for zeolites desilicated with NaOH/TBAOH mixture than with pure NaOH only (Table 2), which is related to the increase in mesopore surface as a consequence of the formation of the pores of narrower diameter (with TBA$^+$ as PDA; see Section 3.2 and Figure 4).

3.3.2. Accessibility of Lewis Acid Sites in Mesoporous Aluminosilicates and Alumina. In the present work, information on the accessibility of the sites interacting with pivalonitrile was achieved from the intensity of pivalonitrile bands but not from intensities of the Si−OH−Al group bands, as it has been reported in the work of Nesterenko.[21] It is worth mentioning that in some cases the band of the Si−OH−Al groups (3300−3800 cm^{-1}) cannot be analyzed because it is covered either by the bands of the Si−OH groups interacting with probe molecules or by the bands of probe molecules themselves (such as pyridine, lutidine, and collidine). Therefore, the intensities of the Si−OH−Al bands free or interacting with CO cannot be measured accurately. Figure 5 A shows, as
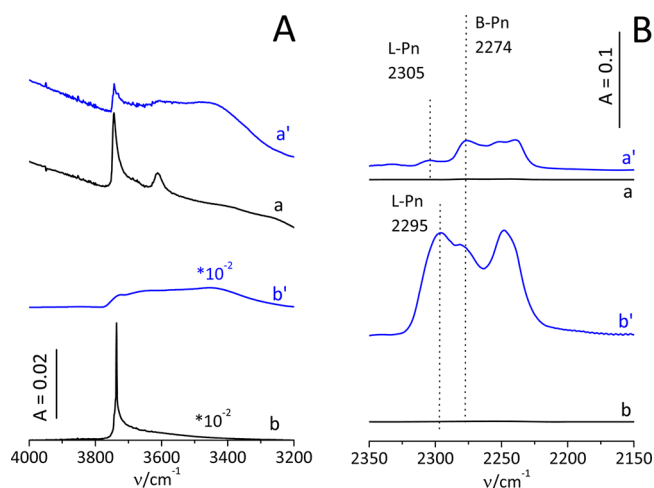

Figure 5. Spectra of OH groups (A) and of adsorbed pivalonitrile (B) in desilicated zeolite HZSM-5 of Si/Al = 164 (a,a′) and in MCM-41 (b,b′). Spectra a and b were recorded before and spectra a′ and b′ − after pivalonitrile adsorption.

an example, the spectrum of the Si−OH−Al groups in zeolite HZSM-5 (Si/Al = 164) before and after pivalonitrile adsorption, where the band of the Si−OH−Al groups (3300−3800 cm^{-1}) is overlapped by the bands of the Si−OH interacting with pivalonitrile as well as nonperturbed spectrum of pivalonitrile adsorbed in the region of the C≡N groups vibration. The difficulties mentioned above can be overcome when using pivalonitrile C≡N diagnostic bands. Pivalonitrile may also be used to follow the accessibility of protonic sites or other acid sites in materials in which the bands of the acidic hydroxyls are not detectable, for example, in mesoporous aluminosilicates or similar materials.[25] In zeolites the presence of the bridging Si−OH−Al groups is confirmed by the IR bands in the region of frequency 3550−3660 cm^{-1}. The intensity of the Si−OH−Al group band depends on both the concentration of hydroxyls and the extinction coefficient of this band. In mesoporous aluminosilicates, such MCM-41 or MCM-48, the presence of a considerable amount of Brønsted acid sites has been identified, mainly by adsorption of the base (pyridine or ammonia) as probe molecules. Nevertheless, it is very difficult to detect the bridging Si−OH−Al group band (around 3600− 3610 cm^{-1}), probably because of the very small value of the extinction coefficient of very weakly acidic hydroxyls band.[25] To illustrate such a possibility, we studied the adsorption of pyridine and pivalonitrile in MCM-41 of Si/Al = 15. The spectra of OH groups in the region of the Si−OH−Al group vibration in this material as well as the spectrum of pivalonitrile adsorbed are shown in Figure 5. The values of total concentrations of sites of Brønsted- and Lewis-type (measured with pyridine) were 265 and 500 μmol/g, respectively, and the same values of the concentrations were obtained with pivalonitrile: 257 and 480 μmol/g for Brønsted and Lewis sites, respectively. It is in line with the fact that protonic sites in mesoporous aluminosilicates, such as MCM-41, are accessible to bulky pivalonitrile molecules.

Additionally, the sorption of pivalonitrile was also performed on mesoporous alumina[25] containing only Lewis acid sites, the concentration of which was previously determined with pyridine. The agreement between the concentrations of Lewis sites detected by both pivalonitrile (590 μmol/g) and by pyridine (600 μmol/g) enforces the accessibility of all of the Lewis acid sites being situated on the surface of mesoporous alumina to bulky molecules. Once more, the validation of our method has been proven.

3.3.3. Transition-Metal Cations Accessibility. The procedure of the quantitative pivalonitrile adsorption has been adapted for the accessibility investigations of Lewis acid sites of different nature, that is, multivalent metal cations hosted in zeolites. Zeolites CoY and CoX of Co/Al = 0.31 and 0.33, respectively, have been selected.[26] In these zeolites, only Co^{2+} cations situated inside supercages are accessible to reagent molecules, including both bulky pivalonitrile and carbon monoxide. Each Co^{2+} cation should be available for both Pn and CO molecules; hence the concentration of Co^{2+} cations determined with those probes should be equal.

The concentration of Co^{2+} cations in supercages has been quantified with CO as probe[26] and compared with the concentration detected by pivalonitrile using extinction coefficient for Lewis acid sites originating from Al atoms (Table 3). The agreement in the concentrations of Co^{2+} cations

Table 3. Chemical Composition and Results of Quantitative IR Studies with CO and Pn as Probe Molecules for Zeolites CoX and CoY

zeolite	Co/Al	chemical analysis Co^{2+} [μmol/g]	concentration of Co^{2+} [μmol/g]	
			determined with CO	determined with Pn
CoY	0.31	1200	585	600
CoX	0.33	1950	459	481

determined with both probe molecules (Pn and CO) is in line with the finding that the number of Co^{2+} cations accessible to Pn is the same as those reached by CO. Therefore, it can be stated that our procedure of Pn sorption can be used to quantify not only the Lewis acid sites but also the sites of redox nature.

Transition-metal cations are active sites in numerous redox reactions; hence the information on their accessibility is important for catalysis. The concentration of Co^{2+} sites in supercages detected by Pn and thereby accessible to reactant molecules was calculated as only half of the total concentration of Co (determined in chemical analysis) in zeolite CoY and ca. 25% for zeolite CoX (Table 3).

In summary, a new method of quantitative studies of the accessibility of both the acid sites of Brønsted- and Lewis-type and metal cations with pivalonitrile as probe molecule was elaborated. Information on the accessibility was obtained from the maximum intensities of the diagnostic IR bands at 2258–2278 and 2305 cm^{-1} of pivalonitrile interacting with protonic and Lewis sites respectively. The main advantage of applied method is the novelty: it is the first quantitative method for the investigation of accessibility of the Brønsted and Lewis sites with hindered pivalonitrile as the probe molecule. The pioneering works of Nesterenko et al.[21] and Thibault-Starzyk et al.[22] were limited to Brønsted sites only. Another advantage is transferability of proposed method. This method not only can be applied for Brønsted and Lewis acid sites (originated

form Al-atoms) but also allows us to study the accessibility of transition-metal cations in zeolites being active sites in many important redox processes.

4. CONCLUSIONS

We offer a new method of investigation of the accessibility both of Brønsted and Lewis acid sites as well as metal cations based on quantitative IR studies of bulky pivalonitrile adsorption. The extinction coefficients of the diagnostic bands of pivalonitrile interacting with both kinds of acid sites were determined, and, consequently, the concentration of sites accessible to pivalonitrile was calculated.

Total concentration of Brønsted and Lewis sites was determined with pyridine, and the sum of both concentrations was very close to Al content. The AF being the ratio of site concentrations determined with pivalonitrile and pyridine was calculated.

The values of the AF increase upon desilication of zeolite and correlate well with the values of mesopore surfaces. The increase in the accessibility is related to the increase in contribution of sites on the external surfaces and in pore mouths in zeolites of high mesopore surfaces. Upon desilication, the sites inside micropores in desilicated materials are also supposed to react more easily with hindered molecules because in zeolites with the expended mesopore system, the average length of micropores is smaller (shorter distances between micropore mouths) than in nondesilicated zeolites.

In zeolites of medium Al content (Si/Al = 32), the accessibility of the acid sites to pivalonitrile was lower than that in highly siliceous zeolite (Si/Al = 164), where all of the acid sites were accessible (AF $\approx$ 1). It may be supposed that in zeolite of Si/Al = 32, that is, of higher concentration of both types of acid sites, bulky pivalonitrile molecules bonded with acid sites located near micropores mouths block the micropore entrance; therefore, sites located deeper inside micropores are not reached by pivalonitrile.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
XRD diffraction patterns and TEM images. The deconvolution data of the spectra of pivalonitrile sorbed in studied zeolites. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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