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## Development of a method for the synthesis of basic catalysts with high number of active species

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ARTICLE INFO	A B S T R A C T	
Keywords: MCF Niobium Ceria Melamine Knoevenagel condensation	Mesoporous silica MCF and metalosilicates Nb/MCF-14 and Ce/MCF-14 were modified with anchoring or melamine followed by (3-chloropropyl)trimethoxysilane functionalization. The texture/structure parameters chemical composition and surface properties of synthesized samples were investigated by XRD, N <sub>2</sub> adsorption/ desorption, XPS, UV-vis, TG, elemental analysis and 2-propanol dehydration and dehydrogenation, whereas the activity of obtained catalysts was tested in the Knoevenagel condensation between benzaldehyde and mal ononitrile. The Knoevenagel reaction required the presence of basic active sites or a pair of acid-base active centers. The novelty of the presented work was the use of mesoporous cellular foam (MCF) also modified with niobium (Nb/MCF-14) or cerium species (Ce/MCF-14) as supports for melamine anchoring. The use of the mentioned supports allowed the investigation of the role of open structure of MCF and metal dopant on mel- amine loading, its stability and reactivity in the Knoevenagel condensation. The obtained results clearly de monstrate that cerium and niobium species loaded into MCF increase significantly the efficiency of melamine loading as well as its stability. The anchoring of melamine to silica and metalosilicates increase the activity of this modifier as a result of formation of secondary amine species. The presence of defected ceria in Mel/Ce/MCF- 14 raises the basicity of anchored melamine due to the electron donating effect of ceria. Consequently, the amine species in melamine are more active in the Knoevenagel condensation than those in Mel/Nb/MCF-14 because niobium species do not change oxidation state as easily as defected ceria.	

#### 1. Introduction

The subject of this paper fits the global trend of synthesis and modification of mesoporous silica, in order to obtain effective heterogeneous catalysts in reactions requiring the presence of available basic active species, such as the Knoevenagel condensation. One of the possibilities of generation of basic active centers in mesoporous silica is the immobilization of specific organic compounds containing amine or imine species [1–5]. The basicity of such species is related to the presence of a lone pair of electrons in the nitrogen atom, which can abstract a proton from the reagent molecules. Thus, amine or imine species work as Brønsted basic sites [6].

The mechanism of the Knoevenagel condensation carried out over amine modified materials has not been fully explained yet. Two mechanisms of this reaction are postulated, in which the ion-pair [7] or imine intermediates [8] are formed. In the ion-pair mechanism the amine species trap a proton from the methylene group of the active methylene compound, in which the carbon atom is strongly acidic due to the neighborhood of an electron-withdrawing group. As a result of this reaction an anion is formed which can attack the carbonyl carbon atom of aldehyde. The obtained intermediate product -  $\beta$ -hydroxyl compound - gives then  $\alpha$ , $\beta$ -unsaturated compound after the elimination of a water molecule [7]. In the second mechanism the amine species are involved in the formation of imine intermediate with aldehyde compound. The obtained imine exhibits high basicity and thus it can deprotonate the active methylene compound. As a consequence,  $\alpha$ , $\beta$ -unsaturated compound is formed after the elimination of a water molecule from  $\beta$ -hydroxyl compound [8].

The increase in basicity of heterogeneous catalysts with basic nitrogen atoms may be obtained by using modifiers with a high number of basic centers. This solution has been used in [4,9], where 3-[2-(2aminoethylamino)ethylamino]propyl-tri-methoxysilane and [3-(2-aminoethylamino)propyl]trimethoxysilane were applied as the basic modifiers of mesoporous silica. The catalysts with a greater number of basic species may be also obtained via a two-step modification of silica, in which (3-chloropropyl)trimethoxysilane (CIPTMS) previously anchored on silica reacts with nitrogen containing compound possessing at least one amine group. The available amine group in the modifier has been used for the reaction with CIPTMS, which leads to formation of the C–N bond between the anchored chlorine precursor and the basic

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Scheme 1. The way of melamine anchoring into supports followed by CIPTMS modification.

modifier. This reaction was used for immobilization of modifiers with a greater number of amine species as melamine [1], piperazine [10] or biguanide [11] and was also used for the synthesis of catalysts modified with imine species, using imidazole and 1H-1,2,3-triazole [3] as the basic compounds.

The functionalization of mesoporous material with specific functional groups possessing basic nitrogen species together with components affecting their basicity strength, could lead to changes in the chemical behavior of the catalyst and thus its activity and selectivity. This concept was applied in the synthesis of mesoporous silica SBA-15 modified with amine together with Zr, Mo or Nb [9], niobiosilicates and cerium modified silicas based on SBA-15 or MCF structure modified with imidazole, triazole and aminotriazole active species [3], or in amino-grafted MCM-41 modified with Nb or Al together with [3-(2aminoethylamino)propyl] trimethoxysilane and 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane [12]. The results presented in the above mentioned papers showed, that the close neighborhood of metal species and basic nitrogen compounds has an impact on the activity of catalysts in the Knoevenagel condensation. Moreover, the presence of niobium, zirconium and molybdenum in silica skeleton increased the efficiency of modifiers loading, which is attractive for increasing catalytic activity.

There is no doubt that the appropriate selection of the modifiers is a key point for the design of effective catalysts. Thus, the choice of organic compounds with a high number of basic nitrogen species and a suitable metal as an additional component, which would increase the efficiency of basic modifier loading, lead to obtain appropriate basic properties addressed to the Knoevenagel condensation. Thus, in this work melamine was the basic modifier and niobium or cerium were the additional components used for mesoporous cellular foam (MCF) modification. The synergistic effect between metal species and aromatic heterocycles such as imidazole, triazole and aminotriazole have been reported in our recent paper [3]. It has been found that niobium Lewis acidity and redox properties of cerium played an important role in the basicity of synthesized samples. However, the specific nature of melamine due to a high number of heteroatoms in its heterocyclic ring and three available amine species [1] suggests that melamine can interact with metal species in a different manner than the above-described modifiers. It is well known that the basicity of aromatic amines can be determined by the presence of electron-donating or electron-withdrawing groups connected to the aromatic ring. The former ones increase the basicity of amine species, while the latter ones lead to the opposite phenomenon [13]. Thus, the presence of niobium and cerium in MCF close to the anchored melamine can affect the basicity strength of this basic modifier as a result of the transfer of electrons between melamine and metal species.

#### 2. Experimental

#### 2.1. Synthesis of silica support - MCF

The synthesis of MCF was performed according to the procedure described in [14]. The surfactant Pluronic P123 (16 g, Aldrich) was dissolved in 600 cm<sup>3</sup> of 0.7 M solution of HCl (35–37 %, POCH) upon vigorous stirring at 35–40 °C. Then, NH<sub>4</sub>F (0.1868 g, Aldrich) and 1,3,5-trimethylbenzene (16 g, Aldrich) were added together to the mixture.

After 1 h of gel stirring at the same temperature, tetraethoxysilane (34.108 g, Aldrich) was introduced. The mixture was then stirred at 35–40 °C for 20 h and heated in an oven at 100 °C under static conditions for 24 h. The solid product was filtered, washed with distilled water (1200 cm<sup>3</sup>) and dried at RT (room temperature). The template was removed by calcination at 550 °C for 8 h under static conditions with a temperature ramp of 1 °C min<sup>-1</sup>.

#### 2.2. Silica modification with niobium or cerium species

The MCF support was modified with niobium or cerium species by using impregnation method as in [15]. At first, niobium(V) ethoxide (Aldrich) or cerium(III) nitrate hexahydrate (Aldrich) was dissolved in dry methanol. The amount of metal precursor was chosen so that to achieve the Si/Nb or Ce molar ratio 14. The dissolved metal sources were then added to the dried silica (drying for 24 h at 100 °C), which was evaporated for 1 h at 80 °C before admission of metal salt solution. The obtained mixture was then stirred in a vacuum evaporator at 60 °C until the methanol was removed from the solid. Then the metalosilicates were dried at 110 °C for 18 h and calcined at 500 °C for 4 h with a temperature ramp of 3 °C min<sup>-1</sup>. The obtained samples are denoted as Nb/MCF-14 and Ce/MCF-14 (the number 14 is the Si/Nb or Ce molar ratio).

## 2.3. MCF, Nb/MCF-14 and Ce/MCF-14 modification with melamine followed by (3-chloropropyl)trimethoxysilane (ClPTMS) anchoring

The modification of the supports with (3-chloropropyl)trimethoxysilane (ClPTMS), as shown in Scheme 1, was made as follows. A portion of 1.3 g of silica or metalosilicate (dried overnight at 100 °C) was put into a glass flask. Then 40 cm<sup>3</sup> of dried toluene and 1.3 cm<sup>3</sup> of ClPTMS (Aldrich) were introduced. The obtained mixture was then stirred for 15 min at room temperature and then heated at 110 °C for 24 h. The solid product was then filtered, washed by 45 cm<sup>3</sup> of dried toluene and dried at 100 °C for 24 h.

The anchoring of melamine to the supports modified with ClPTMS was performed as described below and illustrated in Scheme 1. A portion of 1.81 g of melamine (Aldrich) and 2 cm<sup>3</sup> of triethylamine (added for neutralization of HCl formed during the solid modification) was introduced to the mixture containing 1.8 g of silica or metalosilicate and 40 cm<sup>3</sup> of dried toluene. The obtained mixture was then heated at 110 °C for 48 h. The solid was then filtered, washed with 33 cm<sup>3</sup> of dichloromethane and 33 cm<sup>3</sup> of methanol and finally dried at 100 °C for 24 h. The obtained samples are denoted as Mel/MCF, Mel/Nb/MCF-14 and Mel/Ce/MCF-14.

#### 2.4. Samples characterization

The obtained catalysts were characterized by nitrogen adsorption/ desorption, XRD, elemental analysis, UV–vis, XPS and thermogravimetric analysis.

 $N_2$  adsorption/desorption isotherms were measured using an ASAP 2020 instrument. The catalysts before the analysis were outgassed under vacuum at 120 °C for 10 h. The surface area was calculated by the BET method, while the pore volume and diameter were estimated according to the Broekhoff-de Boer method with the Frenkel-Halsey-Hills

#### approximation [16].

XRD patterns were obtained on a Bruker AXS D8 Advance apparatus using  $CuK_{\alpha}$  radiation ( $\gamma = 0.154$  nm), with a step of  $0.05^{\circ}$  in the wide-angle range.

Elemental analysis was carried out with Elemental Analyzer Vario EL III.

The UV-vis spectra in the range between 800-190 nm were recorded using a Varian-Cary 300 Scan UV-vis Spectrophotometer and Spectralon as a reference sample. Before measurements the solids were dried overnight at 100 °C.

X-ray photoelectron measurements (XPS) were performed on an Ultra High Vacuum (UHV) System (Specs, Germany) equipped with a monochromatic microfocused Al K $\alpha$  X-ray source (1486.6 eV). Binding energies were referenced to the Si 2p peak at 103.4 eV.

TGA measurements were made in air atmosphere using SETARAM SETSYS-12 apparatus in the temperature range 20–1000 °C with a temperature ramp of 5 °C min<sup>-1</sup>.

#### 2.5. Test reactions

#### 2.5.1. 2-propanol dehydration and dehydrogenation

The 2-propanol decomposition was performed using a microcatalytic pulse reactor ( $\emptyset$  6 mm) containing the catalyst bed (0.02 g). The reactor was connected to the column (5% Carbowax20 m) of an SRI 310 chromatograph. The granulated (0.5 <  $\emptyset$  < 1 mm) catalyst placed in the reactor was first activated at 350 °C for 2 h under nitrogen flow (40 cm<sup>3</sup> min<sup>-1</sup>). Then, the 3 µl pulses of 2-propanol (POCH) after introduction into the reactor were vaporized and passed through the catalyst bed under nitrogen flow, 65 cm<sup>3</sup> min<sup>-1</sup>. The reaction was performed in the temperature range between 150–300 °C. The products of the reaction were identified by GC equipped with a FID detector under nitrogen as a carrier gas.

#### 2.5.2. Knoevenagel condensation

All catalysts were tested in the Knoevenagel condensation carried out without any solvent (Scheme 2). A mixture of benzaldehyde (20 mmol, 2.12 g) (Aldrich) and malononitrile (20 mmol, 1.32 g) (Aldrich) together with 0.5 wt.% of the catalyst (preliminary dried overnight at 100 °C) was placed in a quartz reactor in an EasyMax system and heated at 60 °C upon vigorous stirring (200 rpm). The reactions were performed for 5, 15 and 30 min. Products were analyzed by a gas chromatograph (Thermo Scientific) equipped with 60 m VF-5 ms capillary column and a FID detector.

#### 3. Results and discussion

The idea of this work was the synthesis of strong basic catalysts with open structure active in the Knoevenagel condensation under mild reaction conditions. For this purpose, the mesoporous cellular foams were synthesized, modified with metal species (niobium or cerium) and melamine as the precursor of basic nitrogen species. MCF was used as the support because of its attractive structure, made of cells of size ca 35 nm connected by windows of size ca 20 nm. Such a construction of silica avoids diffusional problems during the reactions performed in liquid phase such as the Knoevenagel condensation. The choice of metal species for MCF modification was dictated by the possibility of their interaction with anchored basic modifier - melamine, which was used because of its high number of basic nitrogen atoms.

#### 3.1. Characterization of the materials

#### 3.1.1. Structure/texture properties of the supports

In this work three different supports were used for melamine loading, i.e. silica (MCF) and metalosilicates with niobium (Nb/MCF-14) or cerium species (Ce/MCF-14). The incorporation of metal species did not disrupt the structure of mesoporous cellular foam as shown in Fig. 1. The nitrogen adsorption/desorption isotherms of all supports can be described as type IV according to IPUAC classification [17]. All isotherms exhibit one hysteresis loop of type H1 at a relatively high pressure (p/p<sub>o</sub>), which is typical of mesoporous cellular foam [18]. The nitrogen adsorption allowed also the estimation of texture parameters of synthesized supports presented in Table 1. The surface area and pore volume decreased after niobium or cerium species incorporation into MCF, which confirmed the presence of both metals in MCF.

The XRD patterns shown in Fig. 2 suggest that niobium species did not form a crystalline niobium oxide on Nb/MCF-14 surface [3]. Most probably the formed Nb<sub>2</sub>O<sub>5</sub> was amorphous and thus it gave no signal in the XRD pattern of Nb/MCF-14. The presence of Nb<sub>2</sub>O<sub>5</sub> on the surface of Nb/MCF-14 was verified by the UV-vis and XP spectra shown in Figs. 3 and 4, respectively. The UV-vis spectrum of Nb/MCF-14 (Fig. 3) exhibited three bands, observed after spectrum deconvolution, at 217 nm, 253 nm and 310 nm. The first and the second bands are typical of tetra- and penta-coordinated niobium species, respectively [19,20]. The presence of both bands confirms the inclusion of niobium species into silica skeleton. This conclusion was verified by the XP spectrum of niobiosilicate, which displayed the BE of Nb  $3d_{5/2}$  at 207.5 eV (Fig. 4). This value is higher than that observed for  $Nb_2O_5$  (207.1 eV [21]), which further confirmed the niobium incorporation into silica matrix, as concluded on the basis of the UV-vis measurement. The UV-vis spectrum of Nb/MCF-14, among the bands typical of niobium species included into silica skeleton, showed furthermore the third, less intense, band at 310 nm assigned to extra-framework niobium [19]. To check if some niobium oxide is present in Nb/MCF-14, the XP spectra of oxygen were analyzed (Fig. 4). The deconvoluted O 1s spectrum, apart from the intensive band at 532.8 eV assigned to the oxygen in silanol species of MCF silica support [22], revealed an additional less intense component at 530.0 eV typical of the lattice oxygen in metal oxides [23].

In the case of XRD pattern of Ce/MCF-14 (Fig. 2) the reflexes typical of cerium oxide (structure of fluorite) were detected (JCPDS ICDD PDF Card – 00-043-1002). The CeO<sub>2</sub> crystals were of the size of 14 nm. The UV–vis spectrum of Ce/MCF-14 (Fig. 3), after its deconvolution, shows the two components at 247 nm and 302 nm, which are assigned to the electron charge transfer between oxygen and cerium species at +3 and +4 oxidation state, respectively [15,24]. The presence of cerium species in different oxidation states in Ce/MCF-14 was furthermore confirmed by the XPS Ce 3d spectrum (Fig. 4). The deconvoluted spectrum shows several components at 884.6 eV and 901.6 eV, which evidence the presence of Ce<sup>3+</sup> - O<sup>2-</sup>, and the bands at 881.7 eV, 887.6 eV, 898.7 eV, 905.5 eV and 917.1 eV typical of Ce<sup>4+</sup> - O<sup>2-</sup> [25,26]. The surface Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) ratio for Ce/MCF-14 was 0.41. The presence of cerium species at both oxidation states reaffirm the defected nature of cerium oxide loaded on Ce/MCF-14 surface. This observation



**Scheme 2.** The Knoevenagel condensation between benzaldehyde and malononitrile.

benzaldehyde

malononitrile

benzylidenemalononitrile



Fig. 1. The nitrogen adsorption/desorption isotherms of silica MCF and metalosilicate supports before and after melamine loading.

Table 1			
Texture/structure	parameters	of synthesized	samples

Catalyst	Surface area, m <sup>2</sup> /g	Pore volume <sup>a</sup> , cm <sup>3</sup> /g	Window diameter <sup>b</sup> , nm	Cell diameter <sup>c</sup> , nm
MCF	708 +/- 1.2	2.61	19.8	35.1
Ce/MCF-14	576 +/- 0.9	2.15	19.7	35.4
Nb/MCF-14	573 +/- 0.9	2.27	20.1	32.5
Mel/MCF	177 +/- 0.5	0.81	17.9	32.6
Mel/Ce/MCF-14	150 +/- 0.4	0.64	16.5	32.2
Mel/Nb/MCF-14	141 +/- 0.3	0.61	17.8	33.5

a,c – determined from adsorption branches of N<sub>2</sub> isotherms (BdB–FHH method).

<sup>b</sup> determined from desorption branches of N<sub>2</sub> isotherms (BdB–FHH method).



Fig. 2. The wide-angle XRD patterns of modified samples and melamine.

was moreover verified by the deconvoluted O 1s XP spectrum of Ce/MCF-14, which revealed the three components at 529.7 eV, 532.7 eV and 534.0 eV. The most intense component at 532.7 eV assigned to hydroxyl groups from silanol species in MCF, and the one at 529.7 eV typical of lattice oxygen in metal oxides were also observed for Nb/MCF-14, whereas the band at 534.0 eV was detected only in the spectrum of Ce/MCF-14. The latter band is attributed to the oxygen in defected metal oxides [27] and its presence confirmed that Ce/MCF-14 contained cerium species at +3 oxidation state. The number of surface oxygen vacancies in Ce/MCF-14 can be evaluated from the ratio of  $O_V/O_V + O_L$ , where  $O_V$  and  $O_L$  refer to  $O_2^{-1}$  in oxygen vacancies (V) or in the lattice (L). The surface ratio of  $O_V/O_V + O_L$  for Ce/MCF-14 was 0.80.

The differences in chemical behavior of niobium and cerium species loaded on MCF were investigated in 2-propanol dehydration and dehydrogenation (Table 2). The products formed in this reaction are the indicators of acidity or basicity of tested samples. 2-Propanol is transformed into propene on acidic active centers, whereas acetone is formed on basic active centers [28]. Diisopropyl ether appears if pairs of acid-base centers are present on the catalyst surface. Both, niobium and cerium species loaded into MCF catalyzed the 2-propanol conversion, however Nb/MCF-14 showed higher activity than Ce/MCF-14. The niobium modified silica catalyzed the 2-propanol conversion only to propene, while Ce/MCF-14 exhibited the selectivity also to other products such as acetone and diisopropyl ether. The obtained results proved that the surface of both metalosilicates shows different properties. The surface of Nb/MCF-14 is acidic, while that of Ce/MCF-14 is more basic.

#### 3.1.2. The impact of melamine loaded on the supports

The anchoring of melamine caused significant changes in the shape of nitrogen adsorption isotherms, as shown in Fig. 1. The volume of adsorbed nitrogen decreased significantly for the melamine modified samples, compared to its volume adsorbed on the corresponding supports. The hysteresis loop of the samples modified with melamine is still of type H1. The calculated textural parameters of the materials modified with melamine species (Table 1) show a significant reduction of surface area and pore volume in comparison to the supports without modification. This confirms the anchoring of a modifier to the surfaces of MCF, Nb/MCF-14 and Ce/MCF-14. Moreover, the anchoring of melamine caused a decrease in the windows and cells diameter in the



Fig. 3. The UV-vis spectra of modified MCF materials and melamine.

obtained samples with exception of Mel/Nb/MCF-14. In this sample the cells size increased after melamine loading.

The XRD patterns of melamine modified samples (Fig. 2) confirm the modifier inclusion into the supports by the presence of the reflexes characteristic of melamine. The XRD pattern of Mel/Nb/MCF-14 did not show the reflexes characteristic of niobium oxide. In the XRD pattern of Mel/Ce/MCF-14 the reflexes typical of CeO<sub>2</sub> were still visible. Nevertheless, they were overlapped by the reflexes characteristic of melamine, thus it was impossible to calculate the crystals size of cerium oxide in this material.

The anchoring of melamine was also proven by the UV–vis (Fig. 3) and XPS measurements (Fig. 5). The UV–vis spectrum of melamine showed a band at 203 nm. This band was well resolved in the spectra of Mel/MCF (211 nm) and Mel/Ce/MCF-14 (214 nm), while for Mel/Nb/MCF-14 it could be overlapped by the band characteristic of niobium in tetrahedral coordination (210 nm). The presence of the band typical of free melamine implies that part of this substance used for the supports modification was not reacted with the previously anchored ClPTMS, as shown in Scheme 1, but it is hydrogen bonded to the surface of supports. That could explain the appearance of the reflexes characteristic of melamine in the XRD patterns of the samples modified with this substance. Interestingly, in the UV–vis spectrum of Mel/MCF, an additional band at 237 nm was detected (Fig. 3). The presence of this band could be assigned to the anchoring of melamine by chlorine precursor (ClPTMS) to MCF support as presented in Scheme 1. This band in the

spectra of Mel/Nb/MCF-14 and Mel/Ce/MCF-14 might be covered by the band assigned to niobium in pentahedral coordination (238 nm) for Mel/Nb/MCF-14 or by the band characteristic of the electron charge transfer between oxygen and cerium in +3(242 nm) in the case of Mel/ Ce/MCF-14. The formation of the bond between chlorine precursor and melamine might be verified by N 1s XP spectra shown in Fig. 5. The spectra after deconvolution showed the two components. The first of them at ca 399.4 eV is typical of nitrogen connected to carbon (C=N) in heterocyclic ring, whereas the second band at 397.0 eV corresponds to the nitrogen in amine species [29]. These components in the N 1s XP spectrum of melamine show similar intensities because of the symmetric structure of this substance [29]. In the XP spectra of the samples modified with melamine the intensity of the first band was lower, especially in the case of modified metalosilicates. The probable reason is that one of the amine groups in melamine formed bond with ClPTMS anchored to the supports. As a result, the electrons from the C=N bond in melamine were delocalized within the whole modifier, i.e. melamine and propyl precursor from previously anchored ClPTMS (Scheme 1). Moreover, the band assigned to C=N was shifted towards higher BE in the XP spectra of Mel/Nb/MCF-14 and Mel/Ce/MCF-14, which implies the interaction between niobium or cerium species with anchored melamine.

As mentioned above, the UV-vis spectrum of Mel/Nb/MCF-14 exhibited the bands typical of metal included into silica skeleton, i.e. tetra- (210 nm) and penta-coordinated (238 nm) niobium (Fig. 3). The



Fig. 4. The Nb 3d, Ce 3d and O 1s XP spectra of metalosilicates.

# Table 2 The results of 2-propanol dehydration and dehydrogenation performed at 300 °C.

Sample	Conversion 2-PrOH, %	Selectivity, %		
		Acetone	Propene	Ether
MCF	Traces	0	100	0
Ce/MCF-14	4	15	84	1
Nb/MCF-14	68	0	100	0

intensities of these bands were different than those observed in the spectrum of Nb/MCF-14. The intensity of the first band was lower, while that of the second one was higher. It implies that both bands might be overlapped by the bands typical of melamine, as suggested above. Apart from the differences in intensity of the bands at 210 nm and 238 nm, they occupied different positions. Both bands were shifted to the blue region of UV-vis in comparison to those in the spectrum of Nb/MCF-14. Additionally, the UV-vis spectrum of Mel/Nb/MCF-14 showed the band with a maximum at 280 nm and with a long tail up to 330 nm typical of niobium in extra-framework position. This band was more intense than that observed in the spectrum of Nb/MCF-14. It seems that Nb/MCF-14 modification with melamine followed by ClPTMS anchoring caused the extraction of a part of niobium from the silica skeleton. As a result, greater amount of Nb<sub>2</sub>O<sub>5</sub> was formed on the surface of Mel/Nb/MCF-14. This phenomenon could cause the increase in the cells diameter in Mel/Nb/MCF-14 (Table 1). The differences in the intensity and position of both bands as well as detection of the new band characteristic of octahedral coordinated niobium at UV-vis spectrum of Mel/Nb/MCF-14 proved a strong interaction between melamine and niobium species in the niobiosilicate support.

The impact of melamine on niobium species in Nb/MCF-14 is furthermore manifested in the XP spectra shown in Fig. 6. As concerns the Nb 3d XP spectrum of Mel/Nb/MCF-14, the detected BE of Nb  $3d_{5/2}$  was 207.3 eV. This value is lower than that observed for Nb/MCF-14 (207.5 eV) and is closer to that observed for bulk Nb<sub>2</sub>O<sub>5</sub> (207.1 eV) in which niobium is in extra-framework position. The presence of niobium oxide in Mel/Nb/MCF-14 was evidenced by the O 1s XP spectrum, which showed the component at 530.2 eV typical of lattice oxygen. The presence of melamine in niobiosilicate caused also a shift of BE of O 1s towards higher value (530.2 eV in Mel/Nb/MCF-14 from 530.0 eV in Nb/MCF-14), which might be caused by the transfer of electrons between melamine and niobium oxide localized on the surface of Mel/Nb/MCF-14.

The influence of melamine on metal species was also observed for Mel/Ce/MCF-14. The UV–vis spectrum of this sample, besides the band typical of melamine, showed the bands assigned to the electron charge transfer between oxygen and cerium in +3 (242 nm) and +4 oxidation state (300 nm) (Fig. 3). The positions of both bands were blue shifted in comparison to the spectrum of Ce/MCF-14. Interestingly, the band typical of Ce<sup>3+</sup> - O<sup>2-</sup> was better resolved in the spectrum of Mel/Ce/MCF-14 than in the Ce/MCF-14. However, this band might be overlapped by the band characteristic of melamine anchored to the support by ClPTMS precursor. Nevertheless, the visible differences in the position and intensity of the bands characteristic of both cerium species indicated the interaction between melamine and cerium cations, similarly as was observed for niobium modified sample.

The differences appeared on the surface of Ce/MCF-14 after melamine anchoring were also certified by XPS measurement. The Ce 3d XP spectrum of Mel/Ce/MCF-14 (Fig. 6) exhibited the components assigned to Ce<sup>3+</sup> (883.8 eV and 901.5 eV) and Ce<sup>4+</sup> (882.3 eV, 886.7 eV, 898.6 eV, 906.7 eV and 917.4 eV) bonded with O<sup>2-</sup> as for Ce/MCF-14. The positions and intensities of the listed components were changed with respect to those in the XP spectrum of Ce/MCF-14 (Fig. 4). A significant difference in the band's area was observed for the components at 883.8 eV and 917.4 eV characteristic of the electron charge



Fig. 5. The N 1s XP spectra of melamine modified samples.



Fig. 6. The XP spectra of metalosilicate supports after melamine loading.

transfer between  $O^{2-}$  and  $Ce^{3+}$  or  $Ce^{4+}$ , respectively. The intensity of the first band decreased, while the second one increased in comparison to those in the spectrum of Ce/MCF-14. As a consequence, the surface ratio of  $Ce^{3+}/Ce^{3+} + Ce^{4+}$  decreased by 47% for Mel/Ce/MCF-14 (from 0.41 to 0.22). Consequently, the ratio of oxygen vacancies on the surface of Mel/Ce/MCF-14 also decreased from 0.80 to 0.50. Furthermore, the position of the bands typical of oxygen in oxygen vacancies (534.2 eV) and lattice oxygen in metal oxides (530.2 eV) was shifted to higher BE (from 534.0 eV and 529.7 eV for Ce/MCF-14, respectively) after melamine loading into Ce/MCF-14. A similar phenomenon was observed for Mel/Nb/MCF-14. The differences which appeared for Mel/ Ce/MCF-14 indicated that melamine played a role of an electronwithdrawing modifier, which caused the change in oxidation state of surface cerium species from +3 to +4 (XPS analyses only the surface of the materials). It is well known that cerium cations in defected cerium oxide can exist in two forms, in a more stable tetravalent state and trivalent state having the deficiency of positive charge compensated by oxygen vacancies [30]. Experimental studies have shown that the highly mobile lattice oxygen available at the surface of ceria together with the oxygen vacancies are responsible for the transfer of electrons in the fluorite structure of ceria [31].  $Ce^{3+}$  has one electron in the 4f orbital and this electron is mobile [32]. The close neighborhood of melamine with resonate structure of heterocyclic ring bonded with three amine species to cerium oxide in Mel/Ce/MCF-14 caused the migration of mobile electrons from the surface of ceria to melamine. As a result the very unstable  $Ce^{3+}$  cations in Mel/Ce/MCF-14 were immediately transformed into  $Ce^{4+}$  state. At the same time the number of oxygen vacancies and lattice oxygen on the surface of Mel/Ce/MCF-14 was changed.

#### 3.1.3. The efficiency of melamine loading and its stability

The efficiency of melamine loading can be estimated from the nitrogen content. The weight percentage of nitrogen and moles of anchored melamine calculated from the elemental analysis data are given in Table 3. It is evidenced that the effectiveness of melamine anchoring depends on the composition of the support used. The presence of niobium or cerium in MCF enhanced (more than twice) the modifier loading. It can be caused by the strong interaction between metal species and melamine inferred from the UV–vis and XP spectra (Figs. 3–6). The increase in modifier loading is higher for Nb/MCF-14 than Ce/MCF-14 support. Similar results were obtained in our earlier paper in which the chemical interaction between niobium species and imidazole, triazole or aminopropyl species was proved [3]. A similar interaction can occur with melamine species and thus the visible increase in efficiency of melamine loading in Nb/MCF-14 support was obtained.

The metal species in MCF also have an important effect on the stability of anchored melamine, which is particularly significant for processes performed in liquid phase, such as the Knoevenagel condensation. The stability of anchored melamine was estimated by thermogravimetric analysis whose results are shown in Fig. 7. The TG curves revealed two mass loss events between 270–390 °C and 400–600 °C. The first greater mass loss could be assigned to the decomposition of melamine that did not react with anchored CIPTMS. The chlorine precursor decomposed from MCF and NbMCF-14 at temperature below 300 °C [14]. Melamine melts and decomposes at 347 °C,

#### Table 3

The melamine loading on silica and metalosilicate supports (based on elemental analysis).

Catalyst	N, wt.%	Melamine, mmol/g
Mel/MCF	13.1	2.2
Mel/Ce/MCF-14	41.2	4.9
Mel/Nb/MCF -14	44.2	5.3

however it undergoes sublimation at temperatures below its melting point [33]. The DTG curves presented the maxima of the first mass loss at 324 °C for Mel/MCF, 329 °C for Mel/Ce/MCF-14 and 335 °C for Mel/ Nb/MCF-14. These temperatures are close to the melting point of melamine, thus they could be correlated with the sublimation of unreacted form of this modifier. The second less intense mass loss observed in the DTG curves has its maximum at 476 °C for Mel/Ce/MCF-14 and at 556 °C for Mel/Nb/MCF-14, while for Mel/MCF a broad maximum corresponding to mass loss was detected. This mass loss might be linked to the decomposition of melamine anchored *via* a propyl chain of ClPTMS to the supports (Scheme 1). The formed chemical bonding between these two compounds could increase the melamine stability and thus could be responsible for the shift of the temperature of its decomposition to the higher value.

The temperature of the maximum that corresponds to the decomposition of melamine is an indicator of the modifier stability. It is visible that melamine was more stable on the sample containing niobium than on that with cerium species. The temperature of melamine decomposition was higher by 6 °C for the first mass loss (329 °C in comparison to 335 °C) and by 80 °C for the second mass loss (476 °C compared to 556 °C). The visible difference between Mel/Ce/MCF-14 and Mel/Nb/ MCF-14 might be caused by the change in the oxidation state of cerium species in Mel/Ce/MCF-14 after melamine anchoring. A similar phenomenon of decreasing stability of anchored basic modifier in cerium modified silicas in comparison to niobiosilicates was observed for the samples modified with imidazole species [3].

#### 3.2. Results of the Knoevenagel condensation

It has been already reported that the Knoevenagel condensation between aldehydes and active methylenes proceeds efficiently in the presence of catalysts which exhibit base or acid-base properties [9]. Thus, the synthesis of catalysts containingmelamine, as a basic modifier, and different supports to which it was anchored, such as MCF, Nb/ MCF-14 and Ce/MCF-14, seems to be the appropriate. Melamine contains a high number of basic nitrogen species, which could play a role of active sites in the Knoevenagel condensation, while the used supports exhibit different properties (acid or basic one) and thus they can affect the efficiency of melamine loading and its basicity strength. The performed reactions between benzaldehyde and malononitrile, illustrated in Scheme 2, allowed to support some conclusions drawn from the structural/textural characterization and chemical composition of the synthesized samples. Moreover, the above reactions provided the information that helped explain the differences in the strength of basicity of melamine anchored to the silica and metalosilicates.

The results of the Knoevenagel condensation between benzaldehyde and malononitrile in the presence of the synthesized samples are given in Fig. 8. It is important to note that the selectivity of the reaction was 100% to the main product, benzylidenemalononitrile. It evidenced that anchoring of melamine to MCF, Nb/MCF-14 and Ce/MCF-14 caused a significant increase in the activity of benzaldehyde conversion in comparison to the activity of silica and metalosilicate supports. It is worth noting that melamine was not detected in the reaction mixtures of Mel/MCF, Mel/Nb/MCF-14 and Mel/Ce/MCF-14 by GC-MS. It implies that melamine did not leach from these catalysts during the Knoevenagel condensation. In order to check if the reaction was not limited by external or internal diffusion, the additional reactions were performed in which a mixture of benzaldehyde and malononitrile with Mel/Ce/MCF-14 was stirred at 100 rpm, 200 rpm and 400 rpm. The obtained results clearly demonstrated that the reactions performed over the modified metalosilicate were not controlled by external or internal diffusion because for each reaction a similar benzaldehyde conversion was obtained, ca 87%. Interestingly, the reaction performed over free melamine (2 mg) was not so efficient as for samples modified with this substance. Thus, the role of the support in increasing the basicity strength of melamine was evidenced. This occurrence might be



Fig. 7. The thermogravimetry analysis of melamine modified samples.



**Fig. 8.** The results of the Knoevenagel condensation between benzaldehyde and malononitrile performed for 15 min in the presence of synthesized samples and melamine. The reaction mixture was stirred at 200 rpm with exception of \* - 100 rpm and # - 400 rpm.

correlated with the formation of secondary amine species in the melamine modified materials. The non-anchored melamine has only primary amine species and tertiary amine within its heterocyclic ring, which are less basic than secondary amine [34]. Consequently, the presence of secondary amine groups in melamine anchored to the supports raised the benzaldehyde conversion in comparison to the homogeneous melamine system.

From among the catalysts tested, the highest conversion of benzaldehyde equal to 87.0% was achieved over Mel/Ce/MCF-14. This phenomenon could be due to a higher number of melamine anchored to metalosilicates than to Mel/MCF as shown in Table 3. However, the differences between the benzaldehyde conversion achieved over Mel/ Ce/MCF-14 and Mel/Nb/MCF-14 suggest that the higher activity of the former sample might be caused by the electron donation to melamine by defected cerium oxide in Mel/Ce/MCF-14 as deduced from the Ce 3d and O 1s XP spectra (Fig. 6). It is well known that the electron donating groups increase the basicity of aromatic amines due to displacement of negative charge on the carbon connected to nitrogen in amine group. Consequently, the lone pair of electrons placed in the nitrogen atom of amine species is more reactive [13] as visible for Mel/Ce/MCF-14. Moreover, the ceria in Mel/Ce/MCF-14 still exhibit defected nature as confirmed by the XP spectra (Fig. 6), in which basic mobile oxygen could participate in the reaction besides melamine. The basicity of Ce/ MCF-14 support was confirmed by 2-propanol dehydration and dehydrogenation (Table 2). In contrast, the acidic niobiosilicate (as confirmed by 2-propanol conversion (Table 2)) did not promote the condensation between benzaldehyde and malononitrile as ceria did in Mel/ Ce/MCF-14. This might be caused by different nature of niobium species loaded into MCF support, which are at +5 oxidation state, the most stable state of niobium [35]. Thus, niobium included into MCF and niobium oxide on the surface of Mel/Nb/MCF-14 could not play the role of electron donating species as it did ceria in Mel/Ce/MCF-14.

The activity of samples modified with melamine was moreover investigated at different reaction time (Fig. 9). The conversion of benzaldehyde increased gradually with increasing reaction times for all investigated catalysts. Mel/Ce/MCF-14 showed the highest activity among the tested samples in each reaction time due to its stronger basicity.

As the amount of anchored melamine was different, depending on the type of support used for modifier anchoring (Table 3), a comparison of the activities of Mel/MCF, Mel/Ce/MCF-14 and Mel/Nb/MCF-14 was made on the basis of both benzaldehyde conversion and TOF (turnover frequency) calculated for the reactions performed for 5 min (Fig. 9). Melamine anchored to the metalosilicates was less active than when it was loaded into MCF. However, if melamine was anchored to Ce/MCF-14, its activity increased relative to that of melamine anchored to Nb/



Fig. 9. The influence of reaction time on benzaldehyde conversion performed over synthesized catalysts. Activity of catalysts expressed as turnover frequency (TOF) calculated as mole of benzaldehyde converted on one mole of anchored melamine (mole/mole\*min) for reactions performed for 5 min.

MCF-14 support. This observation confirmed the positive impact of defected cerium oxide in Mel/Ce/MCF-14, leading to increase in the basicity strength of melamine species as postulated above.

In order to investigate the recyclability of the obtained materials modified with melamine species, the catalysts after the Knoevenagel condensation were separated from the reaction mixture, washed with acetone  $(3 \times 5 \text{ cm}^3)$ , dried at 100 °C (overnight) and used in the next reaction runs. The activity of synthesized materials decreased in the next reaction cycle. In the 3rd reaction run, the obtained benzaldehyde conversion for all tested materials was of ca 50%. As melamine was not leached to the solution (it was not detected in the reaction mixture by GC-MS), the decrease in the catalysts activity could be due to the blockage of the active sites by chemisorption of reaction substrates or a product (the catalysts changed their color from white to brown) and by the loss of mass of the catalysts used for the next reaction cycle during the catalyst separation from the reaction mixture.

#### 4. Conclusions

Mesoporous cellular foams modified with niobium or cerium species and functionalized with melamine followed by (3-chloropropyl)trimethoxysilane anchoring were used as efficient catalysts for the Knoevenagel condensation between benzaldehyde and malononitrile. The efficiency of melamine loading was higher when MCF was doped with metal species. Moreover, cerium and niobium species loaded into MCF facilitate the reaction between melamine and chlorine precursor (CIPTMS), which was previously anchored on the surface of metalosilicates. Consequently, the basic modifier was better stabilized in Mel/ Nb/MCF-14 and Mel/Ce/MCF-14 than in Mel/MCF. The activity of melamine in the Knoevenagel condensation increased when it was anchored to silica and metalosilicate supports as a result of the formation of secondary amine species, which are more basic than primary and tertiary amines. The presence of defected ceria in Mel/Ce/MCF-14 increased the basicity of anchored melamine as a result of the electron donating effect of ceria. Therefore, the amine species in melamine in Mel/Ce/MCF-14 catalyzed the Knoevenagel condensation more

efficiently than in Mel/Nb/MCF-14 and Mel/MCF. Niobium species in Mel/Nb/MCF-14 did not donate amine species in anchored melamine as ceria did in Mel/Ce/MCF-14 because of different properties of niobium, which does not change its oxidation state as easily as defected ceria.

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