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Dynamic adsorption-desorption of methyl ethyl ketone on MCM-41 and SBA-15 decorated with thermally activated polymers

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Graphical abstract

Highlights

- Ordered mesoporous silicas were decorated with polyacrylonitrile and novolac resin.

- The thermally activated composites were tested in adsorption of butan-2-one.
- The superficial *ladder-type* polyacrylonitrile enhanced the adsorption capability.
- The mechanism of butan-2-one adsorption was proposed.
- The ketone molecules were adsorbed exclusively in the *keto* tautomer form.

Abstract

Three series of mesoporous adsorbents designed for removal of methyl ethyl ketone vapor (MEK) were synthesized: MCM-41 was decorated with various amounts of novolac resin (Nov) and polyacrylonitrile (PAN), while SBA-15 was modified with PAN. The composites were thermally activated towards an enhancement of MEK adsorption capacity and tested in a fixed bed adsorber. Structural features of parent silicas were investigated by XRD, while textural parameters of the composites were studied by nitrogen adsorption. A surface composition was examined by DRIFT and XPS. It was found that decoration of the silica surface with small amounts of PAN improved the monolayer adsorption capacity. The MEK breakthrough curves and desorption profiles were employed for calculation of the monolayer capacity and total pore volume ($V_{\text{total MEK}}$). The $V_{\text{total MEK}}$ for the materials with smaller pores (MCM-41) were comparable to those determined by nitrogen adsorption, whereas respective values for the solids with larger pores (SBA-15) were underestimated. The mechanism of adsorption of MEK onto the adsorbents was elucidated. The MEK molecules were adsorbed solely in the form of *keto* tautomer. The enhanced MEK adsorption capacity came from the beneficial textural features of the support and the presence of a *ladder-type* PAN structure containing O-groups.

Keywords: MCM-41; SBA-15; novolac resin; polyacrylonitrile; volatile organic compounds; dynamic adsorption

1. Introduction

Since the discovery of the family of liquid crystal-templated M41S silica materials in 1992 [1,2], ordered mesoporous silicas (OMS) have attracted a great interest of many researchers. OMS exhibit the presence of a highly ordered system of mesopores with a well-defined shape and adjustable width. Their special advantage is the opportunity for easy modification of the surface. These beneficial features open up a way to utilize OMS in various fields, such as adsorption, [3–5,17–19], chromatography [6,7], medicine [8,9], optical sensor technology [10,12], and catalysis [13–17]. It should, however, be noted that the majority of the developed applications concerns a potential use of OMS in technologies related to the environmental protection, including removal of hazardous organic and inorganic pollutants from gas or liquid phase by physical adsorption [3,4,18–22] or adsorption followed by catalytic conversion [13]. Obviously, the methods of abatement of pollutants based on reversible adsorption are economically justified due to non-destructive character. Their main advantages are the following: (i) simplicity of an installation construction, (ii) low processing energy input needed for adsorption followed by regeneration of an adsorbent bed, (iii) feasibility of the recovery of valuable adsorbate(s), and (iv) possibility of working in multiple adsorption-desorption cycles without special expensive treatments.

One of the largest and sorely dangerous groups among a variety of air pollutants are volatile organic compounds (VOCs). This group comprises plenty of organic compounds (hydrocarbons and their derivatives) characterized by a boiling point ranging between 50 and 250 °C under ambient pressure. The most widely used technologies for the adsorptive removal of non-methane VOCs in the technological scale include pressure swing adsorption, thermal swing adsorption and combined pressure-thermal swing adsorption [21]. Basically, these methods are based on cycles of adsorption followed by regeneration of an adsorbent and recovery of an adsorbate by a proper adjustment of temperature/pressure variables. The

working adsorbent has to exhibit a high thermal and mechanical stability as well as sufficient and stable efficiency in the removal of respective pollutant(s) in multiple adsorption-desorption work cycles. Recently, much efforts have been paid to test OMS as a prospective alternative to conventional adsorbents (usually microporous activated carbons) used in the elimination of VOCs. It was found that OMS show a high adsorption capacity of both polar and non-polar VOCs [18–24,27,31,32]. Their sorption capability may be easily adjusted by a proper post-synthetic modification of hydrophilicity/hydrophobicity of surface. Moreover, the mesoporosity of these materials eliminates diffusion limitations and simplifies an evacuation of VOCs molecules at relatively low temperatures [23,33,35–37]. Consequently, the lifetime of the adsorbent is prolonged improving the overall economy of the process [22,23]. Among numerous types of OMS, MCM-41 and SBA-15 silicas are the most often studied. The pore framework of both of them is classified as the $p6mm$ space group with the 2D hexagonal arrangement of parallel oriented, one-dimensional cylindrical-shaped open mesopores of a uniform diameter varying in the range of 1.5–20 nm (so-called honeycomb structure) [25]. In general, major differences between these materials is that SBA-15 is characterized by larger mesopores, thicker silica walls and possess a fraction of intrawall micropores [39,41]. Our previous studies [18–20,31,32] have shown that the adsorption capability of OMS in the elimination of VOCs may be enhanced by the decoration of their surface with polymers - polyacrylonitrile (PAN) and poly(furfuryl alcohol) (PFA) - followed by thermal activation. Although adsorption equilibria of organic molecules on mesoporous materials may provide valuable insight into strength of adsorbate-surface interaction, pore size and volume of adsorbent, kinetic of diffusion inside pore structure, such studies are rather scarce in the available literature. The distinctive shapes of breakthrough curves collected for methyl ethyl ketone (MEK) interacting with pristine MCM-41 in a fixed bed mode inspired us to do closer inspection of the isothermal adsorption and temperature-programmed desorption profiles. The

saturation curves may be divided into two well-distinguished regions: (i) mono- and multilayer adsorption, and (ii) capillary condensation step. Such behavior of breakthrough curves for water and various organic compounds on OMS with narrow mesopores (i.e. MCM-41 and MCM-48) was reported elsewhere [21,26–30]. For instance, Park and Knaebel [26] have found unusual two-step breakthrough curves for water vapor adsorbed on silica gel. Instead of the expected sigmoidal profile, they achieved the breakthrough pattern resembling the tangent function, which was strongly influenced by humidity and temperature. Shim and coworkers [21] studied the adsorption equilibria and column dynamics for various polar and non-polar VOCs on MCM-48 as a function of pelletizing pressure. The shape of adsorption isotherms clearly indicated that the increasing pelletizing pressure caused the collapse of the mesoporous structure, although the main pore size remained unaltered. The gradual restriction of the plateau region of breakthrough pattern revealed that this step can be ascribed to capillary condensation in the mesopores. Similar results were reported by Hartmann and Bischof [27] who determined the mechanical stability of MCM-48 based on adsorption of benzene, n-heptane and cyclohexane. It was found that the equilibrium adsorption isotherm of particular VOCs could be employed for a direct prediction of breakthrough profile. Moreover, the total pore volumes calculated from the breakthrough curves and nitrogen adsorption isotherms were consistent. Shim et al. [28] investigated the adsorption of polar and non-polar VOCs and H₂O vapor on wash-coated MCM-48 monoliths. The breakthrough curves for a single component were satisfactorily simulated based on the equilibrium adsorption and axisymmetric model, whereas for multicomponent adsorption the simple extended hybrid Langmuir-Sips model was successfully employed.

This contribution is aimed at three following issues: (i) synthesis and testing of polymer-decorated MCM-41 and SBA-15 silicas designed for adsorptive removal of polar volatile organic compounds in a fixed bed mode, (ii) attempts to estimate the textural parameters from

the adsorption to organic adsorbate in relation to those from nitrogen adsorption, and (iii) understanding the nature of the adsorption phenomenon, including the mechanism of surface-adsorbate interaction and to determine the form in which ketone is attracted on the surface. The mesoporous silicas were modified by deposition of various amounts of novolac resin (Nov) and PAN. Nov was introduced to the pore system by incipient wetness impregnation, whereas the PAN-based composites were prepared by precipitation polymerization of acrylonitrile in an aqueous medium. The obtained composites were subjected to thermal activation at temperatures providing a maximum adsorption capacity of MEK (i.e. at 350 °C for PAN and 225 °C for Nov). The structural and textural parameters and surface chemistry were studied thoroughly using low-angle X-ray diffraction (XRD), low-temperature adsorption-desorption of nitrogen, as well as the infrared (IR) and photoelectron (XPS) spectroscopies, respectively. The MEK breakthrough profiles and temperature-programmed desorption (TPD) profiles recorded in a fixed bed adsorption system were employed for calculation of total pore volume and monolayer capacity. The achieved parameters were discussed in relation to the respective values determined from the results nitrogen adsorption and with regard to the type and amount of polymeric modifier. The relative strength of interactions between MEK molecules and adsorption sites was assessed based on the temperature determined as a maximum of TPD profile. Finally, the mechanism of MEK adsorption on the pristine silicas and polymer/silica composites was elucidated based on IR spectroscopic studies. It was found the interaction of MEK and the silica surface is governed by the mechanism of competitive adsorption of water and ketone molecules. MEK molecules are adsorbed solely in the form of *keto* tautomer.

2. Experimental section

2.1. Synthesis

2.1.1. Materials

All reagents and solvents were commercially available and used without further purification: hexadecyltrimethylammonium chloride ($C_{16}TMACl$; 25% water solution, Sigma-Aldrich), tetraethyl orthosilicate (TEOS; 99.0%, Sigma-Aldrich), poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Pluronic P123; Sigma-Aldrich), ammonia solution (25% water solution; Avantor Performance Materials Poland), phenol (99.0%; Avantor Performance Materials Poland), formaldehyde (37.0% water solution; Avantor Performance Materials Poland), hydrochloric acid (HCl 35% water solution; Avantor Performance Materials Poland), ethanol (99.8%; Sigma-Aldrich), acrylonitrile (AN, 99%; Avantor Performance Materials Poland), 2,2'-azobis(isobutyronitrile) hydrochloride (AIBA, 98%; Sigma-Aldrich), methyl ethyl ketone (MEK, 99.5%; Avantor Performance Materials Poland).

2.1.2. MCM-41

MCM-41 silica was synthesized at a molar gel composition of 1.00 TEOS: 0.16 $C_{16}TMACl$: 2.76 NH_3 : 140.13 H_2O [20]. Amounts of 525.0 cm³ of distilled water, 45.3 cm³ of $C_{16}TMACl$ solution and 44.0 cm³ of ammonia solution were mixed in a 1000 cm³ beaker and stirred with a paddle stirrer (ca. 400 rpm) at room temperature for 30 min. Then, 48.6 cm³ of TEOS (cooled before to 4 °C) was added dropwise (2 drops/s). Next, the resulting white slurry was stirred at room temperature for 1 h. Subsequently, the solid product was filtered, washed with distilled water and dried at room temperature for 72 h. Finally, the structure-directing agent was removed by calcination of the material in an electric muffle furnace at 550 °C for 8 h using a heating rate of 1 °C/min. As the yield of the calcined material reached ca. 9 g, the synthesis was repeated three times. The materials produced in the separate batches were

physically mixed (before, we made sure that the products were very similar in terms of structural (XRD) and textural properties (low-temperature nitrogen adsorption)).

2.1.3. SBA-15

SBA-15 silica was synthesized at a molar gel composition of 1.00 TEOS: 0.02 Pluronic P123: 5.58 HCl: 182.55 water [31]. Amount of 4.00 g of Pluronic P123 was dissolved in 150.0 cm³ of 1.6 M HCl solution at room temperature. Then, 9.1 cm³ of primarily cooled TEOS (4 °C) was added dropwise. The obtained white suspension was stirred at 45 °C for 8 h and aged at 80 °C for next 15 h. Then, the precipitate was filtered, washed with distilled water and dried at room temperature overnight. The structure-directing agent was removed using the same procedure as for MCM-41. The yield of the calcined material reached ca. 2 g. In order to produce the amount of silica needed for modification, the synthesis was carried out nine times, and the calcined materials produced in the separate batches were physically mixed.

2.1.4. Novolac resin (Nov)

Nov was synthesized by acid-catalyzed polycondensation of phenol (PH) with formaldehyde (FA) at a molar ratio PH/FA of 1.42:1.00. Amounts of 66.74 g of PH and 37.2 cm³ of FA solution were mixed at room temperature in a 250 cm³ three-neck round-bottom flask placed in an oil bath and equipped with a reflux condenser and a small dropping funnel filled with 18.3 cm³ of 1 M HCl solution used as a catalyst. A stirrer was turned on (200 rpm), and a half of the acid solution was carefully dropped into the reaction mixture. After the temperature of the mixture reached 90 °C (strongly exothermic effect), the stirrer was turned off. Upon 15 min, the stirrer was restarted and the remaining amount of the catalyst was added dropwise. Then, the stirring and heating were stopped and the reaction mixture was left for the next 30 min. After cooling down, the aqueous phase was decanted and the viscous resin product was

heated up to 100 °C in order to remove the residual water occluded in the polycondensate bulk by distillation under a reduced pressure. Finally, the dry solidified resin was ground in an agate mortar and stored in a sealed vessel in a dark place.

2.1.5. *Decoration of MCM-41 with Nov*

The MCM-41 material was decorated with various amounts of Nov by the single-step incipient wetness impregnation of freshly calcined silica support with an ethanol solution of resin. The intended Nov/MCM-41 mass ratios were 0.05, 0.20, 0.40, 0.60, and 1.20. Prior to the impregnation, the adsorption capacity of MCM-41 for pure ethanol was determined to be 4.3 cm³ per 1.00 g of silica. Each Nov solution was prepared to achieve the adequate amount of resin contained in 4.3 cm³ of solution needed for impregnation of 1.00 g of MCM-41. The impregnated samples were dried at 40 °C for 24 h. The obtained composites were denoted as Nov_x_M, where *x* means the respective resin/silica mass ratio and M = MCM-41.

2.1.6. *Decoration of MCM-41 and SBA-15 with PAN*

The procedure of synthesis of PAN/silica composites (with the intended polymer/silica mass ratios of 0.10, 0.60, 0.80, 1.20 and 2.00) by the precipitation polymerization of AN in an aqueous slurry of silica was described in details in our previous papers [18,19,31]. Briefly, an amount of 3.00 g of freshly calcined silica was introduced into a three-neck round-bottom flask (250 cm³) immersed in an oil bath placed on a magnetic stirrer and equipped with a reflux condenser. Subsequently, adequate amounts of distilled water, AN, and AIBA initiator were added to achieve the total volume of the reaction mixture of 100 cm³. The AIBA/AN molar ratio of 0.004 was kept constant for each synthesis. The intended PAN/silica mass ratio was adjusted using an appropriate monomer volume. In order to remove oxygen dissolved in the reaction mixture, the mixture was initially purged with argon (grade 4.6; 40 cm³/min) for

30 min at room temperature. The polymerization process was carried out at 60 °C for 3 h. The resulting composite was filtered, washed with distilled water and dried overnight at 60 °C. The samples were marked as PAN $_x$ _M and PAN $_x$ _S, where x is the real polymer/silica mass ratio, M = MCM-41, and S = SBA-15. As the real contents of the introduced polymer may differ from those intended due to the formation of water-soluble oligomeric species or remaining unreacted monomer in the reaction mixture, the actual PAN/silica mass ratios were determined by means of thermogravimetric measurements performed in an air atmosphere (by subtracting the masses recorded at 130 and 1000 °C, respectively [18,19]; cf. Fig. S1). As a counterpart, the bulky PAN sample was synthesized by the same method as the composites, but without using the silica support.

2.1.7. Thermal activation

Thermal treatment of the synthesized composites was carried out in a tubular quartz oven under the nitrogen atmosphere (grade 4.6; 40 cm³/min). The temperature regime included the heating ramp of 5 °C/min and an isothermal period of 4 h at the optimal temperature (i.e. this one which provided the highest MEK adsorption capacity). The optimal temperature of activation for the Nov/MCM-41 series was found to be 225 °C (cf. Fig. S2), while the bulky PAN and PAN/silica composites were activated at 350 °C, as reported elsewhere [18].

2.2. Characterization methods

Structural parameters of pristine MCM-41 and SBA-15 were examined by means of low-angle X-ray powder diffraction (XRD) using a Bruker D2 Phaser instrument equipped with a LYNXEYE detector. The diffraction patterns were recorded using Cu K α radiation (λ = 1.54184 Å) in a 2 θ range of 0.80–8.00° with a step of 0.02°.

Textural parameters of the studied materials were determined by low-temperature adsorption-desorption of nitrogen ($-195.8\text{ }^{\circ}\text{C}$). The isotherms were collected using an ASAP 2010 instrument (Micromeritics). Prior to the analyses, the samples were outgassed at $250\text{ }^{\circ}\text{C}$ for 12 h. Specific surface areas were calculated based on the multipoint Brunauer–Emmett–Teller model (S_{BET}) within a relative pressure range of 0.05–0.20. External surface areas ($S_{\text{ext.}}$) were calculated based on slopes of linear functions fitted to standard reduced adsorption plots (α_s) in the regions of $\alpha_s = 1.25\text{--}1.90$ and $\alpha_s = 1.90\text{--}2.50$ for the MCM-41- and SBA-15-supported composites, respectively. Micropore and mesopore volumes were assessed by analysis of y-intercepts of relevant tangent lines fitted to α_s plots in the ranges of $\alpha_s = 0.50\text{--}0.80$ and $\alpha_s = 1.25\text{--}1.90$ for the MCM-41 series, and $\alpha_s = 0.50\text{--}1.20$ and $\alpha_s = 1.90\text{--}2.50$ for the SBA-15 series, respectively [33]. Micropore areas were computed based on the t -plot model (de Boer equation; $p/p_0 = 0.05\text{--}0.20$). For each sample, α_s was plotted vs. adsorption on a standard macroporous LiChrospher Si-1000 silica reference, reported by Jaroniec et al. [34]. Total pore volumes were extracted from the adsorption branches of the isotherms by the single-point model (s-p), using respective data points at $p/p_0 = 0.97\text{--}0.98$. The non-local density functional theory model (NLDFT; adsorption branch of isotherm; cylindrical pore symmetry assumption) was employed for calculation of pore size distribution curves (PSD). Based on the XRD pattern and mesopore volume (α_s model), an average pore diameter of MCM-41 was additionally calculated according to the equation proposed by Kruk et al. [35,36]. In this approach, the average pore diameter (w_d) and thickness of mesopore walls (b_d) were obtained from the following equations:

$$w_d = c \cdot d_{100} \left(\frac{\rho \cdot V_{\text{meso}}}{1 + \rho \cdot V_{\text{meso}}} \right)^{\frac{1}{2}} \quad (1)$$

$$b_d = a_{100} - w_d \quad (2)$$

where:

c – constant; for cylindrical symmetry of pores $c = 1.213$;

d_{100} – (1 0 0) interplanar spacing [nm];

ρ – density of amorphous silica; $\rho = 2.2 \text{ cm}^3/\text{g}$;

V_{meso} – primary mesopore volume (α_s model) [cm^3/g];

a_{100} – (1 0 0) lattice parameter [nm]; for p6mm space group $a_{100} = \frac{2}{\sqrt{3}} \cdot d_{100}$ [nm].

The wall thickness of SBA-15 (D_{wall}) was calculated by subtracting the lattice parameter (a_{100}) and main mesopore diameter (D_{pore}) determined by the NLDFT model.

Mid-infrared spectra for the silicas and composite materials were recorded in a diffuse reflectance mode (DRIFT) in the wavenumber range of 650–4000 cm^{-1} using a Nicolet 6700 FTIR spectrometer equipped with a DRIFT device (EasiDiff™-Pike Technologies) and MCT-A detector. Samples were diluted to 1.5 wt. % with KBr and softly milled in an agate mortar. 200 scans were collected at a resolution of 4 cm^{-1} . The spectrum of liquid MEK was recorded using the same spectrometer equipped with Smart iTR™ Attenuated Total Reflectance (ATR) accessory. The measurement was carried out within the spectral region of 650–4000 cm^{-1} . 200 scans were taken at a resolution of 4 cm^{-1} .

X-ray photoelectron spectroscopy measurements (XPS) were carried out with a Prevac photoelectron spectrometer equipped with a hemispherical analyzer VG SCIENTA R3000. The photoelectron spectra were recorded using a monochromatized aluminum source Al K α ($E = 1486.6 \text{ eV}$) and a low-energy electron flood gun (FS40A-PS) to compensate for charge accumulation on the surface of nonconductive samples. The base pressure in the analytical chamber was 5×10^{-9} mbar. The surface composition was studied based on the integrals and binding energies of C 1s, N 1s, O 1s and Si 2p core levels. The binding energy values of measured regions were referenced to the C 1s core level of 285.0 eV.

Elemental analysis measurements (EA) were performed using a Flash 2000 (Thermo Scientific) organic elemental analyzer (CHN). The oxygen content was calculated by subtracting the contents of all other analyzed elements from 100%.

Thermogravimetric analyses (TG) were carried out using a SDT Q600 thermobalance (TA Instruments). An amount of ca. 20 mg of a dry sample placed in a corundum crucible was heated in an air atmosphere ($100 \text{ cm}^3/\text{min}$) from 30 to 1000°C and a heating rate of $20^\circ\text{C}/\text{min}$.

The amounts of AN monomer attached to the MCM-41 and SBA-15 surface in an aqueous medium were analyzed by means of total organic carbon (TOC) measurements (Shimadzu TOC-Vcph apparatus) of AN solution before and after contact with silica. 1.0000 g of freshly calcined silica was immersed in a 50.00 g of 1.00 wt. % of AN aqueous solution in a round-bottom flask (100 cm^3) placed on a magnetic stirrer. The mixture was stirred vigorously for 30 min at room temperature (20°C). Subsequently, the silica was isolated by filtration and the filtrate was subjected to the TOC analysis. The AN adsorption capacity was calculated based on a decrease in the AN concentration after the contact with silica referred to the mother liquor.

The mechanism of MEK adsorption was investigated by DRIFT spectroscopy. An amount of ca. 0.50 g of previously outgassed adsorbent (200°C , 1 h) placed in a quartz boat was transferred to a glass vessel (1000 cm^3) equipped with a sealed cover and filled with 50 cm^3 of liquid MEK. The boat was held over the liquid in a manner preventing a direct contact of the adsorbent with liquid MEK. Then, the vessel was closed and kept in a laboratory dryer at 40°C for 24 h (pre-adsorption step). After adsorption, the vessel was opened and the saturated adsorbent was divided into six portions which were subsequently exposed to the atmospheric air at 40, 50, 75, 100, 125 and 150°C for 30 min. Finally, each sample was

diluted to 2.0 wt. % with KBr, softly milled in an agate mortar and subjected immediately to a DRIFT measurement carried out by the same procedure as described above.

2.3. Fixed bed adsorption tests

Tests of dynamic adsorption of MEK on the composites in a fixed bed followed by TPD were performed in a home-built system (cf. Fig. S3). This system was designed to work in two following modes: (i) saturation of the bed with adsorbate vapor diluted in a carrier gas at a given temperature, and (ii) thermal desorption in a flow of pure carrier gas. 0.1000 g of an adsorbent sample was weighted in a cylindrical stainless steel adsorber plugged at the bottom with a quartz wool (adsorber length ca. 70 mm; inner diameter 6 mm). The adsorber was subsequently placed in a thermostated oven and the inlet and outlet of the adsorber were connected to the carrier gas line and flame ionization detector (FID), respectively. A constant flow of carrier gas (N_2 ; 20 cm^3/min) was purged through the adsorbent bed and the oven was heated up to 150 °C and hold at this temperature until the signal of FID reached a baseline level (outgassing step). Then, the adsorber was weighted again in order to ascertain the exact mass of the degassed sample and placed back in the oven kept at 40 °C. Next, a flow of carrier gas (N_2 ; 20 cm^3/min), saturated with MEK vapor at 10 °C, was passed through the adsorbent at 40 °C. The breakthrough curve was recorded until the FID signal reached a plateau (the outlet MEK concentration equaled the inlet concentration). Subsequently, MEK dosing was interrupted and the pure carrier gas (N_2 ; 20 cm^3/min) was passed through the saturated bed again at 40 °C in order to remove the loosely (reversibly) adsorbed forms of ketone (i.e. these collected in the pore structure by capillary condensation and/or multilayer adsorption, excluding the monolayer adsorbed directly on the adsorbent surface). The removal of a reversibly adsorbed ketone was completed by the step of a heating from 40 to 50 °C with a rate of 10 °C/min. The main measurement of TPD was then carried out by heating from

50 °C up to 250 °C at a rate of 15 °C/min in a flow of pure carrier gas (20 cm³/min). The identical mass of the adsorbent before and after the entire adsorption-desorption cycle ascertained the quantitative desorption of adsorbate upon TPD. The adsorption capacities were calculated from the integrals of the respective regions of the recorded FID signals. The detector response was calibrated by integration of the desorption profiles collected for precisely defined quantities of MEK.

3. Results and discussion

3.1. Structural characteristics of pristine MCM-41 and SBA-15

The low-angle X-ray diffraction patterns collected for pristine MCM-41 and SBA-15 silicas are displayed in Fig. 1.

Three well-distinguished diffraction lines at $2\theta = 2.34, 4.09$ and 4.72° for MCM-41 and $1.03, 1.74$ and 1.98° for SBA-15, ascribed to the reflections indexed as (1 0 0), (1 1 0) and (2 0 0), respectively, confirm the 2D p6mm symmetry of both synthesized materials (structures of MCM-41 and SBA-15 depicted maintaining relevant proportions are shown as insets in Fig. 1). Furthermore, the presence of the reflection indexed as (2 1 0) observed for MCM-41 at $2\theta = 6.25^\circ$ evidences a high quality of its structure. The d_{100} spacing of 3.8 nm for MCM-41 corresponds to the unit cell parameter a_{100} of 4.3 nm. The MCM-41 wall thickness equals 0.7 nm (assuming primary mesopore volume of 0.76 cm³/g; cf. Table 1), while the calculated pore size of 3.6 nm is consistent with the main pore diameter determined by the NLDFT model (3.8 nm).

The SBA-15 silica exhibits the d_{100} interplanar spacing of 8.6 nm, which corresponds to a lattice parameter $a_{100} = 9.9$ nm. This material is characterized by twofold broader mesopores (7.3 nm) and almost fourfold thicker walls (2.6 nm) compared to MCM-41. These structural

parameters of MCM-41 and SBA-15 remain in a good agreement with the relevant values reported earlier [25,35–37,41].

3.2. *Changes in textural parameters after polymer introduction*

It is pertinent to mention that the modifications did not affect the long-range ordering of the pristine silicas thereby solely the textural parameters will be discussed herein. The low-temperature nitrogen adsorption-desorption isotherms recorded for pristine MCM-41 and SBA-15 silicas and their composites with polymers after thermal activation are displayed in Fig. 2.

The isotherms of parent MCM-41 and the samples with a moderate Nov and PAN content (cf. Fig. 2A,B) exhibit mutually similar behavior and correspond to IV type according to the IUPAC classification [38]. The narrow hysteresis loop suggests the presence of a well-defined mesopore structure with cylindrical-shaped channels uniform in diameter accompanied by the small fraction of slightly larger pores (cf. Fig. 2A'). The BET specific surface area of 1061 m²/g, pores uniform in size close to 3.8 nm and single-point total pore volume of 0.83 cm³/g for pristine MCM-41 (cf. Table 1) are similar to the corresponding parameters demonstrated earlier in the literature [35–37]. The capillary condensation step occurs in all cases at $p/p_0 = 0.20$ – 0.30 and shows slight shifts to the lower relative pressure with increasing polymer content. This fact proves the successful deposition of both polymer modifiers inside the mesochannels of MCM-41. The isotherms recorded for the materials with the highest contents of polymer modifiers reveal their non-porous character, reflected in total pore volumes close to nil as well as the specific surfaces of only a few m²/g. Taking into account the textural parameters of the MCM-41-supported materials compiled in Table 1, one may conclude that both polymer modifiers influenced significantly the porosity of the MCM-41-supported

composites. The coverage of the pore walls with increasing polymer amount resulted in a progressive blocking of mesopores.

In our previous work [19], we proved that the introduction of PAN by the precipitation polymerization in an aqueous slurry results in the formation of irregular plugs of polymer anchored onto the silica walls. Based on our former works on the different polymer/silica composites [19,20], we can state that the homogeneity of deposition of modifier onto the silica surface depends stronger on the nature of the polymer than on the method of its introduction. For instance, it was found that poly(furfuryl alcohol) deposited on MCM-41 by the same procedure of polyreaction in an aqueous medium, is distributed more homogeneously compared to PAN [20]. Although the effect of clogging of silica mesopores with the PAN particles is not clearly evident for narrow-porous MCM-41, it is explicitly visible in the nitrogen isotherms of SBA-15 with broader channels (Fig. 2C). The isotherm of non-modified SBA-15 of type IV with a well distinguished H1 hysteresis loop shows a rapid increase in nitrogen uptake at $p/p_0 = 0.60\text{--}0.75$ due to the capillary condensation in the mesopores. The BET specific surface area of $765\text{ m}^2/\text{g}$, average mesopore diameter of 7.3 nm and total pore volume of $0.89\text{ cm}^3/\text{g}$ (cf. Table 1) are typical values for SBA-15 silicas [15,24,25,31,41]. It is interesting to consider the behavior of the nitrogen isotherms collected for SBA-15 loaded with moderate amounts of PAN (i.e. PAN0.15_S, PAN0.39_S, and PAN0.84_S). Although the shape of the adsorption branches remains unaltered with the little-by-little lower maximum nitrogen uptake at $p/p_0 = 1$, the desorption branches show an additional step and a closure point at $p/p_0 = 0.43$, regardless of the polymer content. This effect clearly indicates the cavitation mechanism observed in broad mesopores clogged by irregular particles of modifier [19].

Obviously, the filling of the pores with the polymer modifier is reflected in the total pore volume accessible for N_2 . As seen in Table 1, the MCM-41 pore system is completely filled

with the modifier (i.e. $V_{\text{total}} \approx 0$) for the polymer/silica mass ratio of 1.20 and 1.31 in the case of Nov and PAN, respectively. This disparity may be caused by differences in both the character of the polymer species after deposition and the density of bulk polymers. In the case of SBA-15 series, the complete filling of the pore system is achieved for the PAN/silica ratio of 1.63. The higher loading of SBA-15 with PAN required for total blocking of its pores compared to MCM-41 clearly corresponds to the higher total pore volume of SBA-15.

A decrease in the external surface area with increasing polymer content was observed for both studied MCM-41 series (cf. Table 1), suggesting the deposition of polymer domains onto the outer surface of the silica particles, which may facilitate coalescence of the material grains. Interestingly, the modification of SBA-15 with small amounts of PAN (i.e. PAN0.05_S, and PAN0.15_S) entailed a slight increase in the external surface area. This may be due to the inhomogeneities of the superficial polymer domains, which may be created in the relatively large pores of SBA-15. The comparative α_s plots are displayed in Fig. 2A'',B'',C''. The y-intercepts of linear functions fitted to the α_s plots at low reduced adsorption values (up to 0.8) for both MCM-41 series are close to zero suggesting the absence of microporosity in the composites. This is consistent with the former studies provided by Silvestre-Albero et al. [39], in which the exclusively mesoporous character of MCM-41 was evidenced. It should also be kept in mind that the temperature of thermal activation of the composites was insufficient to lead to the formation of micropores in the polymer species, as the microporosity of thermally treated resins starts to be formed above 700 °C [40]. In contrast, the SBA-15 and its composites with PAN reveal a small contribution of microporosity, which decreases with increasing polymer content. This microporosity originates from the inherent microporosity of parent SBA-15 (so-called *micropore corona* that is being formed around mesopores during soft-templating synthesis [39,41]).

3.3. Surface composition

The surface composition of the studied materials was investigated by means of DRIFT and XPS. The DRIFT spectra collected for pristine silicas as well as for the polymer-decorated composites before and after thermal activation are gathered in Fig. 3.

The spectra recorded for both parent silicas exhibit the presence of a sharp absorption band at 3745 cm^{-1} , ascribed to the stretching vibrations of SiO–H (isolated terminal silanol groups) [41,42]. The broad band at $3000\text{--}3700\text{ cm}^{-1}$ is attributed to the vibrations of hydrogen-bonded silanol groups, while the bands at 1210 and 1060 cm^{-1} are assigned to the asymmetric stretching vibrations of Si–O–Si and the well-pronounced band at 805 cm^{-1} is ascribed to the bending modes of Si–O–Si moieties. The band at 960 cm^{-1} is attributed to the Si–OH stretching vibrations, whereas the band at 1240 cm^{-1} (partially overlapped with the band at 1210 cm^{-1}) proves the presence of dehydroxylated surface siloxane bridges [42–44]. It should be noted that the intensity of the band at $3000\text{--}3700\text{ cm}^{-1}$ is significantly higher for SBA-15 compared to MCM-41, while the modes at 1240 and 3745 cm^{-1} exhibit higher intensity for MCM-41. This clearly indicates the higher degree of silica condensation and a higher concentration of isolated silanols on the surface of MCM-41, despite the same silica precursor used, calcination regime as well as procedure of sample preparation before the DRIFT measurements. Besides, both pristine silicas exhibit the presence of absorbance at 1625 cm^{-1} , ascribed to the molecular water strongly adsorbed on the silica surface.

The DRIFT spectra recorded for the polymer-covered silicas display the presence of characteristic absorption frequencies of both support and polymer components. The spectra collected for the Nov0.20_M sample before and after activation are displayed in Fig. 3A. Four partially overlapping bands assigned to methyl and methylene groups are observed in the region of $2800\text{--}3000\text{ cm}^{-1}$. These modes are attributed as follows: 2883 cm^{-1} - symmetric

stretching vibrations of CH_2 , 2909 cm^{-1} - symmetric stretching vibrations of CH_3 , 2940 cm^{-1} - asymmetric stretching vibrations of CH_2 , and 2979 cm^{-1} - asymmetric stretching vibrations of CH_3 [45]. A decrease in the intensity of a broad band in the region of $3000\text{--}3600\text{ cm}^{-1}$ after the thermal activation suggests possible partial dehydration of phenolic resin and desorption of moisture. The band at $3040\text{--}3070\text{ cm}^{-1}$ is ascribed to the C–H stretching vibration in aromatic rings. The absorptions at 1605 and 1506 cm^{-1} (C=C stretching vibrations in aromatic rings), remain unaltered after the thermal treatment suggesting the lack of further chemical transformation upon heating.

The deposition of PAN on MCM-41 and SBA-15 supports resulted in a slight decrease in the intensity of the corresponding IR bands. This effect is well pronounced for the absorption mode of isolated silanols at 3745 cm^{-1} . Simultaneously, an evident increase in the intensity of the complex band at $3000\text{--}3700\text{ cm}^{-1}$ is observed. These facts unambiguously indicate that PAN deposited on silica interacts with its surface with the engagement of isolated silanols by the formation of H-bonds (cf. Fig. 3B; inset) [46]. Furthermore, the coating of silica particles with PAN caused the appearance of new absorption bands (cf. Fig. 3B,C). The bands characteristic of methyl and methylene vibrations are found at similar positions as in the case of the Nov-derived materials. The sharp, well-distinguished band at 2241 cm^{-1} is ascribed to the stretching vibrations of $\text{C}\equiv\text{N}$ groups in the polymer chains and the band at 1453 cm^{-1} is assigned to the in-plane bending vibrations of CH_2 [31]. Compared to the Nov series, the thermal activation of the PAN-derived samples caused a stronger chemical alteration of the surface composition regardless of the silica support. The thermal treatment of the PAN0.79 sample at $350\text{ }^\circ\text{C}$ influenced significantly the DRIFT spectrum. The new bands related to the vibrations of primary amine groups (N–H vibration modes) appeared at 3381 and 3214 cm^{-1} . Furthermore, the characteristic nitrile mode at 2241 cm^{-1} is less intense and slightly shifted to 2236 cm^{-1} . This confirms the partial transformation of PAN chains toward so-called *ladder-*

type structure of PAN and its dehydrogenation (Fig. 3B; inset) [31,47]. These moieties were found to be responsible for the enhanced MEK adsorption capacity [18,19,31]. The suppositions regarding the formation of the *ladder* PAN are additionally supported by the appearance of new bands at 1613 and 1582 cm^{-1} attributed to the C=N and C=C stretching modes in aromatic rings. Additionally, the band at 1386 cm^{-1} confirms the presence of conjugated C=N species. The band at 804 cm^{-1} (partially overlapped with the MCM-41 modes) is assigned to the =CH out-of-plane bending vibrations, while the absorptions at 793 and 740 cm^{-1} are ascribed to the bending vibrations of C-H in -C=C-H moieties and the wagging vibrations of =CH species in unsaturated rings, respectively.

The interesting DRIFT results inspired us to deepen the investigation on the interaction between fresh silica surface and monomer when MCM-41 and SBA-15 immersed in the aqueous solution of AN before initiation of polymerization. The TOC analyses performed for the AN solutions after 30 min of contact with freshly calcined silicas showed that the monomer is readily adsorbed onto the surface. The adsorption capacity reached 15.9 and 11.2 μmol of AN per 1 m^2 of silica for MCM-41 and SBA-15, respectively. Interestingly, a slightly higher value for MCM-41 seems to be in line with the higher concentration of isolated silanols as compared to SBA-15. The H-bonded AN molecules may polymerize without disturbance of the hydrogen bonds. The polyreaction may involve either the molecules adsorbed on adjacent silanols or “free” AN available in the reaction medium. The textural features of the PAN-decorated silicas suggest the latter scenario (i.e. formation of surface-attached random aggregates) being more likely.

To better identify the surface composition, XPS spectra were recorded for the parent silicas and chosen PAN/silica composites before and after thermal activation at 350 °C (Fig. S4 and Table 2). Additionally, the composition of bulky PAN and chosen PAN-derived composites before and after activation was investigated by means of elemental analysis (Table 3). As the

Nov-based adsorbents exhibited no significant alteration in the surface chemistry after thermal treatment (cf. Fig. 3A), and the modification of MCM-41 with Nov did not enhance the MEK adsorption capacity (cf. Section 3.4), these materials were not investigated using XPS and EA.

Obviously, in the case of the PAN-decorated samples, the higher amount of polymer in the composite, the lower content of SiO₂ is observed on the surface (Table 2; compare PAN1.31_M and PAN1.63_S, both before thermal treatment). This is also reflected in the higher content of nitrile groups ($E_b = 399.5 \pm 0.5$ eV) [31], which is found to be the exclusive form of nitrogen at the surface of the non-activated composites. After the thermal activation the content of C $\equiv$ N species drops drastically due to denitrogenation and/or transformation of nitrile into *ladder-type* PAN, containing C=N groups ($E_b = 398.1 \pm 0.4$ eV) [48,49]. The deconvolution of XPS spectra in the C 1s region for both, as-made and activated composites, reveals the presence of the three following features: (i) C=C, C–C, CH₂ groups with the content increasing more than double after the thermal treatment (dehydrogenation of *ladder-type* PAN with the formation of C=C bonds) ($E_b = 285.0 \pm 0.1$ eV) [20,31,48], (ii) CN, C–OH, C–O moieties, with the content decreasing more than double after the thermal treatment (slight denitrogenation) ($E_b = 286.3 \pm 0.2$ eV) [20,31,48], and (iii) C=O functional groups ($E_b = 287.6 \pm 0.2$ eV) [20,31,48]. A plausible explanation for the origin of oxygen-containing moieties is the radical polymerization of AN monomers in an aqueous medium, which enables these moieties to be incorporated into the structure of the formed polymer chains. As the presence of oxygen in the polymer structures will affect the C: H: N atomic ratios (for the ideal PAN structure: C₃H₃N), we have made the effort to analyze the elemental composition of bulky PAN and the studied composites before and after thermal activation.

Based on the results of elemental analysis (C, H and N) after normalization of the polymer content to 100%, the empirical formulas of the polymers were determined (Table 3).

As-made bulky PAN evidences a slight deficiency of hydrogen in relation to the ideal PAN structure (C_3H_3N), due to the presence of oxygen moieties. During the thermal activation, dehydrogenation and denitrogenation occur, and the content of oxygen raises. A small different effect is observed for the as-made composites. Both of them exhibit a small excess of hydrogen (compared to ideal PAN), and higher amount of oxygen than in the case of bulky polymer. Nevertheless, the thermal treatment results in a similar degree of dehydrogenation and denitrogenation compared to bulky PAN. In the case of the MCM-41-supported sample, the oxygen content is retained, while for the SBA-15 sample it increases significantly. This is fully in line with the foregoing discussion on the results of DRIFT and XPS. It can therefore be inferred that the changes undergoing during the thermal activation are similar on the surface and in the bulk of PAN.

3.4. *Dynamic adsorption-desorption tests*

An example of breakthrough curve and desorption profile for a MCM-41-supported composite is presented in Fig. 4.

The breakthrough pattern (Fig. 4A) can be divided into two regions: (i) between t_0^a and t_1^a , ascribed to multilayer adsorption taking place prior to capillary condensation, and (ii) between t_1^a and t_2^a attributed to the capillary condensation step. In the desorption profile (Fig. 4B), two parts can also be distinguished. The first one (between t_0^d and t_1^d) is related to the isothermal desorption of reversibly adsorbed MEK (i.e. by capillary condensation and multilayer adsorption, excluding a monolayer adsorbed directly on an adsorbent surface) that

could be removed by purging a saturated bed with a pure carrier gas at the same temperature as during adsorption (i.e. 40 °C). The second part of the desorption curve (the region between t_2^d and t_3^d) represents the TPD profile collected within a temperature range of 50–250 °C at a linear heating rate of 15 °C/min. The transitional region between t_1^d and t_2^d corresponds to heating a sample from 40 to 50 °C with a rate of 10 °C/min, carried out to ensure the complete removal of reversibly adsorbed MEK before TPD.

The experimental breakthrough curves recorded at 40 °C over parent MCM-41 and its Nov-derived relatives are displayed in Fig. 5A.

The decoration of MCM-41 with various contents of resin influenced significantly the shape of MEK breakthrough pattern. The profile recorded for pristine silica exhibits the well-distinguished region of capillary condensation between 22 and 47 min time-on-stream. Once MEK appears in the outlet of the adsorber (at 22 min), its concentration increases rapidly until $c/c_0 \approx 0.6$. The further saturation of the adsorbent results in a gradual filling of the mesopores, accordingly to the mechanism of capillary condensation. This is clearly reflected in the reduced increasing MEK concentration at the adsorber outlet starting from 22 min time-on-stream. The growing content of the Nov modifier results in a gradual shortening of the saturation time. More interestingly, this causes the breakthrough curve to be little-by-little more similar to sigmoidal with the increasing Nov loading, and evidences a decrease in the available adsorbent surface and internal void space. The presented observations remain in line with the nitrogen isotherms in which the gradual extinction of capillary condensation step at $p/p_0 = 0.20$ – 0.30 with the increasing polymer content is clearly evident (cf. Fig. 2A). In the case of the sample decorated with the highest amount of Nov, the capillary condensation step disappears.

The TPD profiles recorded for the Nov series are shown in Fig. 5B. The isothermal purging of the adsorbent bed for 30 min led to complete desorption of reversible adsorbed MEK molecules. The increasing temperature during TPD results in desorption of the remaining monolayer, attracted stronger by the adsorption sites. It should be underscored that these centers may originate from both composite components – polymer modifier and uncovered silica surface.

The breakthrough curves and TPD profiles collected for the PAN-derived series supported on MCM-41 and SBA-15 are demonstrated in Fig. 6.

Surprisingly, contrarily to the Nov-based series, regardless the type of silica support and the amount of PAN introduced into its pore system, the shape of saturation curve remains clearly sigmoidal. A plausible explanation of this effect may be the different manner of deposition of PAN (as irregular plugs) compared to homogeneous films of Nov as mentioned above (cf. Section 3.2.). The presence of randomly dispersed PAN particles creates the constrictions that hinder the diffusion of MEK molecules penetrating the inner voids of the material. As a consequence, the distinctive capillary condensation step in the breakthrough profile cannot be well pronounced.

As it is shown in Fig. 5B and in the insets in Fig. 6, regardless of the type of silica host and the type of polymer modifier, one desorption maximum is observed in the TPD profiles. Furthermore, irrespective of the chemical nature of the modifier and the type of silica support, the higher polymer content, the lower temperature of maximum desorption rate is observed (e.g. at 176 °C for parent MCM-41, 134 °C for Nov0.60_M, 123 °C for PAN1.31_M, 161 °C for parent SBA-15 and 144 °C for PAN0.39_S, cf. Fig. 6; insets). Interestingly, these values are significantly higher compared to the boiling point of MEK under standard atmospheric pressure (i.e. 79.6 °C). Serrano and coworkers [24] postulated that since TPD is carried out

exclusively for a single layer of adsorbate, the relative strength of interaction of adsorbate-adsorption center is directly related to the maximum of TPD peak. Obviously, it should be kept in mind that the latter parameter is also governed by diffusion limitations in the pore system and the inter-grain space. Nevertheless, the ΔT values can be relatively compared within a given series of materials. Hence, in this simple approach, the strength of adsorbent-MEK interaction may be expressed as the difference between the temperature of TPD maximum ($T_{\text{TPD}}^{\text{max.}}$) and the boiling point of adsorbate under the same pressure ($T_{\text{MEK}}^{\text{b.p.}}$) as follows:

$$\Delta T_{\text{MEK}} = T_{\text{TPD}}^{\text{max.}} - T_{\text{MEK}}^{\text{b.p.}} \quad (3)$$

Thus, for the positive ΔT value an adsorbent surface is considered as a *philic* to adsorbate, while the negative ΔT suggests a *phobic* character of a surface [24]. The monolayer capacities of MEK as a function of ΔT_{MEK} calculated for all studied series are demonstrated in Table 4.

The ΔT varies in the range from +37 °C (for PAN1.63_S) to +99 °C (for PAN0.06_M) and depends on the content of polymer modifier and type of silica support. The strongly positive ΔT_{MEK} values clearly evidence their definitely *philic* character to MEK. It is interesting to consider that the higher the polymer content, the lower temperature of the maximum desorption rate is observed. This may seem to be curious in view of the textural features of the adsorbents (cf. Fig. 2; Table 1). It would be reasonable to suppose that narrowing the pores will result in a delay in the desorption of MEK, manifested in the shift of the maximum evacuation rate towards higher temperature (cf. Fig. 6). Apparently, despite the effect of narrowing of the pores with increasing polymer content, the diffusion limitations do not cause delays in MEK desorption. Considering the data compiled in Table 4, one may infer that the

increasing polymer content results in the weaker strength of adsorbent-adsorbate interaction (cf. ΔT_{MEK} values). Moreover, it is worth to note that the interaction between adsorbent and adsorbate is stronger for pristine MCM-41 compared to Nov0.05_M ($\Delta T_{\text{MEK}} = 96$ and 81 °C, respectively), while the loading of MCM-41 with the smallest amount of PAN (i.e. PAN0.06_M) gives rise to enhance strength of this interaction ($\Delta T_{\text{MEK}} = 96$ and 99 °C, respectively).

In the case the SBA-15 series the ΔT_{MEK} for the parent silica (81 °C) is considerably lower than for MCM-41. As shown in the DRIFT results, MCM-41 exhibits a higher content of surface isolated silanol groups engaged in MEK adsorption. The ΔT_{MEK} decreases within the SBA-15 series with the increase in the PAN content to 37 °C for the composite of the highest PAN loading.

The total pore volume ($V_{\text{total MEK}}$) and monolayer volume ($V_{\text{mono MEK}}$), presented in Table 4, were assessed by integration of respective regions of the breakthrough curve and desorption profile according to the Gurvich rule [50] under the assumption of the density of liquid MEK at 40 °C to be 0.7843 g/cm^3 . The real density of liquid adsorbate filling the mesopores can vary due to different packings of adsorbate molecules inside the pore system, but this inaccuracy does not usually exceed a few percents [27,51]. The values of $V_{\text{total MEK}}$ were calculated by integration of the entire adsorption profiles (cf. Fig. 4A; the regions between t_0^a and t_2^a marked in grey), whereas V_{mono} were determined by integration of the TPD profiles within the temperature range of 50 – 250 °C (cf. Fig. 4B; the region between t_2^d and t_3^d marked in grey). The monolayer thicknesses were calculated based on the respective monolayer volumes related to the corresponding BET specific surface areas.

Regardless the nature of the organic modifier introduced into the pore system of MCM-41 and the type of the silica support covered by PAN, the determined pore volumes decrease with the increasing content of polymer modifier. The average MEK monolayer thickness (or

alternatively the number of MEK molecules per specific surface area unit) for the PAN-decorated MCM-41 is higher compared to the Nov-based samples. This suggests the presence of a higher number of adsorption centers on both the series of PAN-decorated silicas compared to the Nov-based MCM-41 series. The total pore volumes and monolayer capacities calculated based on MEK and N₂ adsorption are comparatively displayed in Fig. 7.

It is evident that these values for the Nov-decorated MCM-41 series are comparable, while both PAN-derived series exhibit $V_{\text{total MEK}}$ slightly lower compared to N₂ adsorption (cf. Table 4; Fig. 7B). The reason of this effect may be the aforementioned clogging of pores in MCM-41 by deposited PAN and impeded accessibility to the pore system. Taking into account the pore width of MCM-41 (3.8 nm), additionally lowered by the PAN loading (cf. Table 1), it can be inferred that only five-six molecules of MEK span the pore diameter. Thus, the underestimated total adsorption capacity of MEK compared to N₂ adsorption is understandable. Nevertheless, the average level of compliance of total pore volumes calculated on MEK and N₂ adsorption for both MCM-41-supported series exceeds 90%. Therefore, it can be concluded that the organic vapor breakthrough curves can be successfully employed to assess $V_{\text{total MEK}}$ of polymer-covered MCM-41.

Interestingly, the values of $V_{\text{total MEK}}$ for the SBA-15 series are considerably underestimated. The average value of $V_{\text{total MEK}}$ equals 49% when compared to the respective calculations from the N₂ adsorption isotherms. It should be noted that SBA-15 exhibits significantly larger pores (ca. 7.3 nm) than MCM-41. Besides, it should be kept in mind that the vapor pressure (VP) of MEK in the inlet was relatively low (at the carrier gas saturation temperature of 10 °C the $VP_{\text{MEK}} = 5.6$ kPa). Therefore, the capillary condensation of MEK at 40 °C probably does not occur (cf. Section 3.4). Thus, contrarily to MCM-41, this approach appears to be unsuitable for calculations of total pore volume for the SBA-15 supported composites.

The data depicted in Fig. 7 show that in the case of the Nov-decorated MCM-41 series the monolayer capacity of MEK is the linear function of the respective value calculated on N₂ sorption results, including pristine MCM-41. In contrast, in the case of the PAN-decorated MCM-41 composites, a linear function was fitted, excepting the pristine silica support. A similar trend can be observed for the SBA-15 series. The slopes of the fitted lines equal 0.197 and 0.315 for the Nov- and PAN-covered MCM-41, respectively, while for PAN-decorated SBA-15 the corresponding value equals 0.394. This means that the average adsorption ratio for the Nov series reaches one molecule of MEK per five molecules of N₂, while for both PAN series this ratio equals about one molecule of MEK per three molecules of N₂. This is reasonable when considering the molecular sizes of N₂ and MEK. The present results corroborate our previous reports [18,19,31] concerning the effect of enhanced adsorption of polar organic adsorbates caused by the decoration of silica with PAN.

3.5. Mechanism of interaction of MEK with adsorbent surface

The mechanism of MEK adsorption onto the parent silicas and PAN-derived composites thermally treated at 350 °C was studied by DRIFT spectroscopy. The relevant spectra collected for the preliminary outgassed silicas and the same samples after pre-adsorption of ketone at 40 °C, compared to the liquid adsorbate spectrum, are displayed in Fig. 8.

The spectrum of liquid MEK exhibits four partially overlapping bands ascribed to methyl and methylene groups in the region of 2800–3000 cm⁻¹ (cf. Fig. 8, inset. The respective assignments are provided in Section 3.3.). The characteristic intense and sharp absorption band at 1712 cm⁻¹ is assigned to the stretching vibrations of carbonyl groups. The adsorption of MEK molecules on the surface of MCM-41 and SBA-15 results in a significant decrease in the intensity of the absorption band at 3745 cm⁻¹ (stretching vibrations of isolated silanols)

that suggests the engagement of these entities in ketone adsorption. Simultaneously, especially in the case of MCM-41, an increase in the intensity of the broad band at 3000–3700 cm^{-1} (vibrations of hydrogen-bonded silanol groups) is observed. The latter effect is more pronounced for MCM-41 due to the higher concentration of isolated silanols and, consequently, the lower concentration of hydrogen-bonded ones onto its surface compared to SBA-15 (cf. Section 3.3.). Furthermore, the adsorption causes a shift in the position of the band related to the vibrations of carbonyl in MEK towards lower wavenumbers. More interestingly, for the ketone pre-adsorbed on MCM-41 and SBA-15, the C=O mode shows two well-distinguished components at 1708 and 1693 cm^{-1} after deconvolution using the Lorentzian formalism. Thus, two types of pre-adsorbed MEK forms coexist on the surface of silica, i.e. (i) loosely adsorbed molecules (due to capillary condensation) with the absorption band at 1708 cm^{-1} , and (ii) strongly attracted molecules anchored by H-bonding with the absorption band at 1693 cm^{-1} . It should be noted that in the case of SBA-15, the band at 1708 cm^{-1} is noticeably weaker compared to MCM-41, suggesting the marginal amounts of the “liquid-like” MEK. Moreover, the changes in the relative intensity of these modes during desorption at elevated temperatures (Fig. S5A) clearly indicate the earlier evacuation of loosely bound MEK forms, followed by the desorption of the H-bonded species. This is consistent with the dynamic adsorption study, which revealed the occurrence of the phenomenon of capillary condensation in the case of MCM-41.

The majority of ketone molecules adsorbed on SBA-15 exist as H-bonded forms (IR absorption band at 1693 cm^{-1}).

It is also worth to consider that the intensity of the band at 1625 cm^{-1} (Fig. 8 and S5), attributed to the vibrations of molecular water strongly adsorbed on the silica surface, drops after pre-adsorption of MEK, and increases again during desorption at elevated temperatures (cf. Fig. S5A,B). Apparently, this effect arises from desorption and re-adsorption of water.

These findings allow us to suppose that the interaction of MEK and the silica surface is most likely governed by the mechanism of competitive adsorption of water and MEK molecules with favored adsorption of the latter ones. A similar mechanism of interaction of organic adsorbate-silica interface was reported previously by Yoon and Vivek [52] who established that silica may undergo dehydration when immersed in the aqueous solutions of methanol and ethanol (i.e. replacement of the adsorbed water). The postulated mechanism of reversible adsorption of MEK on a silica surface assuming the competitive adsorption followed by thermal desorption with rehydration is displayed in Fig. 9.

The DRIFT spectra collected for the chosen PAN/silica composites after pre-adsorption and thermal desorption of MEK are presented in Fig. S5A',A'' and B',B'' for the MCM-41- and SBA-15-based materials, respectively. As seen in Fig. S5A',B' the decoration of both silicas with small amounts of PAN does not affect significantly the nature and location of characteristic IR bands of MEK after pre-adsorption when compared to the parent supports. However, MCM-41 exhibits a more distinguished increase in the intensity of the band at 3000–3700 cm^{-1} after modification with PAN and adsorption of MEK. This is due to the low content of hydrogen-bonded silanols in the pristine MCM-41, as well as the intensive absorption modes of polymer modifier appearing in this region after thermal activation (i.e. 3381, and 3214 cm^{-1} , cf. discussion in Section 3.3.). The more interesting difference is the lack of the C=O band at 1708 cm^{-1} for the PAN0.06_M material (Fig. S5A'). This is in full compliance with the results of dynamic adsorption exhibiting the lack of capillary condensation step (cf. Fig. 6A).

The lower intensities of MEK characteristic absorption bands in the case of the composites with the higher contents of PAN (Fig. S5A'',B'') are reasonable due to their lower MEK adsorption capacity (cf. Table 4; Fig. 7). Moreover, the MEK vibration modes are partially

overlapped with these bands characteristic of the polymer modifier. Nevertheless, the shape and positions of respective maxima for the collected spectra are unaltered compared to the composites with the lower PAN content. This allows us to deduce that the mechanism of adsorption remains the same, notwithstanding the PAN content in the composite. The lower adsorption capacities should be attributed to the decrease in the textural parameters which arises from the increasing PAN content. Combining these results one may conclude that both components, i.e. the parent silica support and the surface domains of PAN, contribute in the total adsorption capacity of MEK. Evidently, in both cases, the MEK molecules are adsorbed in the *keto* form. The enhanced monolayer adsorption capacity exhibited by the samples with the lowest PAN loading (i.e. PAN0.06_M and PAN0.05_S) arises from the cumulative effect of the favorable features: textural parameters (high surface area, double-sided open mesopores) and the presence of *ladder-type* of PAN. Undoubtedly, the effect of improved monolayer sorption ability is additionally strengthened by the high concentration of oxygen-containing surface moieties, as was proven by XPS and DRIFT spectroscopic studies as well as elemental analysis.

It is interesting to consider the above findings in view of the report provided by Machowski et al. [32], who studied the adsorption of MEK on poly(furfuryl alcohol) (PFA)-modified MCM-41 and MCM-48 silicas. The authors found out that the modification of the silica surface with small amounts of thermally activated PFA enhances the MEK adsorption ability similarly to PAN but the PFA-modified silica surface attracts the ketone in its *enol* tautomeric form.

4. Conclusion

MCM-41 silica was successfully decorated with various amounts of Nov and PAN. As a counterpart, a series of PAN-decorated composites supported on SBA-15 (with larger pores) was synthesized. The modification of MCM-41 with Nov resulted in the formation of a

polymer film on the silica walls, while PAN accumulated in the pore system exhibited lower homogeneity forming randomly dispersed plugs, regardless the type of silica support. The polymer/silica composites were subjected to thermal activation toward maximization of MEK adsorption efficiency (at 350 °C and 225 °C for PAN and Nov, respectively). The activation of the PAN-derived samples resulted in the formation of so called *ladder-type* of PAN with a considerable content of oxygen-containing moieties. The activated Nov-derived materials did not exhibit any significant chemical transformation of resin. The composites were tested in a dynamic adsorption and TPD of MEK in a fixed bed system. It was found that small amounts of PAN dispersed on the mesoporous support surface enhanced the monolayer adsorption capacity of both modified silicas despite the marginal effect of the surface modification on the MEK *philicity*. On the contrary, the modification of MCM-41 with Nov led to a gradual decrease in the MEK adsorption capacity. Interestingly, the relative strength of interaction of adsorbate-adsorption sites decreased with increasing amount of the polymer modifier. The collected breakthrough patterns and TPD profiles were employed to estimate the textural parameters (i.e. $V_{\text{total MEK}}$ and monolayer capacity) comparatively to nitrogen adsorption. The results revealed that the MEK monolayer capacity is a linear function of the nitrogen monolayer capacity for Nov-modified MCM-41, while for both PAN-decorated series this function is linear excluding the parent support. The proposed approach of calculation of total pore volume based on the MEK adsorption was found to be useful for the materials of relatively small mesopores (MCM-41), but was unsuitable for the solids with larger mesopores (SBA-15) due to the lack of capillary condensation under the conditions of MEK adsorption as used herein.

The mechanism of MEK adsorption was proposed based on the IR studies of pre-adsorbed ketone. The competitive adsorption of water and MEK molecules with favored adsorption of ketone was observed. It was found that the ketone molecules are adsorbed exclusively in the

keto form on the PAN-modified supports. The enhanced adsorption capacity of the samples modified with the lowest PAN amount is the resulting effect of beneficial textural features and the presence of so-called *ladder-type* of PAN structure. Additionally, the presence of beneficial oxygen-containing surface moieties enhances the adsorption capability.

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Appendix: Supplementary data

Supplementary data associated with this article can be found in the on-line version at

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Fig. 1. Low-angle X-ray powder diffraction pattern for pristine MCM-41 (A) and SBA-15 (B). Insets: schematic representation of the relevant structures (all dimensions are drawn maintaining proportions; the microporosity of SBA-15 skipped for clarity).

Fig. 2. N₂ adsorption (filled circles) – desorption (open circles) isotherms (A,B,C), respective PSDs (A',B',C'), and α_s plots (A'',B'',C'') for MCM-41 (a), Nov0.05_M (b), Nov0.20_M (c), Nov0.40_M (d), Nov0.60_M (e), Nov1.20_M (f) (A,A',A''), MCM-41 (a), PAN0.06_M (b), PAN0.17_M (c), PAN0.79_M (d), and PAN1.31_M (e) (B,B',B''), and SBA-15 (a), PAN0.05_S (b), PAN0.15_S (c), PAN0.39_S (d), PAN0.84_S (e), and PAN1.63_S (f) (C,C',C'').

Fig. 3. DRIFT spectra for MCM-41 (a), Nov0.20_M before (b), and after thermal treatment at 225 °C (c); inset: novolac structure (A), the respective spectra for MCM-41 (a), PAN0.79_M before (b), and after activation at 350 °C (c); inset: postulated mechanism of acrylonitrile monomer adsorption on silica (B), and SBA-15 (a), PAN0.84_S before (b), and after activation at 350 °C (c); inset: ideal structures of pristine and activated PAN (*ladder-type*) (C).

Fig. 4. Exemplary MEK breakthrough curve (A) and temperature programmed desorption profile with temperature regime (B) for polymer-decorated MCM-41 (the areas marked in grey correspond to the respective integrals taken for calculations).

Fig. 5. Experimental MEK breakthrough curves recorded at 40 °C (A), and respective desorption profiles (B) for pristine MCM-41 (a), Nov0.05_M (b), Nov0.20_M (c), Nov0.40_M (d), Nov0.60_M (e), and Nov1.20_M (f).

Fig. 6. Experimental MEK breakthrough curves at 40 °C and corresponding TPD profiles (insets) for pristine MCM-41 (a), PAN0.06_M (b), PAN0.17_M (c), PAN0.79_M (d), PAN1.31_M (e) (A), and pristine SBA-15 (a), PAN0.05_S (b), PAN0.15_S (c), PAN0.39_S (d) (B).

Fig. 7. Total pore volumes calculated on N₂ isotherms and MEK breakthrough curves (bars) and respective monolayer capacities (circles) for MCM-41 (a), Nov0.05_M (b), Nov0.20_M (c), Nov0.40_M (d), Nov0.60_M (e), Nov1.20_M (f) (A), MCM-41 (a), PAN0.06_M (b), PAN0.17_M (c), PAN0.79_M (d), and PAN1.31_M (e) (B), SBA-15 (a), PAN0.05_S (b), PAN0.15_S (c), PAN0.39_S (d), PAN0.84_S (e), and PAN1.63_S (f) (C).

Fig. 8. IR spectra collected for liquid MEK (carbonyl band at 1612 cm^{-1}), outgassed silicas and the same samples after pre-adsorption of MEK at $40\text{ }^{\circ}\text{C}$ (dotted lines: lorentzian deconvolution of adsorbed MEK carbonyl band – “liquid-like”, loosely adsorbed, centered at 1708 cm^{-1} , and H-bonded, at 1693 cm^{-1}).

Fig. 9. Postulated mechanism of MEK adsorption on silica: (i) competitive adsorption of MEK with replacement of molecular water (dehydration), (ii) formation of H-bonded MEK-silanol and loosely adsorbed "liquid-like" MEK layer containing the desorbed water, (iii) TPD of MEK – elimination of "liquid-like" MEK layer followed by breaking of MEK-silanol hydrogen bonds, (iv) rehydration of silica surface.

Table 1. Textural parameters of the studied samples calculated based on nitrogen adsorption-desorption isotherms.

Sample	$S_{\text{BET}} (S_{\text{ext.}})$ [m ² /g]	S_{micro} [m ² /g] <i>t</i> -plot	V_{total} [cm ³ /g] <i>s</i> - <i>p</i>	V_{micro} [cm ³ /g] α_s	V_{meso} [cm ³ /g] α_s	D^* [nm] NLDFT
MCM-41	1061 (53)	0	0.83	0.00	0.76	3.8
Nov0.05_M	957 (53)	0	0.74	0.00	0.67	3.5
Nov0.20_M	743 (39)	0	0.55	0.00	0.49	3.5
Nov0.40_M	507 (13)	0	0.34	0.00	0.32	3.5
Nov0.60_M	287 (20)	0	0.19	0.00	0.16	3.2
Nov1.20_M	8 (7)	0	0.01	0.00	0.00	—
PAN0.06_M	944 (33)	0	0.65	0.00	0.61	3.5
PAN0.17_M	690 (26)	0	0.46	0.00	0.42	3.2
PAN0.79_M	343 (20)	0	0.23	0.00	0.20	3.2
PAN1.31_M	16 (7)	0	0.02	0.00	0.01	—
SBA-15	765 (79)	54	0.89	0.04	0.75	7.3
PAN0.05_S	664 (92)	137	0.77	0.07	0.58	7.3
PAN0.15_S	481 (92)	47	0.64	0.02	0.50	7.3
PAN0.39_S	297 (46)	17	0.41	0.01	0.34	6.6
PAN0.84_S	129 (66)	11	0.15	0.01	0.06	6.6
Sample	Si [at.%]	O [at.%]	C [at.%]	N [at.%]		
PAN1.63_S	29 (29)	0	0.04	0.00	0.00	—

* Main pore diameter

Table 2. Atomic contributions (atomic %) of surface moieties detected in parent supports and PAN-silica composites before and after thermal treatment at 350 °C.

			$\frac{\text{C}=\text{C},}{\text{C}-\text{C},}{\text{CH}_2}$	$\frac{\text{CN},}{\text{C}-\text{OH},}{\text{C}-\text{O}}$	$\text{C}=\text{O}$	$\frac{\text{CN}}{\text{nitrile,}}{\text{pyrrolic,}}{\text{pyridone}}$	$\frac{\text{C}=\text{N}}{\text{imine,}}{\text{pyridine}}$
MCM-41	34.4	65.6	–	–	–	–	–
PAN1.31_M as-made	4.0	14.1	21.4	42.1	2.6	15.7	–
PAN1.31_M 350	5.7	10.7	49.0	16.9	1.4	9.3	7.0
SBA-15	41.3	58.7	–	–	–	–	–
PAN1.63_S as-made	1.3	2.7	25.7	48.9	0.5	21.0	–
PAN1.63_S 350	1.0	3.8	52.2	23.2	2.1	6.5	10.6

Table 3. Empirical formulas of bulky polyacrylonitrile and PAN-silica composites before and after thermal treatment at 350 °C calculated based on the elemental analysis (for composites the polymer content normalized to 100%).

Sample	Empirical formula (ideal PAN: C ₃ H ₃ N)
PAN	C _{3.00} H _{2.81} N _{1.00} O _{0.04}
PAN 350	C _{3.00} H _{2.08} N _{0.81} O _{0.28}
PAN1.31_M as-made	C _{3.00} H _{3.29} N _{1.00} O _{0.17}
PAN1.31_M 350	C _{3.00} H _{2.52} N _{0.83} O _{0.17}
PAN1.63_S as-made	C _{3.00} H _{3.39} N _{0.97} O _{0.20}
PAN1.63_S 350	C _{3.00} H _{2.61} N _{0.82} O _{0.94}

Table 4. Adsorption parameters calculated on MEK breakthrough curves at 40 °C and TPD profiles.

Sample	V _{total MEK} ^a [cm ³ /g]	V _{total MEK} / V _{total N₂}	V _{mono MEK} ^b [cm ³ /g]	T _{mono MEK} ^c [nm] (×10 ¹⁸ molec. MEK/m ²)	ΔT _{MEK} [° C]
MCM-41	0.75	0.90	0.20	0.19 (1.24)	96
Nov0.05_M	0.65	0.88	0.18	0.18 (1.20)	81
Nov0.20_M	0.55	1.00	0.14	0.19 (1.26)	81
Nov0.40_M	0.39	1.15	0.10	0.21 (1.34)	66
Nov0.60_M	0.20	1.05	0.06	0.21 (1.38)	54
Nov1.20_M	0.00	—	0.00	—	—

PAN0.06_M	0.47	0.72	0.27	0.29 (1.88)	99
PAN0.17_M	0.46	1.00	0.20	0.29 (1.93)	67
PAN0.79_M	0.15	0.65	0.06	0.19 (1.23)	69
PAN1.31_M	0.02	1.00	0.01	0.48 (3.14)	44
SBA-15	0.35	0.39	0.21	0.30 (1.99)	81
PAN0.05_S	0.42	0.55	0.24	0.38 (2.46)	72
PAN0.15_S	0.34	0.53	0.15	0.32 (2.09)	62
PAN0.39_S	0.17	0.41	0.08	0.27 (1.75)	64
PAN0.84_S	0.03	0.20	0.03	0.25 (1.62)	45
PAN1.63_S	0.01	0.25	0.01	0.44 (2.92)	37

^a calculated on the base of integration of the breakthrough curve in the region of multilayer adsorption and capillary condensation (cf. Fig. 4A; the region of t_0^a and t_2^a);

^b calculated on the base of integration of TPD profile (cf. Fig. 4B; the region of t_2^d and t_3^d);

^c monolayer thickness: $T_{\text{mono MEK}} = V_{\text{mono MEK}} / S_{\text{BET}}$; (number of MEK molecules per specific BET surface unit given in parentheses).