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New Nb and Ta–FAU zeolites—Direct synthesis, characterisation and surface properties

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1. Introduction

Isomorphous substitution of zeolite lattice atoms, i.e. their replacements most often by different metal ions, is of great importance. Thus there is a lot of works on this subject in literature [1]. It is known that the isomorphous substitution of aluminium or silicon in zeolite structure can generate unique properties of the materials obtained. Generally, such modification can be performed by two synthetic routes: (i) incorporation of the desired metal through crystallisation together with silicon and aluminium species under hydrothermal conditions or (ii) post-synthesis modification route depends on the kind of zeolite structure, thermal/hydrothermal stability of zeolite, available metal source, and many other parameters.

The classical example of isomorphous substitution is the preparation of TS-1 material of the MFI structure in which silicon is substituted with titanium [3]. This microporous molecular sieve was found to be very interesting in the liquid phase oxidation of organic compounds with hydrogen peroxide as oxidant. However, there are a lot of works concerning isomorphous substitution of other elements into the zeolite lattice, for example B–MFI [4], Ga–BEA [5], Ge–ITQ-21 [6], Fe–MFI [7], Sn–BEA [8], V–MFI [9], and Zn–CIT-6 [10]. It should be mentioned that the incorporation of the so-called heteroatom into zeolite framework via crystallisation under hydrothermal conditions followed by a thermal or hydrothermal treatment could also lead to the displacement of

ABSTRACT

Niobium and tantalum containing Y zeolites were prepared in a one-pot synthesis and via solid-state ion exchange. The first method led to the incorporation of Nb and Ta into the zeolite framework as documented by XRD, UV–vis, XPS and test reactions. The efficiency of the metal introduction was higher for tantalum than for niobium. The presence of Lewis acid sites was proved by pyridine adsorption and cracking of cumene, whereas basic hydroxyls on the surface were evaluated on the basis of 3-methyl-2-cyclopentenone formation in the cyclisation of acetonyl acetone.

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metals from tetrahedral sites towards the extra-framework positions. This aspect was examined in details for the iron isomorphous substitution into the MFI structure [11].

There are even fewer data concerning metal incorporation into large pore structures such as for example that of faujasite (FAU). A possibility of incorporation of boron, gallium, iron and titanium into the FAU skeleton was described in [2,12,13]. Moreover, the faujasite structure was modified by non-metal element, i.e. by phosphorous, to obtain SAPO-37 sample [14]. This material belongs to the aluminophosphate family and shows interesting properties induced by the presence of phosphorous +5 cations in the skeleton. Taking into account the unique properties of SAPO-37 we focused on the preparation of FAU type zeolites containing transition metals of group five (Nb, Ta-present at +5 oxidation state) instead of phosphorous. We expected to obtain isolated Lewis acid centres by incorporation of Nb and Ta cations at the oxidation state +5. The substitution of these elements into the structure of zeolites ZSM-5 and beta (exhibiting high and medium Si/Al ratios) has been already studied (e.g. [15–17]) but as far as we know there are no reports on their incorporation into the zeolite framework of the large pore and low Si/Al ratio (e.g. FAU structure). Here we have explored this possibility by performing direct synthesis, without organic structure directing agent, of Nb and Ta containing Y zeolites.

2. Experimental

2.1. Preparation of zeolites

Preparation of Nb or Ta containing materials of the FAU structure was based on the modified two-steps procedure reported originally by Ginter et al. [18]. Firstly, the seed gel was prepared



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as follows. Sodium hydroxide (Chempur) and sodium aluminate (Riede-de Haën) were dissolved in H₂O. Afterwards, the sodium silicate solution (Aldrich) was added and the mixture was stirred for about 10 min. The final solution composed of: 10.67 Na₂O:Al₂O₃:10 SiO₂:180 H₂O was let to age at room temperature for 1 day. In the second step, sodium hydroxide and sodium aluminate were dissolved in H₂O then sodium silicate was added upon vigorous stirring. The composition of the obtained feedstock gel was: 4.3 Na₂O:Al₂O₃:10 SiO₂:180 H₂O. Afterwards, a part of the seed gel was added to the feedstock gel to get the final composition of: 4.62 Na₂O:Al₂O₃:10 SiO₂:180 H₂O. The metal source (niobium or tantalum pentaethoxide-Aldrich) was added to both, the seed and feedstock gels. The assumed Si/T ratio (T = Nb or Ta) was 64 or 32. Then, after vigorous stirring, the gel was put to a polypropylene bottle and heated in an oven for 5 h at 373 K. The final product was washed with distilled water and dried at 383 K for 12 h.

For comparison, the modified zeolites were also prepared by post-synthesis method, i.e. solid-state ion exchange, using commercial sodium Y zeolite (Katalistiks) and group five metal oxides. Hydrogen form of the zeolite and Nb₂O₅ (Alfa Aesar) or Ta₂O₅ (Aldrich) were mechanically mixed (the ratio of protons to Nb or Ta was assumed as 5) and heated at 973 K in oven for 8 h (temperature ramp 2 K min⁻¹).

2.2. Catalyst characterisation

X-ray diffraction patterns (XRD) were recorded at room temperature on a Bruker AXS D8 Advance apparatus using Cu K α radiation (λ = 0.154 nm), with a step of 0.05°.

To establish the Si/Nb or Si/Ta ratio X-ray fluorescence (XRF) was applied using MiniPal-Philips. The measurements were done using calibration curves prepared from mixtures of silica and Nb₂O₅ or Ta₂O₅ (Si/Nb or Si/Ta from 5 to 300).

Ultraviolet–visible spectroscopy (UV–vis) was applied. The spectra were recorded using a Varian-Cary 300 Scan UV-Visible Spectrophotometer. Catalyst powders, after dehydration at 673 K for 2 h, were placed into the cell equipped with a quartz window. The spectra were recorded in the range from 800 to 190 nm. Spectralon was used as a reference material.

SEM images were recorded using Scanning Electron Microscopy (Philips SEM 515) operating at 15 kV with coating (gold) of the samples.

Aluminium-27 magic-angle spin solid-state nuclear magnetic resonance (²⁷Al MAS NMR) was applied. The spectra were recorded using Bruker Avance DPX300 spectrometer.

X-ray photoelectron spectroscopy (XPS) were performed with a SSI-X-probe (SSX-100/206) photoelectron spectrometer equipped with a monochromatic microfocused Al K α X-ray source (1486.6 eV) from Surface Science Instruments.

2.3. Pyridine adsorption

Infrared spectra were recorded with a Bruker Vector 22 FTIR spectrometer using an in situ cell. Samples were pressed below $0.2 \text{ tons } \text{cm}^{-2}$ into thin wafers of ca. 10 mg cm^{-2} and placed inside the cell. Catalysts were evacuated at 623 K during 3 h and pyridine (PY) was then admitted at 423 K. After saturation with PY the samples were degassed at 423, 473, 523 and 573 K in vacuum for 30 min at each temperature. Spectra were recorded at room temperature in the range from 4000 to 400 cm^{-1} . The spectrum without any sample ("background spectrum") was subtracted from all recorded spectra. The IR spectra of the activated samples (after evacuation at 623 K) were subtracted from those recorded after the adsorption of PY followed by various treatments. The reported spectra are the results of this subtraction.



Fig. 1. XRD patterns of Nb and Ta containing zeolites prepared in one-pot synthesis.

2.4. Acetonylacetone cyclisation

The materials were tested in the acetonylacetone cyclisation. A tubular, down-flow reactor was used in experiments performed at atmospheric pressure, using nitrogen as a carrier gas. The catalyst bed (0.05 g) was first activated for 2 h at 623 K under nitrogen flow (40 cm³ min⁻¹). Afterwards, a 0.5 cm³ of acetonylacetone (Fluka, GC grade) was passed continuously through the catalyst at 623 K for 0.5 h. The substrate was delivered with a pump system and vaporised before it was passed through the catalyst bed in a flow of nitrogen carrier gas (40 cm³ min⁻¹). The reaction products were collected downstream of the reactor in a cold trap (mixture of 2-propanol and liquid nitrogen) and analysed by gas chromatograph (equipped with a TCD detector and with a silicone SE-30 3 m column heated at 353 K).

2.5. Cumene cracking

The cumene cracking was performed, using a microcatalytic pulse reactor inserted between the sample inlet and the column of a chromatograph. The catalyst bed (0.05 g with a size fraction of 0.5 mm < \emptyset < 1 mm) was first activated at 623 K for 2 h under helium flow (40 cm³ min⁻¹). The cumene (Aldrich) conversion was studied at 623 K using 5 µl pulses of cumene under helium flow (40 cm³ min⁻¹). The reactant and reaction products: propene and α -methyl styrene were analysed using gas chromatograph connected on-line with the microreactor. The reaction mixture was separated in helium flow (40 cm³ min⁻¹) on a 3 m column filled with silicone SE-30 and detected by TCD. The column was heated as follows: 303 K for 2 min then 20 K min⁻¹ to 338 K and kept for 4 min, then 10 K min⁻¹ to 373 K and kept for 18 min.

3. Results and discussion

3.1. Synthesis

Niobium and tantalum containing materials prepared via onepot synthesis from the final solution of: $4.62 \text{ Na}_2\text{O}:Al_2\text{O}_3:10$ SiO₂:180 H₂O:0.15625 (or 0.078125) Nb₂O₅ or Ta₂O₅ showed the faujasite structure as confirmed by XRD patterns shown in Fig. 1. One can observe the same reflections with identical relative intensities for NaY zeolite and all materials modified by Nb and Ta, i.e. NbY-64(32) and TaY-64(32) zeolites. The assumed silicon to niobium or tantalum ratios (Si/T where T=Nb or Ta) were 32 or 64 thus the last number in the material symbol stands for Si/T. The

Unit cell	narameters	(XRD)	metal	molar	concentratio	n (XR	- XPS) and XP	S data of	nre	nared	sami	nles
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Catalyst	Unit cell parameter	Molar ratios			Metal BE in the sample, eV	Metal BE in bulk oxide, eV
		Si/Nb(Ta)—XRF	Si/Nb(Ta)—XPS	Si/Al—XPS		
NaY	24.72	-	-	-	_	_
NbY-64	24.76	>300	730	2.2	208.1	207.1 (Nb ₂ O ₅)
NbY-32	24.77	72	80	2.3	207.9	207.1 (Nb ₂ O ₅)
TaY-64	24.76	78	15	2.3	26.7	26.1 (Ta ₂ O ₅)
TaY-32	24.73	45	7	2.3	26.3	26.1 (Ta ₂ O ₅)

unit cell parameters (a_0) of prepared zeolites, estimated from XRD patterns, are shown in Table 1. In spite of low metal concentration the materials containing niobium or tantalum show higher value of a_0 parameter than NaY sample. However, the difference is small, therefore it is not strong evidence for the incorporation of these metals into zeolite structure. When a metal is incorporated into the zeolite structure during the one-pot synthesis three possibilities can be considered: (i) the metal is not able to occupy any positions in the zeolite structure, (ii) the metal is located in the zeolite skeleton and tetrahedrally coordinated with oxygens (like silicon and aluminium) and (iii) the metal occupies extra framework positions as cations or metal oxides.

Crystalline niobium(V) oxide and tantalum(V) oxide show main XRD peaks at 2θ ca. 22.6, 28.3 and 36.6°. For the zeolites with both Si/T ratios used in this work no XRD reflections from crystalline metal oxide phases were observed in XRD patterns. The real amount of tantalum in the final material is ca. 5 and 8 wt% (calculated for Ta(V) oxide) for TaY-64 and TaY-32, respectively. As XRD starts to be sensitive from amount of crystalline phases of ca. 5 wt% one can expect that if all or significant part of tantalum introduced into the zeolite existed in the form of extra framework oxide, the XRD pattern should have contained peaks from the metal oxide phase. To examine more deeply if tantalum is present in the form of oxide on the material surface the XRD patterns of Ta₂O₅, NaY and tantalum containing zeolites prepared by one-pot synthesis as well as by post-synthesis method are shown in Fig. 2. The peaks corresponding to Ta₂O₅ are indicated in the figure. One can observe that the material prepared by post-synthesis technique exhibits all the characteristic peaks related to tantalum(V) oxide phases. For TaY-32 only a very broad peak can be seen at 2θ ca. 28.3°, however no other peaks which could origin from metal oxide phases are observed. Therefore, the difference of tantalum state in the final material depending on the preparation technique is clearly seen.



Fig. 2. XRD patterns of Ta containing zeolites prepared in one-pot synthesis and post-synthesis methods.

However, basing on XRD patterns, the presence of some tantalum oxide in TaY-32 sample should not be excluded.

The lack of peaks related to metal oxide phases in XRD patterns of NbY and TaY zeolites prepared in one-pot synthesis does not exclude the possibility of the presence of such phase in the material, because small metal clusters and/or small quantities of oxides could not be detected by the XRD technique. To examine in detail the possibility of the presence of extra framework metal oxides in the samples prepared, the UV-vis spectra of zeolites were recorded. Fig. 3 shows the spectra of tantalum containing Y zeolites prepared by both, one-pot and post-synthesis methods as well as of bulk tantalum oxide (as a reference sample). The spectra of tantalum containing zeolites prepared in the one-pot hydrothermal synthesis are characterised by a band at 221 nm, which is typical of tetrahedrally coordinated tantalum species. The zeolite containing tantalum incorporated via post-synthesis method shows a different spectrum with a broad band and an adsorption maximum at ca. 270 nm. This band is typical of octahedrally coordinated tantalum. e.g. in tantalum(V) oxide [19]. It is seen as the main band for bulk tantalum(V) oxide (Fig. 3). The UV-vis spectra of niobium containing Y zeolites prepared by synthesis and post-synthesis methods are shown in Fig. 4. Moreover, the spectrum of niobium(V) oxide is also included in the figure. The octahedral coordinated niobium species gives a characteristic adsorption band at ca. 330 nm. The band at similar position is observed for both, niobium(V) oxide and Y zeolite modified by post-synthesis technique (Nb_2O_5/Y) . In the case of NbY-32 the band corresponded to octahedral coordinated niobium species is not observed. Therefore, one can exclude the presence of niobium oxide in this sample and confirm the tetrahedral coordination of niobium species. Thus UV-vis spectra confirmed the XRD results.



Fig. 3. UV-vis spectra of tantalum containing Y zeolites and Ta₂O₅.



Fig. 4. UV-vis spectra of niobium containing Y zeolites and Nb₂O₅.

The incorporation of niobium or tantalum into the faujasite structure could disturb the location of at least part of aluminium present in the synthesis mixture in the framework positions or even displace aluminium located in the framework positions to extra-framework ones. To check the location of aluminium in the zeolites prepared in one-pot synthesis ²⁷Al MAS NMR spectroscopy was applied and the spectra are shown in Fig. 5. The zeolites prepared in hydrothermal synthesis show a characteristic peak at ca. 54 ppm, which is attributed to tetrahedrally coordinated aluminium. Moreover, the peak typical of octahedrally coordinated aluminium (at ca. 0 ppm) is not detected for all samples, which proved that all aluminium species were incorporated into the zeolite lattice. The location of aluminium in the framework positions confirms the well-developed crystallinity of the zeolite structure. Moreover, SEM images of tantalum and niobium-containing samples (Fig. 6) show that the particles of zeolites are similar in size and shape. One cannot observe the presence of some separated phases



Fig. 5. MAS ²⁷Al NMR spectra.

which could inform about the formation of metal oxide in the extra framework positions for samples with Si/Nb(Ta) ratio=64. However, the presence of such phase should not be excluded for lower Si/Nb(Ta) ratio, especially in the case of tantalum containing sample. The average particle size of zeolites estimated from SEM images is between 0.5 and 1 μ m. The same particle sizes for all materials were also inferred from XRD patterns, according to Scherrer's equation. It points out that both the nature of the heteroatom (Nb or Ta) and the silicon to metal (Nb or Ta) ratio did not impact on the crystal morphology.

The efficiency of Nb or Ta incorporation into the faujasite structure in the one-pot synthesis was examined by XRF using calibration curves. The real Si/T ratios in the final zeolites are shown in Table 1. It is well marked that the assumed and real Si/T ratios are a little bit higher for TaY-64(78) and for TaY-32(45). This demon-



Fig. 6. SEM images of: (A) NbY-64; (B) NbY-32; (C) TaY-64; (D) TaY-32.



Fig. 7. Spectra of pyridine adsorbed at 423 K followed by evacuation at 473 K for 0.5 h: (a) TaY-32; (b) TaY-64; (c) NbY-32; (d) NbY-64.

strates that tantalum is rather easily incorporated into the zeolite. It is not the case for niobium containing samples. For NbY-32 sample the efficiency of niobium incorporation is ca. 50% and even much lower for NbY-64. However, much more difficult incorporation of niobium into the zeolites does not exclude the possible location of Nb in the zeolite framework. The results of efficiency of metal incorporation obtained from XRF (which are related to the bulk) are different from those estimated by XPS (Table 1). Whereas for niobium containing samples XRF and XPS data are quite similar, for tantalum zeolites the amount of Ta estimated by XPS is higher. It suggests the higher concentration of tantalum species on the materials surface. However, as evidenced by UV–vis spectroscopy described above tantalum does not show the octahedral coordination, therefore the presence of tantalum oxide could be suggested only basing on XRD and SEM results.

3.2. Metal state and location

Information concerning the metal location in zeolite framework or extra-framework positions can be deduced from its coordination. Tetrahedrally coordinated species should be found for the framework located metals, whereas octahedrally coordinated ones should be related to the extra-framework species. As shown in the ²⁷Al MAS NMR spectra described in the previous section, all aluminium species are present in tetrahedral sites. Thus they are located in the skeleton of zeolites. Moreover, the Si/Al ratio estimated from XPS results (Table 1) is almost the same for all the samples. The sodium amount was also estimated in the final material and expressed as Al/Na ratio. The obtained value was ca. 1, however the difference of sodium content in all samples was small (in the range of experimental error) and therefore is out of discussion. For niobium and tantalum incorporated via the one-pot synthesis the UV-vis spectra pointed out the same metal coordination as for aluminium. i.e. tetrahedral. Moreover, no octahedral niobium or tantalum species were found, contrary to the samples prepared by the post-synthesis method. Therefore, the tetrahedral coordination of Nb and Ta species in zeolites obtained in one-pot hydrothermal synthesis suggests the location of both metals in the zeolite framework.

For further investigation of the metal state and location in the niobium and tantalum-containing Y zeolites XPS spectroscopy was applied. The results obtained for these samples as well as for bulk niobium(V) and tantalum(V) oxides are collected in Table 1. Only



Fig. 8. Spectra of: (a) pyridine adsorbed at 423 K; and after evacuation at: (b) 423 K; (c) 473 K; (d) 523 K; (e) 573 K.



Fig. 9. Spectra of: (a) pyridine adsorbed at 423 K; and after evacuation at: (b) 423 K; (c) 473 K; (d) 523 K; (e) 573 K.

one metal oxidation state was found for both niobium and tantalum and it was estimated as +5. The incorporation of metals at the oxidation state +5 into the zeolite framework changes the local lattice charge by the formation of positively charged tetrahedral species. This could imply the formation of Lewis acids sites in niobium and tantalum-containing zeolites. Indeed, the presence of Lewis centres was concluded on the basis of pyridine adsorption followed by FTIR measurements (described below). It should be mentioned that the origin of such centres cannot be assigned to the aluminium species since they are present in framework positions.

The information concerning the metal location in the zeolite can also be understood from its binding energy. The data in Table 1 show the XPS binding energies obtained for materials prepared in hydrothermal synthesis and for the bulk niobium(V) and tantalum(V) oxides. It can be found that the energies recorded for niobium and tantalum-containing zeolites were higher than those characteristic of bulk metal oxides. The increase in the binding energy can be attributed to different surroundings of niobium or tantalum species in zeolites than in bulk niobium(V) or tantalum(V) oxides. Different neighbourhoods of metal species can be obtained when Si-O-Nb or Si-O-Ta link is created. Such links are formed when the transition metal is incorporated into the zeolite framework, thus the XPS results support the conclusion about the location of metals (Nb and Ta) in the zeolite framework. The lower binding energies for Si/Nb(Ta) = 32 than those for Si/Nb(Ta) = 64 can be explained by the higher concentration of transition metal when the Si/Nb(Ta) ratio is lower. Such an increase in the concentration can induce the interaction between two Nb or Ta species leading to decreasing binding energy. This effect is more pronounced for tantalum zeolites. In spite of low number of Ta atoms calculated per unit cell, such an interaction is possible. It can occur mainly on the materials surface, where a higher concentration of tantalum was estimated from XPS (Table 1). These results can also give some important information concerning the isolation of metal species in the zeolites. As one can observe the difference of binding energies between Nb₂O₅ or Ta₂O₅ and niobium or tantalum included to zeolite, respectively, increases with the decrease of metal content estimated on the materials surface.

3.3. Pyridine adsorption

Aiming the identification of the type of acidic centres present on the zeolite surfaces, infrared spectroscopy combined with the adsorption of pyridine was applied. After the interaction of pyridine with Lewis acid sites (LAS) the characteristic bands at ~1450 and \sim 1610 cm⁻¹ appear [20]. The intensity of the first band is related to the number of LAS, whereas the position of the second band characterises the strength of LAS [20]. Pyridine also interacts with Brønsted acid sites (BAS), which is manifested by the infrared band at \sim 1550 cm⁻¹ and two other bands in the 1620–1640 cm⁻¹ range. Moreover, pyridine can also interact with hydroxyls on the zeolite surface forming weak hydrogen bounds and giving adsorption bands at 1596 and 1445 cm⁻¹. The spectra after pyridine adsorption at 423 K followed by evacuation at 473 K for 0.5 h are shown in Fig. 7. For all zeolites prepared in the one-pot synthesis, the bands at 1598 $\rm cm^{-1}$ and 1444 $\rm cm^{-1}$ dominate. The first band at 1598 $\rm cm^{-1}$ is assigned to the pyridine adsorbed via weak hydrogen bound on hydroxyl groups which do not exhibit strong acidity or are not acidic (e.g. silanol groups and/or Nb-OH, Ta-OH species). The second band at 1444 cm⁻¹ covers both species, i.e. pyridine adsorbed on LAS and hydrogen-bounded pyridine. The overlapping of both bands does not allow to calculate the number of LAS. However, the existence of LAS centres can be validated by the weak band typical of pyridine adsorbed on LAS at ca. 1610 cm⁻¹. Moreover, for all samples the band at 1490 cm⁻¹ is observed. This band is assigned to pyridine adsorbed on both Lewis and Brønsted acid sites. When the BAS are not present or exist at a low concentration, the intensive band at 1490 cm⁻¹ can testify of the presence of LAS. This is the case for all materials prepared. Only the spectrum of NbY-64 (Fig. 7d) shows a distinct band at 1550 cm⁻¹, which is typical of pyridine adsorbed on BAS centres. Such centres were also observed on NaY zeolite prepared according to the procedure applied in this work. This band is hardly seen for NbY-32 and TaY-64 zeolites (Fig. 7b

Table 2	
The estimation of LAS strength of niobium and tantalum containing zeolites.	

Catalyst	Lewis acid s	Lewis acid sites occupied by pyridine after evacuation at					
	423 K	473 K	523 K	573 K			
NbY-64	100%	51%	34%	7%			
NbY-32	100%	55%	20%	3%			
TaY-64	100%	64%	20%	2%			
TaY-32	100%	48%	11%	2%			

and c) and invisible for TaY-32 sample (Fig. 7d). Therefore, one can postulate that LAS centres and OH groups are the dominant ones on the surface of NbY and TaY zeolites.

The strength of Lewis acid centres can be estimated on the basis of the drop of intensity of IR bands after evacuation of adsorbed pyridine at different temperatures. Figs. 8 and 9 reveal the results of such evacuation for TaY and NbY, respectively. Due to the low concentration of BAS in the samples, the intensity of the band at 1490 cm⁻¹, after evacuation at different temperatures, can give an information concerning the LAS strength. The decrease of LAS calculated from the areas of 1490 cm⁻¹ band are also shown in Table 2. The increase in the tantalum content (from Si/Ta = 78 to Si/Ta = 45 for TaY-64 and TaY-32, respectively) leads to a weaker chemisorption of pyridine demonstrated by the lower intensity of the 1490 cm⁻¹ band after evacuation at a desired temperature. The same is observed for niobium containing Y zeolites. The strength of LAS lowers when Ta or Nb forming Lewis acid centres can interact with each other, as can happen at higher concentration of metal atoms.

3.4. Acetonylacetone cyclisation

For the evaluation of the acid/base properties in the reaction conditions, the acetonylacetone transformation was carried out. In the presence of acid centres 2,5-dimethylfuran (DMF) is formed, whereas the presence of basic centres leads to the formation of 3-methyl-2-cyclopentenone (MCP) [21,22]. If acid centres dominate on the catalyst surface the selectivity ratio MCP/DMF is <1. The ratio of MCP/DMF > 1 indicates that basicity is dominant. When MCP/DMF ~ 1, the catalyst has both acid/base character.

The results of acetonylacetone cyclisation carried out on niobium and tantalum containing Y zeolites prepared by the one-pot synthesis are shown in Table 3. It can be pointed out that the higher metal concentration in the sample the higher the conversion of acetonylacetone is observed for the desired nature of metal (Nb or Ta). For the materials with the assumed Si/T ratio of 64, the niobium containing sample shows a little bit higher activity (23% of acetonylacetone conversion) than the tantalum-containing one (19% of acetonylacetone conversion) in spite of the fact that the real molar concentration of Nb is much lower than Ta (Table 1). Therefore, the higher conversion for NbY-64 sample can be explained by the presence of Brønsted acid sites observed for this material (Fig. 7d). The participation of BAS present in NbY-64 sample in

Table 3

The conversion and selectivity in the acetonylacetone cyclisation at 623 K.

Catalyst	Conversion, %	Selectivity, %		Yield, %	6	MCP/DMF
		DMF	MCP	DMF	МСР	
NbY-64	23	33	67	7.6	15.4	2
NbY-32	39	3	97	1.2	37.8	32
TaY-64	19	7	93	1.3	17.7	13
TaY-32	56	1	99	0.6	55.4	99

 $Catalyst-0.05\ g;\ acetonylacetone\ volume-0.5\ cm^3;\ reaction\ time-0.5\ h.\ DMF-2, 5-dimethylfuran;\ MCP-3-methyl-2-cyclopentenone.$

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Average conversion and selectivity in cracking of cumene at 623 K.

Catalyst	Conversion of cumene, %	Selectivity, %	
		Propene	α -Methyl styrene
NbY-64	12	61	39
Nb Y-32	10	48	52
TaY-64	8	42	58
TaY-32	2	0	100

Catalyst-0.05 g; cumene pulse = 5 µl; total He flow-40 cm³ min⁻¹.

the reaction is strongly supported by the much higher selectivity to DMF (33% for NbY-64 and 7% for TaY-64). Among all the catalysts studied, NbY-64 reveals several times higher yield of DMF. For niobium and tantalum zeolites with the Si/T ratio of 32, the conversion observed can be related to the real metal (Nb or Ta) concentration in the zeolite (Table 1). The TaY-32, which shows real Si/Ta = 45, is more active than NbY-32 (Si/Nb = 72). However, not only the amount of transition metal influences the activity but also the nature of metal. If one compares TaY-64 and NbY-32 samples having similar numbers of tantalum and niobium species, different conversions of acetonylacetone are observed, i.e. 19% and 39%, respectively. The higher conversion on NbY-32 zeolite should be related to the privileged role of Brønsted acid centres present in NbY-32 material, as confirmed by the results of cumene cracking described below.

Analysis of the products distribution clearly indicates that with increasing number of Nb or Ta atoms in the zeolite framework, the yield of MCP increases. It means that the number of basic OH groups active in the production of MCP increases with increasing number of metal (Nb or Ta) atoms. The indicator of basicity, i.e. MCP/DMF ratio changes significantly depending on the number and nature of transition metal (Table 2). This phenomenon supports the location of Nb and Ta in the zeolite framework and their +5 oxidation state compensated by four oxygens from the tetrahedra and one basic OH group. The formation of Nb(V)^{$\delta+$}-OH^{$\delta-$} in the case of the isomorphous substitution of niobium into mesoporous molecular sieves was reported before and supported by different experimental techniques [23].

3.5. Cumene cracking

Cracking of cumene is the test reaction used mainly for characterisation of strong acidic centres [24,25]. When strong Brønsted acid centres are involved in the catalytic process, the main products formed are benzene and propene. The transformation of cumene can also take place in the presence of electron-transfer centres. In the later case, it leads to the formation of different products, primarily styrene and α -methyl styrene.

The results of cumene cracking reaction carried out on Nb and Ta containing zeolites are shown in Table 4. The lowest activity was observed for TaY-32 sample (2% of cumene conversion). The same catalyst showed 100% selectivity to α -methyl styrene. It is important to stress that for this sample, not even traces of Brønsted acid sites were detected by pyridine adsorption. The presence of only Lewis acid sites that can act as electron-transfer centres leads to the high selectivity to α -methyl styrene. The other samples which contain at least traces of BAS are more active in cracking of cumene. Moreover, they show also a significant selectivity to propene. This product dominates for the sample showing the highest number of BAS, i.e. NbY-64.

According to the real number of Nb and Ta atoms in the zeolite framework, the samples can be ordered as follows: NbY-64 \ll NbY-32 \leq TaY-64 < TaY-32. With increasing number of these atoms, the selectivity to α -methyl styrene increases because it is related to the number of Lewis acid sites. In the same order the strength of

acid centres decreases, as shown in the study of pyridine adsorption/desorption, and it reflects the decrease in cumene conversion.

4. Conclusions

To the best of our knowledge the Nb and Ta containing FAU zeolites have been successfully synthesised for the first time. Tantalum is easier included into the faujasite structure than niobium. For assumed Si/Nb(Ta) ratio = 64, niobium and tantalum were found to be present exclusively in the tetrahedrally coordinated positions indicating the introduction of Nb and Ta (both in an oxidation state of +5) into the zeolite skeleton. XPS binding energies confirmed that these metals are located in environments other than in bulk oxides, i.e. in the zeolite skeleton. The excess of local positive charge in the zeolite framework in which Nb or Ta is located can be compensated by basic OH groups. These are active in the formation of MCP in acetonylacetone cyclisation. The Lewis acid centres were present in all zeolites prepared in this work and their presence was confirmed by pyridine adsorption and by the results of the cumene cracking reaction.

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