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Application of ToF-SIMS to the study of surfactant removal from AuNbMCM-41 and AuMCM-41 materials

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ABSTRACT

This work is focused on the application of time-of-flight secondary ion mass spectrometry (ToF-SIMS) in investigation of the surfactant removal process from AuNbMCM-41 and AuMCM-41 catalysts (MCM-41 “*Mobil Composition of Matter*”, ordered mesoporous materials discovered by Mobil R&D Corporation). The samples investigated were prepared by co-precipitation in the presence of a cationic surfactant (cetyltrimethylammonium chloride—$CH_3(CH_2)_{15}N(Cl)(CH_3)_3$) and the incipient wetness impregnation methods. The results obtained showed that the time-of-flight secondary ion mass spectrometry appears to be a very useful tool for the investigation of the residual organic template on the surface of ordered mesoporous materials of MCM-41 type. It was demonstrated that the calcination of AuNbMCM-41 and AuMCM-41 catalysts at 550 °C caused a complete removal of the surfactant from the surface of the material investigated. Moreover, it was shown that the use of bismuth liquid metal ion gun in ToF-SIMS experiments permitted obtaining higher emission intensity (more than one order of magnitude when compared to the Ga^+ primary ion source) of secondary ions originating from the surfactant molecules and may facilitate an interpretation of the results obtained.

1. Introduction

MCM-41 materials with hexagonal arrangement of parallel mesopores belong to M41S family of mesoporous molecular sieves discovered in 1992 [1]. They have promising applications in adsorption, ion exchange and catalysis (e.g., acid catalysis, liquid phase redox catalysis). Moreover, they are attractive as host molecules for various guests (e.g., drugs). MCM-41 materials exhibit extremely high surface areas (>1000 $m^2\,g^{-1}$) and large, but well defined, pore sizes in the range of 2.0–30 nm. They are synthesized through a templated mechanism employing ammonium surfactants (cetyltrimethylammonium chloride or bromide). At the right concentration, the ammonium surfactants form lyotropic liquid crystals with hexagonal mesophases, after the removal of surfactant by calcination, the mesoporous materials retain the same geometries. Originally MCM-41 materials were synthesized in the siliceous form, but the composition can be modified by the introduction various elements together with siliceous into the framework of MCM-41 molecular sieves, for instant aluminum, vanadium, niobium, etc., changing the physico-chemical properties of the material.

The total removal of cationic surfactant used in the synthesis of MCM-41 mesoporous molecular sieves is a very important task. For further catalytic application of such materials it is essential to know if the residual fragments of partially decomposed template remain on the surface of metalosilicate samples, which can hold the surfactant more strongly than silicate MCM-41 [2]. The use of, e.g., IR, NMR, ESR or TGA techniques allows us to estimate the presence of organic fragments in the bulk materials [1–3]. However, for catalysis it is significant to know whether the organic molecules are on the catalyst surface. Therefore, in this work we propose the application of the time-of-flight secondary ion mass spectrometry (ToF-SIMS) for this purpose.

ToF-SIMS is widely used in the studies of different groups of solid materials, including biological samples, medicines, polymers and materials used in electronic industry [4–7]. However, secondary ion mass spectrometry can also be very useful in characterization of the catalyst surfaces [8–10]. In the studies of catalysts ToF-SIMS permits: determination of chemical composition of the catalyst surface including identification of impurities, investigation of the distribution of metal or other catalyst components on the sample surface, investigation of the nature of interactions between the metallic phase and the support, comparison of a metal oxidation degree after catalyst treatment in various conditions (temperature, atmosphere, etc.), study of catalyst deactivation processes, in such a case changes

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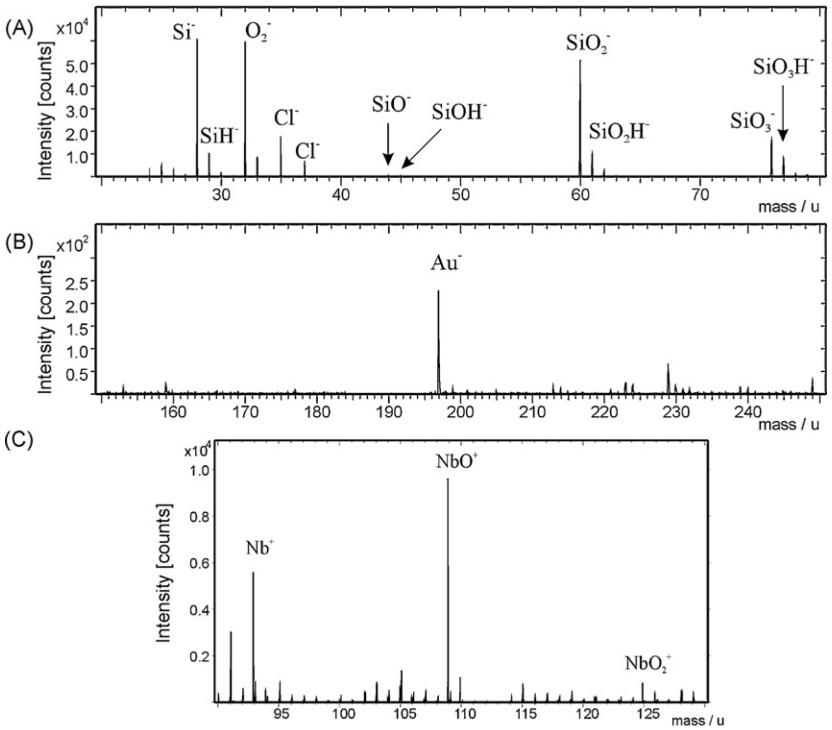

Fig. 1. Fragments of negative (A and B) and positive (C) ion mass spectrum of calcined AuNbMCM-41 catalyst prepared by the co-precipitation method.

in the composition of the upper layer of the investigated surface (formation of new compounds, increase in the quantity of various contaminants and catalyst poisons) can be determined [7,11].

Moreover, it appears that the secondary ion mass spectrometry permits also determination of the presence of organic precursors of catalysts on the surface analyzed and to investigate the process of their decomposition. It can be realized owing to the unique possibilities of ToF-SIMS, among others a possibility of obtaining not only elemental but also molecular information from 1 to 3 uppermost layers of the surface studied with high sensitivity.

The principles of the time-of-flight secondary ion mass spectrometry were presented in several works [12–14] and they will not be discussed here. However, it should be mentioned that a fast development of this technique offers a possibility to gain richer information from the surface analyzed as a result of the use of new primary ion guns (Bi_n, Au_n, C_{60}, SF_5, etc.). It is generally known that during ToF-SIMS measurements performed with using cluster ion sources apart from higher sensitivity and lower fragmentation some problems related to the large spot size of the cluster ion beam occur. It appears that only cluster ion sources (such as Bi_n, Au_n)

Table 1
Selected emission intensity ratios obtained from secondary ion mass spectra of AuNbMCM-41 catalyst prepared by the incipient wetness impregnation (IMP) and the co-precipitation (COP) methods.

Emission intensity ratio	AuNbMCM-41		
	IMP calc.	COP as prepared	COP calc.
$SiOH^-/SiO^-$	1.4	4.6	1.2
SiO_2H^-/SiO_2^-	0.21	0.56	0.20
SiO_3H^-/SiO_3^-	0.54	1.74	0.52
SiO_3^-/SiO_2^-	0.39	0.22	0.40
SiO^+/Si^+	0.032	0.002	0.037
NbO^+/Nb^+	1.16	0.74	1.26
NbO_2^+/Nb^+	0.10	0.04	0.11

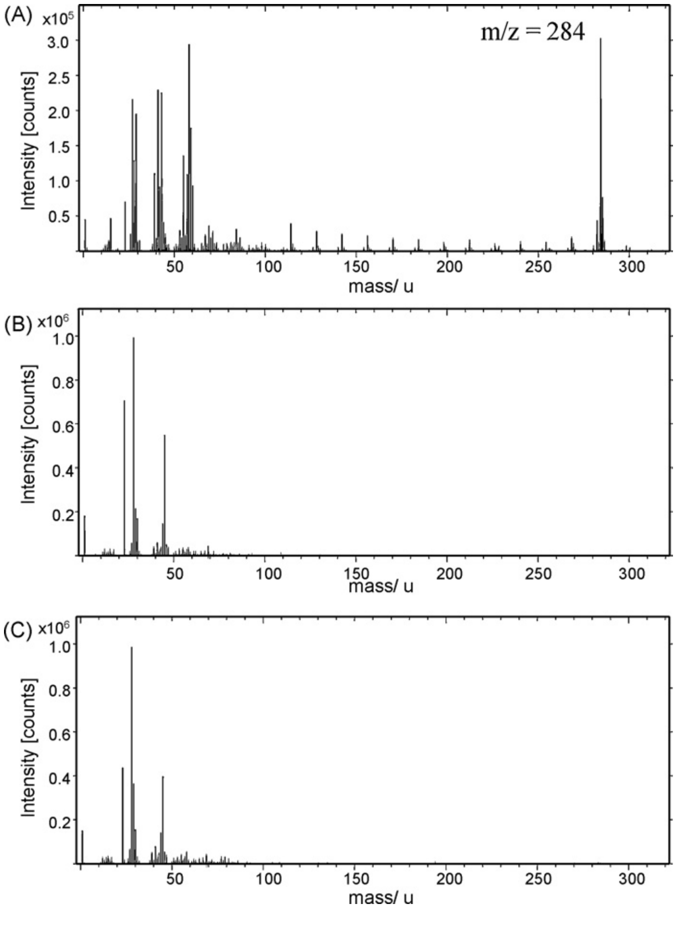

Fig. 2. Secondary ion mass spectra collected from the surface of AuNbMCM-41 catalyst: (A) as made, (B) calcined samples prepared by the co-precipitation method and (C) calcined material prepared by the incipient wetness impregnation method.

Table 2
Intensity of selected ions corresponded to the presence of the surfactant obtained from the mass spectra (performed using Ga^+ and Bi_3^+ primary ion beams) of as made AuNb-MCM-41 catalyst prepared by the co-precipitation method.

Type of ion	Intensity [counts]	
	Ga^+ beam	Bi_3^+ beam
Surfactant molecule—Cl ($m/z = 284$)	270173	3315061
$C_{16}H_{34}^+$ ($m/z = 226$)	5833	68930
$C_{12}H_{26}^+$ ($m/z = 170$)	11164	137754

allow to combine high lateral resolution with high cluster current (in fact, an application of C_{60}^+ primary ions made it possible to obtain the best sensitivity and lowest fragmentation during the experiments, but the large spot size of the primary ion beam caused that such a kind of clusters was not suitable for surface imaging). The literature data shows that the use of the cluster bismuth ion gun gives a possibility to achieve higher emission intensity of secondary ions coming from the surface of the sample investigated than Au_n primary ion source and guarantees an easy operation of the instrument connected with satisfactory lifetime and stability of cluster ion beam [7]. Owing to that more data concerning the distribution and transformation of complex molecules on the surface studied can be obtained.

The most important drawbacks of ToF-SIMS in the investigations of heterogeneous catalysts are matrix effect, fragmentation reactions and quantification problems. In spite of the fact that in some cases a comparison of the emission intensity of selected signals originating from different catalysts (after spectra normalization) enables obtaining semi-quantitative information from the surface of the material investigated, it is usually impossible to compare data acquired in the measurements of the catalysts supported on different carriers (i.e., Al_2O_3, SiO_2, molecular sieves, etc.). Moreover, it should be mentioned that the quality of ToF-SIMS images depends not only on the kind and parameters of primary ion guns or the operation mode of the mass spectrometer but is also connected with the properties of the material investigated and sample topography. Due to the fact that a lot of supported catalysts are powders it appeared that initial pressing them into the pellets makes it possible to achieve richer information from the surface investigated (much better mass resolution, higher emission intensity of secondary ions).

This work is focused on the studies of the process of surfactant removal from AuNbMCM-41 and AuMCM-41 materials using the time-of-flight secondary ion mass spectrometry. In this paper the possibilities of ToF-SIMS in the analysis of decomposition process of catalyst organic precursors are discussed and the performance of two different (gallium and bismuth) primary ion sources in such investigation is compared.

2. Experimental

2.1. Samples preparation

MCM-41 and Nb-containing MCM-41 mesoporous molecular sieves were synthesized according to the procedure described in Ref. [1] and modified with gold according to Refs. [15,16]. The Au/MCM-41 and Au/NbMCM-41 catalysts (with gold loading of 1 wt%) were prepared by incipient wetness impregnation of the support with $HAuCl_4$ (Johnson Matthey) (IMP). The amount of solution used was chosen in such a way that the liquid filled up only the pores of the mesoporous support. After this impregnation, the catalysts were dried at 100 °C for 5 h and calcined at 550 °C for 3 h in air. The alternative, direct synthesis of AuMCM-41 and AuNbMCM-41 (COP) was performed in the same manner as in the previous case. The only difference was the admission of $HAuCl_4$ and niobium oxalate—Companhia Brasileira de Metalurgia e Mineração (in the case of the sample containing Nb) as the sources of gold and niobium, respectively, into the gel containing sodium silicate (Si source-Aldrich) and the template (CTACl – cetyltrimethylammonium chloride – $CH_3(CH_2)_{15}N(Cl)(CH_3)_3$ – Aldrich). The Si/Au atomic ratio was 256 (corresponding to 1 wt% of Au).

2.2. Instrumental

ToF-SIMS measurements were performed using an ION-TOF GmbH (Münster, Germany) instrument (TOF-SIMS IV) equipped with 25 kV pulsed liquid metal Ga^+ and cluster bismuth (Bi_3^+) primary ion guns in the static mode (primary ion dose not higher than 10^{13} ions/cm^2). Both primary ion sources worked in the same conditions with the exception of primary ion current which varied from 1 pA in the case of Ga^+ to about 0.4 pA for Bi_3^+. To obtain the plain catalyst surface, the powder samples were pressed into pellets before the measurements. The pellets were attached to the sample holder using a double-sided tape. For each sample, three spectra and images were collected (from different areas). The analyzed area corresponded to a square ranging from 500 μm × 500 μm to 200 μm × 200 μm. A pulsed electron flood gun was used for the charge compensation.

3. Results and discussion

The investigation presented in this work is a continuation of our studies of gold catalyst containing MCM-41 and NbMCM-41 mesoporous molecular sieves described in Refs. [15,16]. In the previous cases the samples were characterized among other techniques by XRD, FTIR, N_2 adsorption/desorption, TEM and DTA/DTG methods. Moreover, catalytic activity tests (in acetonylacetone cyclization/dehydration, NO reduction with propene and methanol

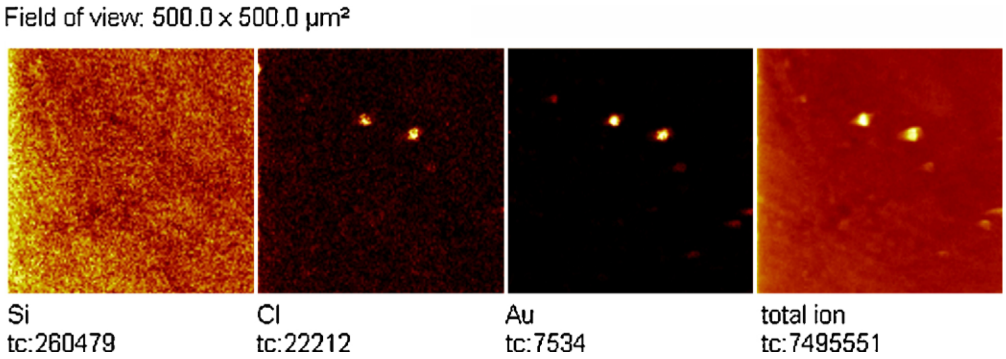

Fig. 3. ToF-SIMS images of a distribution of selected negative ions on the surface of AuMCM-41 catalyst prepared by the incipient wetness impregnation method. Bright color indicates investigated ions.

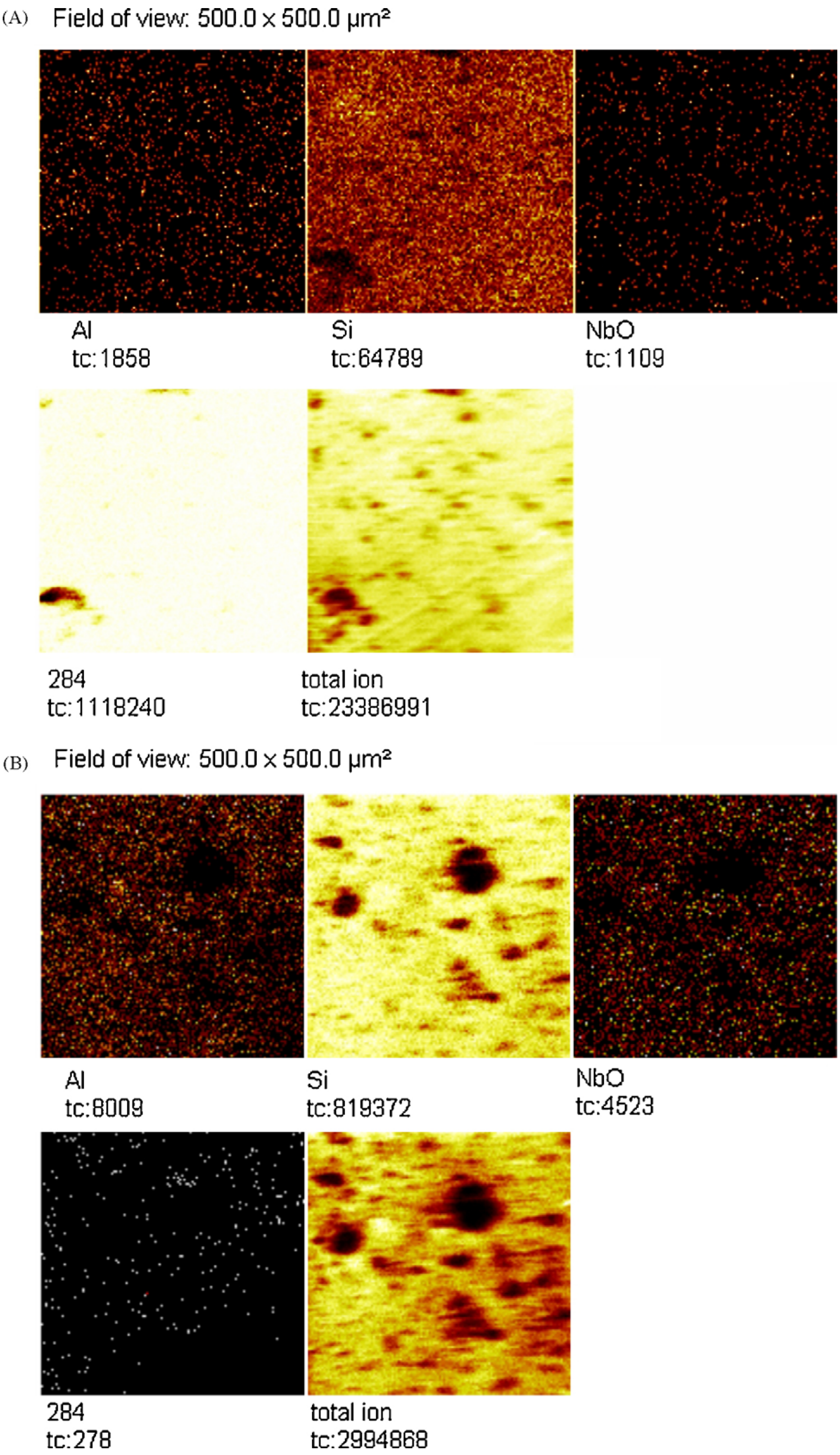

Fig. 4. ToF-SIMS images of a distribution of selected positive ions on the surface of (A) as made and (B) calcined AuNbMCM-41 catalyst prepared by the co-precipitation methods. Bright color indicates investigated ions.

oxidation reactions) were conducted. This publication is devoted to the surface investigation performed by the time-of-flight secondary ion mass spectrometry which gives new potential in the characterization of catalytic systems.

The secondary ion mass spectra collected from the surface of AuMCM-41 and AuNbMCM-41 catalysts show ions originating from molecular sieves such as Si^-, SiH^-, SiO^-, $SiOH^-$, SiO_2^-, SiO_2H^-, SiO_3^- and SiO_3H^- (Fig. 1A). Moreover, the signals corresponding to the presence of chlorine isotopes (at $m/z = 35$ and 37) are observed. The peak at $m/z = 197$ (Fig. 1B) confirms the introduction of gold onto the surface analyzed. In contrast to the results of ToF-SIMS studies of Au/Al_2O_3 and Au/TiO_2 catalysts described in Ref. [17] in this case the ions corresponding to the presence of Au–O bonds are not evidenced. It suggests the existence of only metallic gold on the surface of investigated catalysts. The previous studies of AuMCM-41 catalyst [15] showed that some part of gold atoms may be bonded to chlorine ions or surrounded by them. The ToF-SIMS experiment demonstrated that the amount of chlorine observed on the catalyst surface was considerably greater for the sample prepared by the co-precipitation method. Additionally, the ToF-SIMS results showed that in the case of the catalyst prepared by the co-precipitation method the formation of Au–Cl bonds (which had a great impact on the catalytic activity of the investigated materials) was caused by the calcination process. The same phenomenon was observed for the samples containing Nb. In this case $AuCl^-$ ions were observed only on the secondary ion mass spectrum collected from the surface of calcined catalyst prepared by the co-precipitation method. Analysis of the ToF-SIMS spectra of AuNbMCM-41 catalyst revealed also signals corresponding to the presence of Nb-containing species. In this case Nb^+, NbO^+ and $NbO_2{}^+$ ions ($m/z = 93$, 109 and 125) were detected (Fig. 1C). It suggests that niobium exists in the oxidized form on the catalyst surface. A comparison of the average values of emission intensity ratios $SiO_xH^-/SiO_x{}^-$ ($x = 1$–3), SiO^+/Si^+ and $NbO_y{}^+/Nb^+$ ($y = 1$–2) (Table 1) indicates that the composition of the uppermost layers of the surface of catalysts investigated may change in the calcination process, leading to decrease in the amount of hydrogen and an increase in the quantity of oxygen surrounding silicon and niobium atoms.

The main part of the studies described in this work was to analyze the process of surfactant removal from AuMCM-41 and AuNbMCM-41 catalysts. The secondary ion mass spectrum of as made AuNbMCM-41 sample (Fig. 2A) prepared by the co-precipitation method (in the presence of cationic surfactant - cetyltrimethylammonium chloride) revealed a very intensive signal at $m/z = 284$, which corresponds to the molecule of the surfactant without Cl atom. Moreover, a series of less intensive peaks coming from ions of masses differing in 14 units was also observed. They correspond to the fragments of surfactant molecule formed by successive detachment of $-CH_2-$ groups during the measurement. The above mentioned ions were not noted in the secondary ion mass spectra of the catalyst prepared by the incipient wetness impregnation and co-precipitated sample calcined at 550 °C (Fig. 2B and C). It directly confirms the lack of organic compounds on the surface of the sample prepared by the incipient wetness impregnation and the removal of the surfactant from the surface of the catalyst prepared by the co-precipitation method submitted to calcination. The same phenomenon was observed in the ToF-SIMS spectra of AuMCM-41 catalyst, which confirmed the presence of signals assigned to the surfactant only for as prepared sample made by the co-precipitation method. The differences among mass spectra were also observed in the region of lower masses ($m/z = 0$–100). In the case of the material with the cationic surfactant on the surface a series of peaks corresponding to C_xH_y fragments ($x = 1$–6) was the most intensive (Fig. 2A), while for samples without the surfactant molecules the signals originating from Na^+ ($m/z = 23$) (contamination), Si^+ ($m/z = 28$) and $SiOH^+$ ($m/z = 45$) ions were the most abundant (Fig. 2B and C).

In further part of the study the performances of two different (liquid metal Ga^+ and cluster bismuth $Bi_3{}^+$) primary ion sources in investigations of the surfactant removal were compared. Three representative ions originating from the surfactant molecule were selected for this purpose—$C_{12}H_{26}{}^+$ ($m/z = 170$), $C_{16}H_{34}{}^+$ ($m/z = 226$) and positively charged surfactant molecule without chlorine atom ($m/z = 284$). The results obtained for as made AuNbMCM-41 catalyst prepared by the co-precipitation method revealed that the intensity of the above mentioned ions was more than one order of magnitude higher when the beam of $Bi_3{}^+$ primary ions was used than for monoatomic Ga^+ primary ion gun (Table 2). It is in agreement with the data obtained in the ToF-SIMS studies of other organic molecules and confirms the advantage of the cluster bismuth ion gun over the monoatomic primary ion source in measurements of more complicated organic compounds [18,19].

The time-of-flight secondary ion mass spectrometry makes it also possible to estimate the distribution of particular substances on the surfaces investigated. It can be done by analysis of surface images of secondary ions collected from the samples measured. The earlier studies of AuMCM-41 and AuNbMCM-41 catalysts [15,16] showed that the preparation method of the material investigated may considerably influence the dispersion of gold species on the catalyst surface. It was demonstrated that the use of the incipient wetness impregnation method leads to poor dispersion of Au (agglomerates in the size of several micrometers—Fig. 3) while the co-impregnation method permits getting uniform distribution of gold on the catalyst surface.

Secondary ion images allow observing not only the dispersion of metal but also the distribution of other catalyst components on the surface studied. As mentioned earlier, the application of the polyatomic primary ion gun causes an increase in the emission intensity of secondary ions in the higher mass range. Owing to this, surface imaging can be also used to investigate the process of surfactant removal. ToF-SIMS images of as prepared catalysts obtained by the co-precipitation method revealed that the surfactant (cetyltrimethylammonium chloride—$CH_3(CH_2)_{15}N(Cl)(CH_3)_3$), whose location can be determined on the basis of the differences in the intensity of the signal at $m/z = 284$, is distributed homogenously on the surface studied (Fig. 4A). In the other samples, calcined catalysts prepared by the co-precipitation and the incipient wetness impregnation methods, the surface images of the surfactant demonstrated very weak signal at $m/z = 284$ mainly originating from the background (i.e., Fig. 4B). It is in agreement with the above described results and confirms the removal of the surfactant from the surface in the calcination process.

4. Conclusions

Besides the application of ToF-SIMS to determination of the surroundings of gold and niobium atoms in the catalyst structure, the detection of chlorine and its interactions with Au, and the estimation of gold dispersion, the time-of-flight secondary ion mass spectrometry appears to be a very useful tool for investigation of the residual organic template on the surface of ordered mesoporous materials of MCM-41 type. It was demonstrated that in the case of AuNbMCM-41 and AuMCM-41 catalysts prepared by the co-precipitation method the calcination of samples at 550 °C caused a complete removal of the surfactant from the surface of the material investigated. However, it could not be excluded that some part of the organic material remained inside the pores of the catalysts or in the subsurface region. Moreover, it was shown that the use of cluster bismuth ion gun in ToF-SIMS experiments enabled higher emission intensity (more than one order of magnitude when compared to the liquid metal Ga^+ primary ion source) of secondary ions originating from the surfactant molecules, which may facilitate interpretation of results.

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