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Niobium-containing catalysts—the state of the art

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Abstract

This review article is devoted to the materials containing niobium, which have been discovered or developed in the past few years and exhibit the potential application in heterogeneous catalysis. Niobium oxides and mixed oxides as well as sulfides, nitrides (oxynitrides), carbides (oxycarbides), and phosphates are considered. Among the catalytic processes in which Nb-containing materials were tested, liquid and gas phase oxidation is described in details, and the role of niobium in the prevention of the catalyst from SO_2 poisoning is mentioned.

Keywords: Niobium oxides; Mixed oxides; Sulfides; Carbides; Phosphates; Oxidation in liquid and gas phase; SO_2 poisoning

1. Introduction

The past decade has brought an increasing interest in niobium-containing materials, which can be applied within many fields [1]. The heterogeneous catalysis is one of them and it is so wide area of the possible application in this field that the growing focus on niobium catalysts has been recently noted in many research groups.

The development of studies within synthesis, characterization and application of Nb-containing catalysts was possible thanks to the great progress of the spectroscopic as well as the other physical techniques which allow the analysis of Nb state in the solids.

Niobium compounds exhibit special properties not shown by the compounds of neighboring elements of niobium in the periodic table. Some of them, like stability or strong metal support interaction (SMSI) are very important for a good quality catalyst.

The unfavorable feature of niobium oxides, the biggest group of Nb compounds applied in heterogeneous catalysis, is a low mobility and reducibility of niobium species. The melting point of Nb_2O_5 is very high (1785 K). However, for catalysis and catalysts a very important is the Tamman temperature in which the surface atoms began to diffuse. For Nb_2O_5 it is 893 K, i.e. higher than the temperature of typical catalytic reactions (473–873 K) [2]. If one compare the Tamman temperature of Nb_2O_5 with that of V_2O_5 (482 K), it is understandable that vanadium oxides have found a wider applications than that of niobium equivalents. The low Tamman temperature causes that the surface V(+5) species become very mobile and readily spread out over other oxide surfaces. This is, of course, favorable feature of catalysts and catalysis. However, in some cases, if the catalysts are applied in liquid phase reactions or have to work at very high temperatures during the reaction or regeneration, vanadium can be too easy released from the catalyst surface. For such kinds of processes, the niobium-containing oxides seems to be more attractive catalysts. The semiconductor properties of Nb_2O_5 are lower than that of V_2O_5 which also determine the application of Nb compounds in catalysis.

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The last decade has brought an interest in niobium oxides exhibiting mesoporous structure, prepared as single or mixed oxides, as well as other niobium catalysts such as sulfides, nitrides and oxynitrides, carbides or phosphates. The review of new materials containing niobium, their characterization and application in various catalytic processes is drawn in this paper. The main focus is concentrated on the materials discovered or developed in the last few years and processes studied at that time.

2. Catalysts

Taking into account the chemical nature of the materials, niobium-containing catalysts can be classified as shown in the diagram (Fig. 1). There is no doubt that the biggest group of the catalysts bases on Nb oxides species. In this group the wide variation of Nb–O connection, structure, combination with the other oxides is widely described in the literature. As a result of these different structures and properties, niobium compounds exhibit unique activity, selectivity and stability for many different catalytic reactions [1]. The new insight to each group of niobium catalysts will be given below.

2.1. Niobium oxides

The development of catalysis on Nb-containing materials in the last few years underwent in the direction of synthesis of bulk niobium oxides exhibiting the higher surface areas than that of the oxides prepared using the traditional methods. Moreover, it focused on the production of mixed oxides in which the reducibility of niobium species, one of the behaviors determining the catalytic properties, changes if Nb is bounded to the other element via oxygen.

The examples of papers published in the last 5 years and describing the new Nb oxide-containing materials, their characterization and catalytic application are shown in Table 1.

2.1.1. Bulk niobium oxides—active phase and a support

It has been described earlier that bulk Nb(V) oxides consists mainly of NbO_6 units which may be present as distorted as well as undistorted species [43]. Moreover, NbO_7 and NbO_8 units appear occasionally. Wachs et al. [2] describing the molecular structure and reactivity of the group V metal oxides compared the physicochemical properties of bulk Nb_2O_5 (T-phase) and V_2O_5. The reducibility of Nb_2O_5 is more difficult than that of vanadium oxide. The reduction of Nb_2O_5 with hydrogen is initiated at ~1073 K. However, for the reduction of bulk Nb_2O_5 to bulk Nb_2O_4 the temperature of ~1573 K is needed. The surface area of bulk niobium oxide used by the authors was very low ($1.9\,m^2\,g^{-1}$), lower than that of V_2O_5 ($3.5\,m^2\,g^{-1}$). Even so, bulk Nb_2O_5 possessed about five times greater the number of specific surface active sites than bulk V_2O_5 due to the different surface morphologies of both oxides. The number of active sites was estimated on the basis of methanol

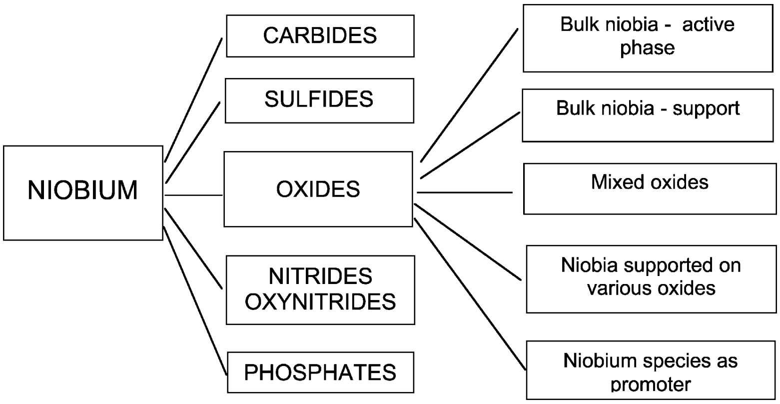


Fig. 1. Chemical nature and niobium species in the heterogeneous catalysis.

Table 1
New niobium oxide-containing catalysts studied in the last 5 years (1997–2001; those published to 1999 are widely described in [1])

Material	Preparation	References
Porous niobium oxide	Preparation by the exfoliation of $H^+/K_4Nb_6O_{17}$ with TBA^+OH^-, precipitating the exfoliated two-dimensional niobate sheets and MgO followed by removal of MgO	[3]
Thin film of mesoporous niobium oxide of Nb-TMS-1 type	PLD technique	[4,5]
Macro-mesoporous niobium(V) oxide	Synthesis by a ligand-assisted vesicle templating strategy	[6]
Reduced mesoporous niobium oxide (reduced Nb-TMS-1)	Reduction with one-dimensional potassium fulleride wires in the channels	[7,8]
	Reduction with low-dimensional bis(benzene) vanadium	[9]
	Reduction with Na-naphtalene	[10]
Niobosiliceous mesoporous molecular sieve of MCM-41 type	Synthesis by use a template—cetyltrimethylammonium chloride, niobium oxalate (or ammonium–oxalate complex or chloride) and sodium silicate	[11–22]
	Synthesis by the use a template—alkyltrimethyl surfactant, tetramethylammonium silicate, and niobium ethoxide	[23,24]
Niobium oxide microporous molecular sieve Nb-TMS6	Prepared by the use of bifunctional templating molecules	[25]
Niobium silicate microporous molecular sieves of the MFI structure, denoted NbS-1 or NbZSM-5	Hydrothermally synthesis using tetrapropylammonium hydroxide as the organic template, tetraethyl orthosilicate and niobium ethoxide	[26,27]
Microporous niobium silicate denoted AM-11	Prepared from niobium oxalate and tetraethyl orthosilicate by autoclaving a mixture of these materials at 473 K	[28,29]
Microporous titanoniobosilicate denoted ETNbS-10	Prepared from sodium silicate, Na, K, Ti chlorides and niobium oxalate autoclaved at 503 K	[30]
Modified perovskite structural oxide, $HLaNb_2O_7$ (HLa)	HLa intercalated with *n*-amines of different carbon chain length using in pillaring ZrO_2 or TiO_2	[31]
Nb(V) oxide	One-step non-hydrolytic condensation reactions starting from VO(O *i*-Pr)$_3$ and $NbCl_5$	[32]
TiO_2 supported vanadium-niobium oxide	Wet impregnation of TiO_2 (anatase)	[33]
$(Mo + V + Nb)/TiO_2$	Wet impregnation of TiO_2	[34]
MoO_3/Nb_2O_5	Wet impregnation of Nb_2O_5 with ammonium heptamolybdate	[35]
Mo–V–Sb–Nb–O	Mixed metal oxides prepared from ammonium metavanadate, antimony trioxide, ammonium heptamolybdate, and oxalic acid	[36]
V_2O_5/Nb_2O_5	Supporting procedure	[37,38]
Co/Nb_2O_5 (cobalt niobiate: $Co_2Nb_5O_{14}$ and $CoNb_2O_6$)	Wet impregnation with cobalt nitrate	[39]
Nickel niobiate/SiO_2	Wet impregnation of niobia—silica system with nickel naphtanoate	[40,41]
Nb_2O_5/SiO_2 or Al_2O_3 or ZrO_2 or TiO_2	Wet impregnation with niobium oxalate/oxalic acid	[42]

chemisorption and the formation of methoxy species. It was stated that bulk niobia exhibits 100% acidic character in contrast to bulk vanadia characterized by 90% of redox properties.

2.1.1.1. Oxides exhibiting high surface areas. The increase of the surface area in niobium oxides is a very important task for the improvement of the catalytic activity of the materials. Montes and co-workers [44] obtained solid Nb_2O_5 with large surface area oscillated between 27 and 132 $m^2\,g^{-1}$ depending on the preparation conditions. They have used $NbCl_5$ as the starting material and did not apply special thermal treatments. Several preparation variables such as pH, H_2O to Nb hydrolysis ratio and calcination temperature have been studied. The pH of the hydrolysis step did not influence the obtained materials, whereas a hydrolysis ratio of 80 moles of H_2O per mole of Nb gave rise to the highest surface area. All materials exhibited the Nb=O bond in highly distorted octahedral NbO_6 (the IR band near 850 cm^{-1}). After calcination at 673 K, acid centers were mostly Brønsted sites, but at increasing temperatures the relative importance of the Lewis centers increased. The described niobia was active in the aldol condensation of acetone. The acidic reaction routes producing mesytilene and acetic acid are controlled by the Brønsted acid centers.

Porous niobium oxide was prepared from a layered compound $K_4Nb_6O_{17}$, by using a soft chemical method [3]. $K_4Nb_6O_{17}$ consists of octahedral units of NbO_6 which form a two-dimensional layered structure via bridging oxygen atoms. The layers are negatively charged, and K^+ ions existing between the layers compensate their negative charge. The exfoliated niobate sheets could be precipitated by addition cations such as H^+ [45]. It allows the authors [3] to create the new types of porous niobium oxides from two-dimensional niobate sheets, obtained from exfoliation of $H^+/K_4Nb_6O_{17}$ with TBA^+OH^-, precipitated by MgO fine particles. The composite was acidic or thermal and acidic treated, and depending on the treating route various materials were obtained as shown on the scheme drown in Fig. 2. If the acidic treatment follows on the evacuation at 573 K the more open structure than that without evacuation is formed. The highest surface area (145 $m^2\,g^{-1}$) was found for the material evacuated at 573 K and acidic treated. This material showed the pore size distribution between 4 and 10 nm. This range corresponds to the space ensured by the MgO particles, whereas the range between 2 and 4 nm registered for the other porous niobium oxides corresponds to the space ensured by TBA^+. Porous niobium oxides exhibit high photocatalytic activity for H_2 evolution from various alcohol aqueous solutions.

Search for new niobium oxide catalysts characterized by higher surface areas resulted in the synthesis of mesoporous niobium(V) oxides denoted in the literature [46–48] as Nb-TMS. Antonelli and Ying [46–48] proposed the synthesis of niobium oxide mesoporous material in such a way that the surfactant head group is directly ligated to the metal alkoxide prior to hydrolysis and condensation. This permits the required interaction between the organic and inorganic phases before the introduction of water. Another key feature of this ligand-assisted templating (LAT) approach is that the metal was directly connected to the inorganic precursor without a charge-matching or hydrogen bonding-interaction. Depending on the surfactant chain length as well as the surfactant: Nb source ratios one can obtain hexagonal, cubic or layered material [1]. Using octadecyl amine as a template and $Nb(OEt)_5$ as a niobium source with 0.75:1 ratio the authors [47] obtained hexagonal arranged mesostructured niobium oxide denoted Nb-TMS-1. By changing the octadecyl to $Nb(OEt)_5$ ratio to 1.0:1 and 1.25:1, the new structures were produced: Nb-TMS-3 (cubic) and Nb-TMS-4 (layered), respectively. The highest surface area of Nb-TMS-1 was 434 $m^2\,g^{-1}$ [46]. Recently, Antonelli and co-workers [7,8] reported the possibility of the reduction of niobium oxidation state in mesoporous niobium(V) oxide (Nb-TMS-1) by the encapsulation of one-dimensional potassium fulleride wires in the oxide mesopores; or by the use of low-dimensional bis(benzene) vanadium [9]; or reduction with Na-naphtalene [10]. The reduction of niobium on the walls to 4.4+ exhibits a great importance for the potential application of these materials in the catalytic processes.

Mesoporous niobia can be prepared also using amphiphilic triblock copolymers as the structure-directing block species [49]. Using Pluronic F127 [$EO_{106}PO_{70}$-EO_{106} - poly(ethyleneoxide) - b-poly(propyleneoxide)-

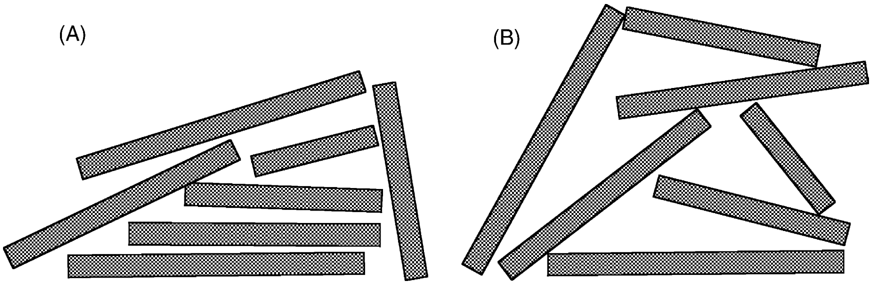


Fig. 2. Scheme of the porous niobium oxide prepared by exfoliation of $H^+/K_4Nb_6O_{17}$ with TBA^+OH^- and mixing with MgO: (A) by acid treatment, (B) by acid treatment followed on evacuation at 573 K [3].

b-poly(ethyleneoxide) with a general formula of $EO_nPO_mEO_n$] a cubic mesophase was built, whereas a hexagonal mesophase was obtained when Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) was used.

The combination of an LAT with a *vesicle templating* strategy, i.e. adding the appropriate amount of a salt to niobium ethoxide/amine gel, allows the formation of a continuous macroporous structure of niobium oxide with mesopores aligned perpendicularly to the macropore axis [6]. The BET surface area of this material was 713 $m^2 g^{-1}$ and the Horvath-Kawazoe pore size was 2.3 nm.

The interesting pulsed laser deposition (PLD) method has been also applied for the preparation of mesoporous Nb-TMS-1 [4,5]. This techniques leads to the production of thin films which generally exhibit low crystallinity. The crystallinity can be improved through reorganization induced by a brief hydrothermal treatment.

The high surface area is characteristic not only for niobia mesoporous molecular sieves but also for microporous materials. A synthesis of the microporous niobium oxide molecular sieve, Nb-TMS-6, through the use of bifunctional templating molecules was performed by Sun and Ying [25]. Unlike Nb-TMS-1 and Nb-TMS-3, which displayed long-range packing of mesopores in hexagonal and cubic arrangements, respectively, the packing of micropores in Nb-TMS-6 appeared to be rather disordered with no clearly defined crystal phases [1].

2.1.1.2. Active species.

In all niobium oxides presented above, does not matter how they are prepared, niobium species (oxide or hydroxide) plays a role of active phase in catalysis. Mostly the acidic properties of niobium oxides are referred. The acidic character of hydrated niobium oxide ($Nb_2O_5{\cdot}nH_2O$), niobic acid, is well known ($H_o \leq -5.6$) [50] and has been recently summarized by Ushikubo [51]. Jehng and Wachs [52] studied the acidity of bulk and supported Nb_2O_5 by Raman and IR of adsorbed pyridine and concluded that the highly distorted surface NbO_6 octahedral sites corresponds to the Lewis acid sites (the Raman band between 850 and 1000 cm^{-1}). Furthermore, the slightly distorted surface NbO_6 sites, as well as NbO_7 and NbO_8 sites are associated with Brønsted acid centers (Raman bands in 500–700 cm^{-1} region).

Hydrated niobium(V) oxide can be prepared in several ways. The starting material used for the oxide synthesis as well as impurities and the preparation method influence not only the textural properties but also the structure (crystalline phase) and hence the acidic properties of Nb_2O_5 [53]. The strength of the acidic sites depends on the preparation methods leading to the formation of various structures. The surface characteristics of metal oxides prepared by the microwave cold plasma heating procedure are different from those prepared by the electric furnace heating method [54–56]. Studying various metal oxides of such elements as Ca, Mg, La, Zn, Al, Nb, Ti, B, Si, Ta, W, Mo, Sugiyama et al. [56] stated that the most effective catalyst for the vapor-phase Beckmann rearrangement of cyclohexanone oxime was niobium oxide prepared by plasma-heat treatment. It was thought that a complex oxide such as Nb_2O_5–NbO_2–NbO was formed on the surface of the sample prepared by plasma treatment and that the acid characteristic was varied by this structure. Since the acid strength was weakened, oxime and lactam were easily desorbed from acid sites. As a result, the lactam selectivity of the plasma treated sample was improved. This is a well illustration of the improvement of the catalytic efficiency by the decrease of the acidic strength.

The different binding energy of niobium in various niobium oxides determines its properties (among others the oxidation state and its stability). The stabilization of niobium influences the catalytic properties of Nb oxides. To achieve the material active in the redox catalysis, too high stability of Nb is unfavorable because it decreases the reducibility of niobium. The discovered possibility of Nb reduction in mesoporous niobium oxide, Nb-TMS-1, by various agents [7–10] opens the new area in the catalytic application of these materials. On the other hand, if one wants to apply Nb oxides for the reaction carried out in the liquid phase, the higher stability of niobium species protects the catalysts from leaching of the active phase. Moreover, the level of Nb stability determines the strength of active centers.

2.1.1.3. Niobia as a support.

The preparation of niobium oxides exhibiting the high surface areas opened new possibilities in their application as supports for various active phases. Niobia is a typical SMSI oxide. It has been already used as an oxide support for a lot of metals. The list of papers devoted to the application of niobium oxide as a support still increases. The following metals supported on niobia has been already described in the literature: Ru [57], Rh [58,59], Pt [60–63], Pt–Sn [64], Re [57], Ni [40,41,65–67], Cr [57,68], W [57], Co [39,69,70], V [38,57,71,72], P [71], Ge [71], Mo [34,35,57,71], Sb [71], Pb [71], Bi [71], Ce [73], and Fe [74]. The properties of the niobia are improved by the addition of these elements, while its high selectivity is still maintained. These kinds of niobia which exhibit high surface areas gives rise a higher dispersion of metals which enhances the catalytic activity of the materials.

The example is niobia supported vanadia catalyst. A metal oxide (i.e. V_2O_5) species can be deposited over a large surface area of a niobia support by the reaction of the surface hydroxyls of niobia with, e.g. vanadium triisopropoxide. A comparison of the reactivities of surface vanadia species loaded on various oxide supports in the methanol oxidation reaction reveals that niobia supported vanadia species are among the most active catalytic systems for this reaction [75]. This high reactivity is associated with the facile reduction of the bridging V–O–Nb bond and reflects the favorable redox potential of the niobia support compared to less reducible supports such as silica and alumina. The redox potential of the niobia support also enhances the redox properties of other reducible surface metal oxide species (V, Cr, Mo, and Re) [76].

The strong interaction between niobia surface and supported metal not always is favorable for the catalytic process. For some reactions, like oxidation of ethene, niobia supported vanadia catalysts do not exhibit the sufficient activity (when one compare with the other supports applied—alumina, zirconia, titania) due to solid-state reaction between the surface vanadia species and the niobium oxide support [38]. That reaction affects the nature of the active sites, which are associated with the V–O support bond.

2.1.2. Mixed oxides and niobia supported on various oxides

The main approach to use mixed oxides containing niobium and niobia supported on various oxides is the catalytic application of their redox properties as well as Lewis acidity of niobium species.

Niobium oxide has been already supported on various oxides: silica [18,40,77–83], alumina [84–87], magnesia [84,87], titania [84,85,88,89], zirconia [84,85]; and zeolites: Y-type [90–92] and ZSM-5 [90,93]. Recently, mesoporous molecular sieves of MCM-41 and MCM-48 type containing silica or aluminosilica lattices have been also applied as effective supports for niobium oxide species [1,18,21,22]. It is known [94] that if the support surface exhibits basic properties, a highly distorted NbO_6 groups are formed, whereas acidic surfaces lead to the formation of slightly distorted NbO_6, NbO_7, and NbO_8 groups. The surface niobia species depends not only on the nature of the support but also on the surface coverage. It has been stated by Jehng and Wachs [52,76] that fourfold coordinated surface NbO_4 species appear at very low surface coverages ($\theta_{Nb} \ll 1$), fivefold coordinated surface NbO_5 species are present at intermediate surface coverages ($\theta_{Nb} < 1$), and sixfold coordinated surface NbO_6 exist at high surface coverages ($0.5 < \theta_{Nb} < 1$). The formation and location of the surface niobium oxide species are controlled by the substrate's surface hydroxyl chemistry. Therefore, on silica, only NbO_4 is present because high surface coverages cannot be achieved on this support due to the low number and reactivity of the silica surface hydroxyls [52].

Most frequently silica and alumina are used as supports for Nb oxides. The addition of niobia to alumina increases the surface acidity of the alumina [94]. Lewis acidity was found in all of the supported niobium oxide systems, while Brønsted acid sites (BAS) were only detected in niobia supported on alumina and silica.

There is no doubt that the catalytic properties of niobia supported on metal oxides depend on the nature of the support. The identity of the support strongly affects the reactivity of the surface niobium oxide species and determines whether its sites are active for redox or acid catalysis. Wachs and co-workers [42] applying Raman spectroscopy analyses of niobia supported on magnesia, titania and zirconia provided the evidence that the NbO_x surface species consists of Nb=O form (the band at $980\,cm^{-1}$) as well as Nb–O–Nb species characterized by the bands at 880 and $935\,cm^{-1}$. Moreover, the infrared spectra in the hydroxyl region indicated the creation of new OH groups (non-acidic or weakly acidic) in niobia supported on zirconia and titania (Nb–OH, Nb–OH–Zr, Nb–OH–Ti). Similar bridged OH groups were also found in niobosilica mesoporous Nb/MCM-41 molecular sieves prepared by sol–gel method [12,15,17] and will be discussed later.

The surface niobium oxide overlayer is quite stable even at high calcination temperatures due to the strength of the surface niobium oxide–support interaction (SOSI) [94]. However, if this interaction is too strong, as in the case of basic oxide supports such as magnesia or bismuth oxide, after the acidic Nb^{5+} introduction the chemical reaction occurs between both oxides [76]. In such a case mixed oxides are formed. If the interaction of niobium with the support is not too strong, it can lead to grafting or anchoring of Nb on the oxide surface. Both, grafting or anchoring are kinds of solid-state interaction. Therefore, sometimes there is not too big difference between the catalytic properties of mixed oxides and those obtained by niobia supported on metal oxides. In the latter case, it is easier to adjust the number of active niobia species located on the surface available for reagents taking part in the catalytic processes. On the other hand, the stability of grafted species usually is lower than that formed on the surface of mixed oxides prepared, e.g. by sol–gel method.

The formation of anchored Nb dimers on silica was mentioned by Ichikuni and Iwasawa [83]. However, most authors (e.g. Wachs et al.) indicated and agree that only isolated Nb species can be formed on silica due to the low number of OH groups on its surface.

The reaction schemes of Nb(V) oxide grafted on silica are shown in [95] and are as follows:

$$\mathrm{NbCl_5} + 5\mathrm{C_2H_5OH} \overset{\mathrm{CCl_4}}{\rightarrow} \mathrm{Nb(OC_2H_5)_5} + 5\mathrm{HCl} \qquad (1)$$

$$n \equiv \mathrm{SiOH} + \mathrm{Nb(OC_2H_5)_5} \overset{\mathrm{CCl_4}}{\rightarrow} (\equiv\mathrm{SiO})n\mathrm{Nb(OC_2H_5)}_{5-n} + n\mathrm{C_2H_5OH} \qquad (2)$$

$$(\equiv\mathrm{SiO})n\mathrm{Nb(OC_2H_5)}_{5-n} + (5-n)\mathrm{H_2O} \rightarrow (\equiv\mathrm{SiO})n\mathrm{Nb(OH)}_{5-n} + (5-n)\mathrm{C_2H_5OH} \qquad (3)$$

The described grafting can lead to the creation of the active species or can produce an useful support for the immobilization of organometallic active phase [95].

Niobium, in mixed oxides and niobia supported on various oxides, usually exist in the oxidation state +5, and it is well known that its reducibility is difficult and depends, among others, on the surrounding of Nb species. Some catalytic reactions, as isomerization and oligomerization of olefins, require the reduced forms of niobium species. Wada and Morikawa [96] observed the activity in these reactions of Nb^{4+} species formed on the pure niobium oxide or the mixed oxides with silicon by the reduction with hydrogen or photoreduction. The reduction of Nb^{5+} to Nb^{4+} with hydrogen requires very high temperatures as mentioned earlier [2], and it depends on Nb coordination and surroundings. The hydrogen reduction of niobium located in the framework of mesoporous molecular sieves, Nb/MCM-41, occurs at temperatures higher than 1100 K, whereas niobium species introduced via impregnation of siliceous MCM-41 is reduced at lower temperature (920–950 K) [T]. Prakash and Kevan [26] effectively reduced Nb located in the framework of MFI zeolite structure by γ irradiation.

The last years has brought the increasing interest in niobium-containing mesoporous molecular sieves. Mesoporous molecular sieves of MCM-41 type (a member of M41S family) discovered in 1992 [97] initiated the production of various metal substituted metallosilicates of MCM-41 structure, which are in fact mixed oxides. Niobosilicate mesoporous molecular sieve, denoted Nb/MCM-41 was the first time synthesized in 1997 [11,12,23]. Niobium species in this material can play various functions in heterogeneous catalysis: active phase, support or promoter. Mesoporous molecular sieves (M41S) prepared through supramolecular templating have a highly defined mesopore structure and extremely large surface areas. The member of M41S family, MCM-41 material, possesses a hexagonal array of uniform mesopores. The local structure and bonding of MCM-41 materials are amorphous in nature, similar to amorphous silica [98]. The other representing of M41S family, MCM-48, exhibits three-dimensional arrangement of mesopores forming the cubic structures.

Hydrogen forms of Nb/MCM-41 indicate the presence of bridged Nb–OH–Si groups presenting the acidic character [12]. The number of BAS calculated from the FTIR studies after adsorption and desorption of pyridine is about four times lower on H-Nb/MCM-41 than on H-Al/MCM-41 material. Moreover, the strength of BAS is lower on H-Nb/MCM-41 than on H-Al/MCM-41, which was concluded on the basis of the pyridine chemisorp-

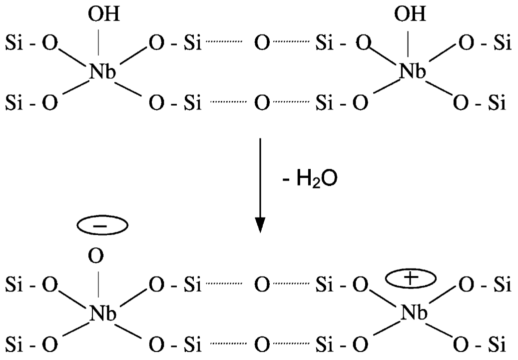


Fig. 3. Dehydroxylation of H-Nb/MCM-41 mesoporous molecular sieve [17,21,22].

tion strength and the activity in the test reactions. H-Nb/MCM-41 materials were inactive in the cumene cracking which requires the presence of strong BAS, whereas the H-Al/MCM-41 catalyst was active in this reaction.

Moderate strength Lewis acid sites are generated during the dehydroxylation of hydrogen forms of Nb-containing mesoporous molecular sieves (H-Nb/MCM-41 materials) [12]. The formation of the active species is proposed to occur according to the scheme presented in Fig. 3 [17,21,22]. In fact, the electron is not located on one oxygen but on the whole number of oxygens in the surrounding of Nb, as well as positive charge is used for the indicating of a hole center which works as an electron trap.

Such materials can be useful catalysts for processes requiring the presence of Lewis acid sites where a high acid strength induces the undesirable side reactions and/or coke formation. Thus, they have been proposed as catalysts for the synthesis of thiols and organic sulfides from alcohols and hydrogen sulfide [1,13,15,17].

The same material exhibits a very high activity in the oxidation of organic compounds with hydrogen peroxide [1,13,15,17,18,21,22,99,100]. The oxidizing properties of the Nb/MCM-41 materials are proposed to be due to the presence of an active lattice oxygen, which is formed during the dehydroxylation of the molecular sieves (see Fig. 3) and was identified by ESR measurements [21]. The generation of this active oxygen is accompanied by the formation of Lewis acid sites as established by FTIR studies following pyridine and lutidine adsorption [12]. The infrared spectra scanned after adsorption of NO provide us with additional evidence for the existence of Nb^+ and NbO^- species on the surface of dehydroxylated Nb/MCM-41 [15,21]. The experimental data, which allowed drawing the scheme presented in Fig. 3 are summarized in Table 2.

The nature of active species formed on the surface of Nb/MCM-41 materials depends on both, Nb source [21,24,101] and Si/Nb ratio [21]. The $Nb–O^-$ paramagnetic center is well detected by ESR spectra (a sharp ESR signal at $g = 2.0025$) on both Nb/MCM-41 (Si/Nb = 32) prepared from niobium oxalate and from niobium chloride [21] although their oxidation properties differ, which will be discussed in the next section. The concentration of Nb species strongly influences the oxygen species formed on the surface. If one applies Si/Nb ratio of 16 in Nb/MCM-41 prepared from niobium oxalate, the ESR spectra varies from those registered for Si/Nb = 32 samples [21]. The ESR signals observed for Nb/MCM-41 (Si/Nb = 16) with $g = 2.0010$,

Table 2
The results of spectroscopic investigations of Nb/MCM-41 prepared according to the procedure described in [11,12] (niobium oxalate used as Nb source, Si/Nb = 32) and activated under vacuum

Technique	Comments	References
Electron spin resonance (ESR)	Activation at 723 K, spectra recorded at 77 K. A sharp signal with $g = 2.0025$ due to a hole localized on an oxygen atom existing near niobium atom, i.e. NbO^- species	[15,21]
Infrared spectroscopy (FTIR) followed by pyridine (Py) and lutidine (Lu) adsorption and desorption	Activation at 673 K. Number of BAS[a] and LAS[a] calculated per 1 g of the catalyst on the basis of IR bands observed after desorption of Py at 423 K and extinction coefficient of Py. BAS = 7; LAS = 522	[12]
Infrared spectroscopy (FTIR) followed by NO adsorption	Activation at 723 K. NO adsorbed at room temperature. Bands at 1629 cm^{-1} due to $Nb–O^-NO$ and 1808 cm^{-1} from Nb^+NO	[21]

[a] BAS (LAS)—Brønsted (Lewis) acid sites.

2.0049, and 2.039 became attributed to O_2^- radical, and another one with $g = 1.987$ assigned in the literature to the lattice defects [102] formed by the desorption or dissociation of oxygen (in [103] due to photo-irradiation under vacuum). The signal intensity decreased with O_2 introduction and heating at 723 K. It was caused by the readsorption of oxygen on the surface of the sample. The described behavior can be explained by the high concentration of Nb–O^- species in Nb/MCM-41 (Si/Nb = 16, prepared from Nb-oxalate) which results in the easier release of oxygen than that from the sample with Si/Nb = 32. The $g_{zz} = 2.039$ of O_2^- radicals well correlates with that calculated by Che and Giamello [103] for O_2^- interacting with M^{4+} cations. Therefore, one can suppose that with a high Nb content (Si/Nb = 16) the partial reduction of Nb^{5+} to Nb^{4+} occurs under evacuation leading to the interaction with O_2^-. It has been also considered that the higher content of Nb in Nb/MCM-41 materials causes partially location of Nb oxide species in the extra framework position.

Recently, Wachs and co-workers [24] examined Nb/MCM-41 molecular sieves synthesized from Nb-etoxide and supported Nb_2O_5/SiO_2 systems. They used in situ Raman and UV-Vis-NIR diffuse reflectance spectroscopies for the structural characterization and demonstrated that similar surface Nb oxide species are present in both Nb/MCM-41 and Nb_2O_5/SiO_2 catalysts and they are sensitive to the environmental conditions (ambient or dehydration). Under dehydrated conditions, the Nb cations in Nb/MCM-41 and 1% Nb_2O_5/SiO_2 are predominantly composed of isolated NbO_4 units, while polymerized surface niobia species and/or bulk Nb_2O_5 are formed at high Nb loadings on SiO_2. Both types of materials present Nb–O–Si bonds in their structures.

Although, the niobium surface species in supported forms and incorporated into the framework during the synthesis can posses a similar structures, their stability and reducibility properties can be different. In fact, it was documented [21] that the reduction with hydrogen is easier when the supported Nb/MCM-41 sample is investigated (it occurs at 920, 943 K depending on Nb source), while that of Nb in the framework occurs very difficult (the reduction peaks in H_2-TPR profiles appear above 1000 K). The stability of niobium incorporated into the framework of Nb/MCM-41 material is higher than that observed for Nb impregnated siliceous MCM-41. In the latter case niobium is easier leached under liquid phase reaction conditions [18]. The distinguish between Nb located in the framework and extra framework positions in Nb/MCM-41 materials can base on H_2-TPR and FTIR measurements in the skeletal range. The Si–O–Si vibrations observed in the 1020–1100 cm^{-1} range are perturbed in the various manner depending on the location of the niobium cations (framework or extra framework) and their interaction with Si–O–Si vibrational mode [20]. The appearance of two IR bands in the transmission window (850–1000 cm^{-1}) on the Nb(from oxalate)MCM-41 (Si/Nb = 16) sample evacuated at 723 K indicates the presence of two various Nb species interacting with T–O–T vibration. It was proposed that they are NbO^- and Nb^+ in the framework which shift a band (1020–1100 cm^{-1}) of a skeletal vibration of Si–O with various $\Delta\nu$ depending on the strength of the interaction, determined by the ion charge. The discussed Nb species origin from the framework, because the chemisorbed molecules (NO) raise the intensity of the perturbed vibrational bands. It can occur only when niobium is localized in the framework (Si–O–Nb), because its interaction with NO molecule lengthens Nb–O bond and shortens Si–O bond causing the increase of the perturbation effect. This effect runs in an opposite way if Nb is localized outside the framework (as in the impregnated samples). This is because of the strong interaction of Nb-extra framework species with the adsorbate (NO) weakness its interaction with the skeletal T–O–T vibrations reducing the intensity of the perturbed IR bands.

The existence of various types of framework and extra framework Nb species was confirmed by the results of the H_2-TPR studies. The samples prepared from Si and Nb sources exhibit both extra framework and framework positions, both occupied by various Nb species, which present various possibility of the reduction. Framework Nb species are reduced at a higher temperature than that of the reduction of the extra framework niobium cations. The reduction temperature depends on a kind of Nb salts used for the synthesis of Nb/MCM-41 materials. It is lower for the framework Nb if the sample is prepared from niobium oxalate than when $NbCl_5$ is used for the synthesis of mesoporous sieves. The role of the anion nature in the Nb source on the properties of the final material is proved by the H_2-TPR experiments.

Niobium-containing mixed oxides and niobium supported on various oxides are used not only in catalysis where niobium species plays a role of the active phase, but also in such processes in which Nb species acts as a support of promoter.

Niobium-containing mesoporous molecular sieves (Nb/MCM-41) have been already used as supports for metals such as Cu [16,17,19,20], Ni [17,104,105], and Fe [106]. The metal–support interaction causes the changes in the reducibility of both niobium and supported metal species. That, of course, determines the catalytic activity. Moreover, the modification of niobium-containing MCM-41 material with nickel leads to the higher dispersion of metal (after reduction with H_2) than that noted for pure siliceous or alumino-silica samples used as a support for Ni [105].

2.1.3. Niobium oxide species as additive

Small amount of niobium oxide species added to the catalyst (usually mixed oxides) can play a role of a promoter. It can be a structural promoter, as in Pd/Al_2O_3 system [107], where niobia favors the ideal Pd^0/Pd^{2+} surface ratio thanks to the existence of NbO_x polymeric structures near the monolayer.

The redox potential of niobia enhances the redox properties of some metal oxides (V, Cr, Mo, etc.) if they are supported on niobia. In such a case Nb_2O_5 plays a double role, a support and a promoter. However, if niobia is applied as a support for vanadia the solid-state reaction between vanadia layer and the underlying support inhibits the activity of the catalyst [38]. To obtain a promoting effect usually a low quantity of niobium oxide species should be added. Nb–V–Si [32] and Mo–V–Sb–Nb [36] oxide systems can be examples of materials in which niobium species acts as a promoter. In the latter material, the authors identified $SbVO_4$ and $Mo_{0.61–0.77}V_{0.31–019}Nb_{0.08–0.04}$ phases.

The addition of surface niobia species to vanadia/titania catalysts does not change the molecular structure or redox properties of the surface vanadia species. However, the surface niobia species may or may not influence the catalysts' activities. Specifically, (i) reactions requiring only one surface vanadia redox site are not influenced by the surface niobia species (e.g. methanol oxidation) and (ii) reactions requiring adjacent surface redox and acid sites are enhanced by the surface niobia species (e.g. the selective catalytic reduction (SCR) of NO with ammonia).

2.2. Niobium phosphates

Niobium phosphates, which exhibits a higher acidic strength ($H_o \leq -8.2$) than niobic acid, have been widely studied in the past [1]. Hydrated niobium phosphate, $NbOPO_4 \cdot nH_2O$, consists of layers of composition $NbO(H_2O)PO_4$ in which NbO_6 distorted octahedra are connected in their equatorial planes by PO_4 tetrahedra via sharing corners.

Recently, the deep spectroscopically (FTIR, UV-Vis) studies of the active centers on the niobium phosphate catalysts were carried out by Carlini and co-workers [108]. In both, niobic acid and niobium phosphate, Nb is octahedral, but impregnation of niobia with phosphoric acid converts Nb into a higher coordination species. The basic structural units of amorphous niobium phosphate studied by the authors, are NbO_6 distorted octahedra and tetrahedral orthophosphate species, similar to those present in the bulk of crystalline $NbPO_5$. All phosphate-containing samples, bulk and impregnated, indicate the presence of both terminal POH and NbOH groups. The POH groups of bulk amorphous niobium phosphate are characterized by a slightly stronger Brønsted acidity than those of the impregnated material, whereas NbOH sites appearing to be weaker as Brønsted acids than POH groups. The Lewis acid strength is similar for both kinds of niobium phosphate samples and are assigned to coordinatively unsaturated Nb^{5+} sites. All of these materials exhibit a high activity in the dehydration of fructose to 5-hydroxymethyl-2-furaldehyde (HMF), but bulk niobium phosphate inhibits the polymerization of HMF making this catalyst more promising from the practical point of view [108,109].

A new family of mixed vanadium phosphorus–niobium phosphorus (VPO–NbPO) catalysts was prepared and characterized [110,111]. In this kind of catalysts exhibiting the redox properties, Nb in VPO phases and V in NbPO particles were observed. The interaction between vanadium and niobium species modifies the V^{5+}/V^{4+} balance in a favorable way. It has been concluded that doping by Nb creates superficial defects, responsible for C–H *n*-butane activation, which have been observed as associated with Lewis acid sites of low acidity. This is the reason for the enhancement of the *n*-butane conversion in the oxidation process. Selectivity to maleic anhydride is not modified by Nb doping while CO_2/CO is increased due to the higher V^{5+}/V^{4+} ratio [111].

2.3. Niobium nitrides, carbides, sulfides

Small atoms, such as carbon, nitrogen or oxygen, dissolved interstitially in the lattice of early transition metals produce a class of compounds with unique physical and chemical properties [112] such as electronic, magnetic and refractory. These materials are referred to as metal (oxy)nitrides and (oxy)carbides. Their catalytic activities have been compared to those of noble metals. There are not yet too many papers devoted to these kinds of catalysts. Niobium in nitrides does not reach the oxidation state +5, and the following compounds exist: Nb_2N-β-phase (hexagonal), Nb_4N_3-γ-phase (tetragonal), and NbN-δ-phase (cubic) [113]. Another subnitrides, Nb_5N_2 and Nb_3N_2 clusters, can be produced in molecular beam with laser vaporization of niobium in nitrogen atmosphere at 300 K [114].

Nitrides are commonly prepared by the direct interaction between transition metals and dinitrogen or ammonia. They are also prepared by nitridation of a Nb oxide precursor [1].

Taking into account the possible use of niobium nitrides in catalysis one ought to obtain the materials exhibiting high surface areas. Brayner et al. [112] prepared extruded niobium oxynitrides with macropores and tested them in the cyclohexane dehydrogenation reaction. The materials were active, but they were less stable than molybdenum and tungsten oxynitrides when exposed to air. The authors correlated this feature with a faster superficial oxidation process. Niobium oxynitrides do not show a sufficient activity also in hydrazine decomposition [115]. In both, laboratory and industrial scales their activity were lower than that of tungsten oxynitride and Shell catalyst. The authors stated that modification in thruster design and/or granulometry of niobium oxynitride can improve system performance. The increase in the catalytic activity can be reach by the supporting of the active phase on the appropriate material. The alumina supported niobium oxynitrides exhibiting the surface areas of 179–190 $m^2\,g^{-1}$ and prepared by chemical vapor deposition (CVD) method were tested in thiophene hydrodesulfurization (HDS). The catalysts revealed low activity in the initial stage of the reaction, but the activity increased after 200–300 min from the started point to ca. three times the initial activity. The activity of the niobium nitride catalysts decreases by sulfur accumulation on the surface and nitrogen released from niobium nitride.

Niobium carbides can be prepared by a variety of methods including direct union of the elements at high temperature (e.g. in solar furnace) or by self-propagating high-temperature reaction, carburization of oxides by carbon or methane–hydrogen mixtures, carburization of niobium pentahalide, spray-dried-powder technique or by mechanochemical synthesis or by plasma-chemical process [116]. Five solid-phase regions exist in the niobium–carbon system: a solid solution of carbon in niobium (b.c.c.), Nb_2C (h.c.p.), NbC (f.c.c.), ζ-Nb_4C_{3-x}, and ζ-NbC_{1-x} [117]. The composition range of Nb_2C is very limited at low temperatures, whereas NbC varies from $NbC_{0.7}$ to $NbC_{0.99}$.

Niobium carbides, like nitrides, were tested in hydrotreating processes. Bimetllalic Nb–Mo carbide was applied in hydrodenitrogenation (HDN) and HDS carried out in a high pressure reactor system [118]. The HDN activity for quinoline was high and independent on Mo–Nb composition, whereas HDS process was more sensitive to Mo–Nb ratio. The bimetallic compounds show enhancement in the activity and stability compared to the corresponding monometallic carbides.

It seems that still it is far way from the application of niobium oxynitrides and carbides in heterogeneous catalysis. However, the study on the use of niobium nitrides and carbides in heterogeneous catalysis should be developed, because the related substances based on the other early transition metals have already indicated their high catalytic activity.

Niobium sulfide has been found to be an interesting new active phase for HDS [119–121]. It possesses unique acidic properties useful in hydrotreating reactions [122]. Unsupported niobium sulfides are usually prepared by direct combination of the elements in evacuated silica tubes followed by intercalation–deintercalation treatment to improve the surface area [123]. NbS_x with x = ca. 1.5 or 1.7 have been obtained earlier from Nb_2O_5 and H_2S at 973 K [124].

Unsupported niobium trisulfide exhibits a better activity in the HDS of thiophene than molybdenum disulfide [121]. If it is supported together with Ni on carbon, the catalyst exhibits the high HDS activity and the presence of Ni decreases the selectivity for hydrogenation. The nature of the support and the sulfurizing agent strongly influence the niobium sulfide phase and its catalytic activity. Allali et al. [120] applied carbon and γ-alumina as supports for niobium sulfide and depending on the preparation and activation methods identified various phases: NbS_3, NbS_2, and $Nb_{1-y}S$. Generally niobium sulfides are sensitive to supports effects.

Niobium sulfide was used as a dopant phase to the traditional NiMo hydrotreating catalyst (i.e. alumina supported) and caused the enhancement of the HDS and HDN activity [119]. The authors indicated that niobium is present as NbS_2 layers, well dispersed on the support and in close contact with the other active components. NbS_2 plays a role of an additional active phase.

3. Processes

The catalytic reactions in which niobium-containing materials have been already studied are summarized in the review paper [1]. They are as follows: dehydration of alcohols, dehydrogenation, oxidative dehydrogenation, oxidation, ammoxidation, oxidative coupling of methane, esterification, alkylation, isomerization, hydrogenolysis, disproportionation of hydrocarbons (methathesis), hydrogenation, NO decomposition and reduction, HDS and hydrodenitrification, fine chemicals syntheses, photocatalysis. From 1999 (the date of the review paper has been published), the main focus has been done on the oxidizing properties of Nb-containing materials. Therefore, in this section the role of niobium species in the oxidation processes will be discussed. Moreover, the effect of Nb in the protection of the catalysts against sulfur dioxide poisoning will be shown.

3.1. Oxidizing activity

In the last few years, niobium-containing catalysts have been studied in the liquid phase oxidation of organic sulfides [15,17,18,21,22,99], cyclohexene [22,100], α-pinene [101], as well as in the gas phase selective oxidation of ethane [38], propane [36], *n*-butane [110,111], oxidative dehydrogenation of propane [32–34], oxidation of alcohols [24,125,126], and ammoxidation of 3-picoline [35].

The behavior of most oxidation catalysts can be interpreted within the framework of a redox mechanism (reduction–oxidation). That is a general agreement that partial oxidation of organic compounds almost exclusively involves redox cycles during which lattice oxygen oxidizes the organic molecule leaving a reducing center that is oxidized by O_2, i.e. the so-called Mars–van Krevelen mechanism. It can be illustrated as follows:

$$\text{Cat-O} + \text{R} \rightarrow \text{RO} + \text{Cat} \qquad (4)$$

$$2\text{Cat} + \text{O}_2 \rightarrow 2\text{Cat-O} \qquad (5)$$

Contrary, there is no agreement on the role of “electrophilic” adsorbed oxygen (O_2, O_2^-, or O^-) and also the details of the activation mode of C–H hydrocarbon bonds are under discussion. Peroxometal and oxometal pathways are proposed for the transfer of oxygen to the reactant [127]. Peroxometal pathways usually involve early transition elements with d^0 configuration. The existence of oxometal or peroxometal pathways depends also on the nature of the substrate.

There are the following factors, which should be considered in the discussion of the oxidizing activity of niobium-containing catalysts:

(1) reducibility of niobium,
(2) isolation of niobium species,
(3) leaching of niobium,
(4) presence and mobility of active oxygen,
(5) acidity of the catalyst,
(6) Nb source used in the catalyst preparation,
(7) Nb–O–T angle.

3.1.1. Reducibility of niobium

The oxidizing activity of metal oxides is determined by the reverse oxidation–reduction availability of metal. It is known that vanadium is easier reduced than niobium and it is one of the reasons of its wider application in the oxidizing catalytic reactions. The increase of niobium reducibility is reached by changing of Nb surrounding, i.e. moving from bulky niobium oxides to supported or mixed oxides. The well example is Nb/MCM-41 mesoporous molecular sieve exhibiting a very high activity in the liquid phase oxidation of organic sulfides and cyclohexene [22,100,128]. The interaction of niobium with the other elements can lead to the increase of the reducibility of niobium species. If this effect is reached by location of metals (Cu, Ni) in the extra framework positions in Nb/MCM-41 material [20,105] the reducibility of niobium is enhanced but not the oxidizing properties of the material because the active centers are covered by metal cations.

3.1.2. *Isolation of niobium species*

The concentration of niobium on the support or in the mixed oxides determines the distance between two niobium active species, which influences the oxidizing activity. In the liquid phase reactions with hydrogen peroxide as an oxidizing agent, the presence of niobium dimers or oligomers on the support can be responsible for the decomposition of peroxide. Therefore, the isolated Nb are required for the high activity in these processes. The interesting effect was reached by Kapoor and Raj [101] by the grafting of MCM-41 and MCM-48 with niobium salts. The authors compared the activity of grafted materials and synthesized Nb/MCM-41 and Nb/MCM-48 and they found the much higher activity of the grafted samples in the oxidation of α-pinene. They correlated this feature with the isolation of niobium sites and their existence in tetrahedral structure. It is worthy of note that the authors synthesized Nb/MCM-41 sieves containing 2.0 wt.% of niobium. However, if the concentration of Nb in the skeletal of synthesized Nb/MCM-41 was not too high (for instance $Si/Al = 32$ or 64) a very high sulfoxidation [15,17,18,21,22,99] and epoxidation [22] activity were observed. Suo and co-workers [100] applying Nb/MCM-41 containing 1.43 wt.% of Nb also detected the high activity in the oxidation of cyclohexene with hydrogen peroxide.

The activity of Nb-containing catalysts in the gas phase oxidation does not depend on the location of niobium in the siliceous matrix. Wachs and co-workers [24] did not observe the significant difference in the reactivity of Nb/MCM-41 and Nb_2O_5/SiO_2 in the oxidation of methanol. The spectroscopic studies performed by the authors revealed that under dehydrated conditions, the Nb cations in Nb/MCM-41 and 1% Nb_2O_5/SiO_2 are predominantly composed of isolated NbO_4 units, while the Nb cations in the supported Nb_2O_5/SiO_2 catalysts possess polymerized NbO_x species and/or bulk Nb_2O_5 with the increasing Nb loading.

It is worthy of notice that only the surface niobia species on silica give rise to methanol oxidation products (primarily formaldehyde and methylformate), while the surface niobia species on alumina, titania and zirconia primarily lead to the formation of acidic products (dimethyl ether). Thus, the nature of the oxide support controls the redox properties of the surface niobia species [75,76].

The isolation of niobium species on the catalyst surface is an important factor only in that case when Nb species plays a role of an active phase. In the reactions such as oxidative dehydrogenation of propane or selective oxidation of hydrocarbons in a gas phase, niobium is a promoter, which enhanced the activity of, for instance, vanadium in the catalyst. Isolation of Nb in this case is not considered, but the amount of promoter is usually negligible and therefore, dimers are not formed.

3.1.3. *Leaching of niobium*

In the reactions performed in the liquid phase, the leaching of the active phase is possible. To reduce this problem, the well immobilization of redox-active elements in a solid (inorganic) matrix is necessary. Arends and Sheldon [127] stressed that it can be achieved by isomorphous substitution of metal ions in framework positions of molecular sieves, which is equivalent to the sol–gel production of mixed oxides, but performed with using of the organic template. Amorphous mixed oxides are also formed as a result of impregnation (gafting). Alternatively, metal complexes can be tethered to the surface of solid, e.g. silica, via a spacer ligand. It was indicated that niobium isomorphously substituted to siliceous MCM-41 mesoporous molecular sieve is more stable (resisted from leaching) than Nb grafted on MCM-41 by impregnation if the materials were used in the sulfoxidation with hydrogen peroxide [18].

3.1.4. *Presence and mobility of active oxygen*

Bulk niobium(V) oxide exhibits the redox activity if niobium oxide anions (up to $Nb_6O_{15}^{-}$) are generated by laser ablation [125,126]. Metal–oxygen double bond is responsible for its activity in the gas phase oxidation of methanol [126]. In the first step alcohol condenses at a cluster metal–oxygen double bond to yield Nb(OH)(OCH_3). Nb oxidation state does not change in this step. The so-formed niobium–hydroxyl bond is the new reactive site in the cluster, and undergoes ligand switching in a follow-up collision to yield a bis-methoxy cluster and neutral water. These results confirmed the earlier hypothesis that higher order Nb–O bonds are the catalytic active centers on Nb oxide surface.

Wachs and co-workers [24] studying the oxidation of methanol on silica supported niobia and Nb/MCM-41 molecular sieves evidenced that the presence of Nb–O–Si bonds in the structure of both kinds of materials determine their oxidation activity. Such bonds influence not only the reducibility of niobium but also the activity of oxygen, which can be trapped on Nb. There is not doubt that niobium incorporated to the molecular sieve framework has an oxidation state +5 [15,21,26]. The results obtained in my group [15,21] strongly support our earlier hypothesis about the formation of an active oxygen radical on niobium incorporated into the framework of mesoporous molecular sieve of MCM-41 type. It is formed according to the scheme presented in Fig. 3. This oxygen oxidizes, for instance, NO after its adsorption at room temperature to nitrate/nitrite species [21]. It exhibits also the high activity in the sulfoxidation and epoxidation reactions. The formation of NbO^- species is accompanied by the generation of week Lewis acid sites [12,21], which also are involved in the catalytic oxidation.

3.1.5. *Acidity*

The role of the acidic centers in the oxidation processes has been pointed out earlier [129]. Acid–base properties depend on the covalent/ionic character of metal–oxygen bonds and are involved in some steps of the oxidation reactions such as the activation of the C–H hydrocarbon bonds, the step associated with the evolution of alkoxide species and the desorption/overoxidation of the partial oxidation products. Thus, they participate with the cation redox properties in determining the selective/unselective catalyst behavior.

A key factor for performing selective oxidation catalysis is to allow the desired product to desorb without further transformation and overoxidation. So, the catalyst should not react too strong with these compounds. This can be well illustrated by the epoxidation of cyclohexene on Nb/MCM-41 molecular sieves. If the material exhibiting a week acidity was applied, the high yield of epoxide was registered [12,22], whereas the similar material, but produced from niobium chloride, showing the higher acidity, indicated the high production of glycols [100]. It is known that the epoxide ring is opened on the enough strong acidic center. Therefore, the strength of the acidic sites (if present) cannot be too high for the selective oxidation to epoxy product.

3.1.6. *Niobium source*

As mentioned above, the synthesis of Nb/MCM-41 from niobium(V) chloride [100] led to the other catalytic selectivity in the oxidation of cyclohexene than that of the material produced from niobium oxalate [22,128]. The latter exhibits the higher epoxidation activity. This behavior depends also on the nature of reactant. Kapoor and Raj [101], who studied the epoxidation of α-pinene on niobium grafted silica, compared the activity and selectivity of materials grafted with niobium oxalate and niobium ethoxide. The samples grafted with niobium ethoxide showed a reasonable increase in catalytic activity and H_2O_2 efficiency if compared with that observed on Nb-oxalate grafted material.

A nature of Nb source influences also the oxidizing properties of Nb/MCM-41 sieves in relation to the adsorbed molecules, e.g. NO [21]. The formation of nitrato/nitrito species upon nitrogen(II) oxide adsorption on Nb/MCM-41 at room temperature (IR bands below 1600 cm^{-1}) depends on Nb source and changes in the following sequence:

$$\begin{aligned}&\mathrm{Nb(oxalate)MCM\text{-}41}\\ &\quad > \mathrm{Nb(ammonium\text{–}oxalate\ complex)Nb/MCM\text{-}41}\\ &\quad > \mathrm{Nb(chloride)MCM\text{-}41}.\end{aligned}$$

This order is in agreement with the activity in the *n*-dibutyl sulfide oxidation in a liquid phase, and also with the physical parameters of the materials; namely, a pore size and a pore volume. Pore size in mesoporous materials determines the T–O–T angle [130].

3.1.7. *Nb–O–Si angle*

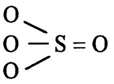
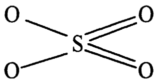
V–O–Si bond angle in V/MCM-41 mesoporous molecular sieves has been considered in relation to the redox activity of the samples in the liquid phase oxidation of cyclohexene [129]. The bond strength is closely related to the electron density of the active metal sites. The latter is "tuned" by the pore size through variation of V–O–Si bond angles. The higher T–O–T bonds angle the higher pore size in MCM-41 materials can be registered. The electron density depending on the T–O–T angle affects the effective redox potential on metal sites. The maximum activity is achieved for the metal for which reactants presumably have an intermediate strength of adsorption. Therefore, the authors [130] observed the volcano curve for the dependance of the activity on the pore size of V/MCM-41 mesoporous sieves.

The same seems to be true for Nb/MCM-41 as indicated and discussed in [128]. This behavior is closely connected with the influence of Nb source on the redox activity, because the niobium source determines the texture and structure of the MCM-41 mesoporous molecular sieves [131].

3.2. *Effect of niobium in the catalysts on the SO_2 poisoning in the removal of nitrogen(II) oxide*

Ushikubo [51] mentioned about the role of niobia additive in the prevention of the catalyst poisoning with sulfur dioxide. It was related to the environmental catalysis, namely the reduction of NO_x with NH_3 in the presence of SO_2. The efficiency of ammonia as a reducing agent on the removal of NO_x decreases because NH_3 reacts with SO_3 that is formed by the oxidation of SO_2. Hence, it is preferable that the oxidation of SO_2 is prevented. $(VO)_2(SO_4)/SiO_2$ catalyst promoted by Nb_2O_5 is effective for the suppression of oxidation of SO_2 under the conditions of NO_x removal. During the removal of hydrocarbons of diesel exhaust, the effective for the suppression of SO_2 oxidation is Pd supported on Nb_2O_5 or Pd/Ta_2O_5.

The effect of sulfur dioxide on nitric oxide adsorption and decomposition on Cu-containing micro- and mesoporous molecular sieves has been recently studied [20]. Cu-ZSM-5 zeolite as well as Cu-Al/MCM-41 mesoporous molecular sieves are poisoned by SO_2 in the decomposition of NO, whereas Cu-Nb/MCM-41 catalysts are active in NO decomposition after SO_2 adsorption. The reason of the poisoning effect is the formation of sulfate species. Two kinds of these species were identified:


(I) and

(II)

The species (I) was formed on Cu-ZSM-5 and Cu-Al/MCM-41 but not on Cu-Nb/MCM-41. On the latter only species (II) was registered. This species does not poison the catalytic activity. Niobium located in the extra framework position (in Nb impregnated siliceous MCM-41) does not prevent the material from the poisoning effect by the adsorption of SO_2.

4. Perspectives

A visible progress has been made in the last decade in the study of Nb-containing catalysts. New materials basing on new structures have been synthesized. Thanks to the development of the spectroscopic and other physics techniques, the processes, which occur on the solid surfaces are better investigated. Therefore, a wider application of Nb-containing solids in sorption and catalytic processes is likely to come.

Greater studies of multimetallic compounds, their synthesis, characterization, and application are required. The revision of earlier studied catalysts, especially those containing niobium species as an additive, should be made applying the new and developed characterization techniques. It allows the understanding of the reaction mechanisms on the molecular level.

The future of niobium-containing catalysts seems to be dominated by their application in the redox processes. Especially interested is the application of mesoporous molecular sieves containing niobium in the liquid phase oxidation (hydroxylation, epoxidation). The stability of niobium species in these processes should be detailed studied. It gives hope for their practice use in the fine chemistry.

Nb nitrides are a new class of materials studied in heterogeneous catalysis. However, they are not enough stable in catalysis (for instance, nitrogen is easily released by sulfur). Therefore, the focus should be done on the appropriate support, which will stabilize Nb nitrides.

The increasing interest in niobium chemistry gives hope for further advances and it seems likely that this area will continue to produce exciting results also in heterogeneous catalysis for years to come.

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References

[1] I. Nowak, M. Ziolek, Chem. Rev. 99 (1999) 3603.
[2] I.E. Wachs, L.E. Briand, J.M. Jehng, L. Burcham, X. Gao, Catal. Today 57 (2000) 323.
[3] R. Abe, K. Shinohara, A. Tanaka, M. Hara, J.N. Kondo, K. Domen, J. Mater. Res. 13 (1998) 861.
[4] M.E. Gimon-Kinsel, K.J. Balkus Jr., Stud. Surf. Sci. Catal. 117 (1998) 111.
[5] M.E. Gimon-Kinsel, V.L. Jimenez, L. Washmon, K.J. Balkus Jr., Stud. Surf. Sci. Catal. 117 (1998) 373.
[6] D.M. Antonelli, Micropor. Mesopor. Mater. 33 (1999) 209.
[7] B. Ye, M. Trudeau, D. Antonelli, Chem. Mater. 13 (2001) 2730.
[8] B. Ye, M. Trudeau, D. Antonelli, Adv. Mater. 13 (2001) 29.
[9] X. He, M. Trudeau, D. Antonelli, Inorg. Chem. 40 (2001) 6463.
[10] M. Vettraino, M. Trudeau, D. Antonelli, Inorg. Chem. 40 (2001) 2088.
[11] M. Ziolek, I. Nowak, Zeolites 18 (1997) 356.
[12] M. Ziolek, I. Nowak, J.C. Lavalley, Catal. Lett. 45 (1997) 259.
[13] M. Ziolek, I. Nowak, P. Decyk, J. Kujawa, Stud. Surf. Sci. Catal. 117 (1998) 509.
[14] M. Ziolek, I. Nowak, P. Decyk, O. Saur, J.C. Lavalley, Mater. Res. Soc. (1999) 833.
[15] M. Ziolek, I. Sobczak, I. Nowak, P. Decyk, A. Lewandowska, J. Kujawa, Micropor. Mesopor. Mater. 35–36 (2000) 195.
[16] M. Ziolek, I. Sobczak, I. Nowak, M. Daturi, J.C. Lavalley, Appl. Catal. B 28 (2000) 197.
[17] M. Ziolek, I. Nowak, I. Sobczak, A. Lewandowska, P. Decyk, J. Kujawa, Stud. Surf. Sci. Catal. 129 (2000) 813.
[18] M. Ziolek, A. Lewandowska, M. Renn, I. Nowak, P. Decyk, J. Kujawa, Stud. Surf. Sci. Catal. 135 (2001) 366.
[19] M. Ziolek, I. Sobczak, I. Nowak, P. Decyk, J. Stoch, Stud. Surf. Sci. Catal. 135 (2001) 151.
[20] M. Ziolek, I. Sobczak, I. Nowak, M. Daturi, J.C. Lavalley, Top. Catal. 11 (2000) 343.
[21] M. Ziolek, I. Sobczak, A. Lewandowska, I. Nowak, P. Decyk, M. Renn, B. Jankowska, Catal. Today 70 (2001) 169.
[22] M. Ziolek, A. Lewandowska, B. Kilos, I. Nowak, Fourth World Congress on Oxidation Catalysis, Berlin/Potsdam 2001, Book of Extended Abstracts, vol. II, p. 79.
[23] L. Zhang, J.Y. Ying, Ceram. Process. 43 (1997) 2793.
[24] X. Gao, I.E. Wachs, M.S. Wong, J.Y. Ying, J. Catal. 203 (2001) 18.
[25] T. Sun, Y. Ying, Angew. Chem. Int. Ed. Engl. 37 (1998) 664.
[26] A.M. Prakash, L. Kevan, J. Am. Chem. Soc. 120 (1998) 13148.
[27] I. Sobczak, P. Decyk, M. Ziolek, M. Daturi, J.C. Lavalley, L. Kevan, A.M. Prakash, J. Catal. 207 (2002) 101.
[28] J. Rocha, P. Brandao, A. Philippou, M.W. Anderson, J. Chem. Soc., Chem. Commun. (1998) 2687.
[29] A. Philippou, P. Brandao, A. Ghanbari-Siahkali, J. Dwyer, J. Rocha, M.W. Anderson, Appl. Catal. A 207 (2001) 229.
[30] J. Rocha, P. Brandao, J.D. Pedrosa de Jesus, A. Philippou, M.W. Anderson, Chem. Commun. (1999) 471.
[31] T. Matsuda, M. Udagawa, I. Kunou, J. Catal. 168 (1997) 26.
[32] F. Barbieri, D. Cauzzi, F. De Smet, M. Devillers, P. Moggi, G. Predieri, P. Ruiz, Catal. Today 61 (2000) 353.
[33] P. Viparelli, P. Ciambelli, J.C. Volta, J.M. Herrmann, Appl. Catal. A 182 (1999) 165.
[34] F.C. Meunier, A. Yasmeen, J.R.H. Ross, Catal. Today 37 (1997) 33.
[35] K.V.R. Chary, T. Bhaskar, G. Kishan, K.R. Reddy, J. Phys. Chem. B 105 (2001) 4392.
[36] S.A. Holmes, J. Al-Saeedi, V.V. Guliants, P. Boolchand, D. Georgiev, U. Hackler, E. Sobkow, Catal. Today 67 (2001) 403.
[37] M.A. Banares, X. Gao, J.L.G. Fierro, I.E. Wachs, Stud. Surf. Sci. Catal. 110 (1997) 295.
[38] M.A. Banares, M.V. Martinez-Huerta, X. Gao, J.L.G. Fierro, I.E. Wachs, Catal. Today 61 (2000) 295.
[39] F.B. Noronha, C.A. Perez, M. Schmal, R. Frety, Phys. Chem. Chem. Phys. 1 (1999) 2861.
[40] M.M. Pereira, E.B. Pereira, Y.L. Lam, M. Schmal, Catal. Today 57 (2000) 291.
[41] M.M. Pereira, E.B. Pereira, Y.L. Lam, C.A.C. Perez, M. Schmal, Appl. Catal. A 197 (2000) 99.
[42] L.J. Burcham, J. Datka, I.E. Wachs, J. Phys. Chem. B 103 (1999) 6015.
[43] J.M. Jehng, I.E. Wachs, Chem. Mater. 3 (1991) 100.
[44] M. Paulis, M. Martin, D.B. Soria, A. Diaz, J.A. Odriozola, M. Montes, Appl. Catal. A 180 (1999) 411.
[45] K. Domen, Y. Ebina, S. Ikeda, A. Tanaka, J. Kondo, J.N. Maruya, Catal. Today 28 (1996) 167.
[46] D.M. Antonelli, J.Y. Ying, Angew. Chem. Int. Ed. Engl. 35 (1996) 426.
[47] D.M. Antonelli, A. Nakahira, J.Y. Ying, Inorg. Chem. 35 (1996) 3126.
[48] D.M. Antonelli, J.Y. Ying, Curr. Opin. Colloid Interf. Sci. 1 (1996) 523.
[49] P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B.F. Chmelka, G.M. Whitesides, G.D. Stucky, Science 282 (1998) 2244.
[50] K. Tanabe, Mater. Chem. Phys. 17 (1987) 217.
[51] T. Ushikubo, Catal. Today 57 (2000) 331.
[52] J.M. Jehng, I.E. Wachs, Catal. Today 8 (1990) 37.
[53] E.I. Ko, J.G. Weissman, Catal. Today 8 (1990) 27.
[54] K. Sugiyama, Y. Nakano, H. Aoki, Y. Tekeuchi, T. Masuda, J. Mater. Chem. 4 (1994) 1497.
[55] Y. Nakano, K. Sugyiama, S. Ogasawara, K. Enomoto, T. Matsuda, J. Mater. Chem. 5 (1995) 527.
[56] K. Sugiyama, G. Anan, T. Shimada, T. Ohkoshi, T. Ushikubo, Surf. Coat. Technol. 112 (1999) 76.

[57] J.M. Jehng, A.M. Turek, I.E. Wachs, Appl. Catal. A 83 (1992) 179.
[58] K. Kunimori, H. Shindo, D. Nishio, T. Sugiyama, T. Uchijima, Bull. Chem. Soc. Jpn. 67 (1994) 2567.
[59] S.I. Ito, T. Fujimori, K. Nagashima, K. Yuzaki, K. Kunimori, Catal. Today 57 (2000) 247.
[60] R. Brown, Ch. Kemball, J. Chem. Soc., Faraday Trans. 92 (1996) 281.
[61] A. Kudo, M. Steinberg, A.J. Bard, A. Campion, M.A. Fox, T.E. Mallouk, S.E. Webber, J.M. White, J. Catal. 125 (1990) 565.
[62] D.A.G. Aranda, A.L.D. Ramos, F.B. Passos, M. Schmal, Catal. Today 28 (1996) 119.
[63] F.B. Passos, D.A.G. Aranda, R.R. Soares, M. Schmal, Catal. Today 43 (1998) 3.
[64] F.B. Passos, D.A.G. Aranda, M. Schmal, Catal. Today 57 (2000) 283.
[65] E.I. Ko, J.M. Hupp, F.H. Rogan, N.J. Wagner, J. Catal. 84 (1983) 85.
[66] D.G. Blackmond, E.I. Ko, J. Catal. 94 (1985) 343.
[67] G. Marcelin, E.I. Ko, J.E. Lester, J. Catal. 96 (1985) 202.
[68] D.S. Kim, I.E. Wachs, J. Catal. 142 (1993) 166.
[69] R.R.C.M. Silva, M. Schmal, R. Frety, J.A. Dalmon, J. Chem. Soc., Faraday Trans. 89 (1993) 3975.
[70] F.B. Noronha, A. Frydman, D.A.G. Aranda, C. Perez, R.R. Soares, B. Morawek, D. Castner, C.T. Campbell, R. Frety, M. Schmal, Catal. Today 28 (1996) 147.
[71] R.H.H. Smits, K. Seshan, J.R.H. Ross, Symposium on Catalytic Selective Oxidation, American Chemical Society, Washington, DC, 1992, p. 1121.
[72] T.C. Watling, G. Deo, K. Sheshan, I.E. Wachs, J.A. Lercher, Catal. Today 28 (1996) 139.
[73] R. Brayner, D. Ciuparu, G.M. da Cruz, F. Fievet-Vincent, F. Bozon-Verduraz, Catal. Today 57 (2000) 261.
[74] M.D. Phadke, E.I. Ko, J. Catal. 100 (1986) 503.
[75] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 323.
[76] I.E. Wachs, J.M. Jehng, G. Deo, H. Hu, N. Arora, Catal. Today 28 (1996) 199.
[77] E.I. Ko, R. Bafrali, N.T. Nuhfer, N.J. Wagner, J. Catal. 95 (1985) 260.
[78] P.A. Burke, E.I. Ko, J. Catal. 129 (1991) 38.
[79] N. Ichikuni, Y. Iwasawa, Catal. Today 16 (1993) 427.
[80] T. Tanaka, H. Nojima, H. Yoshida, H. Nakagawa, T. Funabiki, S. Yoshida, Catal. Today 16 (1993) 297.
[81] H. Yoshida, T. Tanaka, T. Yoshida, T. Funabiki, S. Yoshida, Catal. Today 28 (1996) 79.
[82] T. Beutel, V. Siborov, B. Tesche, H. Knözinger, J. Catal. 167 (1997) 379.
[83] N. Ichikuni, Y. Iwasawa, Proceedings of the 10th International Congress on Catalysis, 1992, Elsevier, Amsterdam, 1993, p. 477.
[84] J.M. Jehng, I.E. Wachs, J. Mol. Catal. 67 (1991) 369.
[85] J. Datka, A.M. Turek, J.M. Jehng, I.E. Wachs, J. Catal. 135 (1992) 186.
[86] J.M. Jehng, I.E. Wachs, Catal. Today 16 (1993) 417.
[87] T. Tanaka, T. Yoshida, H. Yoshida, H. Aratani, T. Funabiki, S. Yoshida, J.M. Jehng, I.E. Wachs, Catal. Today 28 (1996) 71.
[88] R.Y. Weng, J.F. Lee, Appl. Catal. A 105 (1993) 41.
[89] R.M. Pitman, A.T. Bell, Catal. Lett. 24 (1994) 1.
[90] Y.F. Chang, G.A. Samorjai, H. Heinemann, J. Catal. 154 (1995) 24.
[91] M. Ziolek, I. Nowak, H.G. Karge, Stud. Surf. Sci. Catal. 94 (1995) 270.
[92] M. Ziolek, I. Nowak, Mater. Res. Soc. (1999) 997.
[93] P.T. Wierzchowski, L. Zatorski, Catal. Lett. 9 (1991) 411.
[94] J.G. Weissman, Catal. Today 28 (1996) 159.
[95] C.A. Pessoa, Y. Gushikem, L.T. Kubota, Electrochim. Acta 46 (2001) 2499.
[96] Y. Wada, A. Morikawa, Catal. Today 8 (1990) 13.
[97] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[98] C.-Y. Chen, H.-X. Li, M.E. Davis, Micropor. Mater. 2 (1993) 17.
[99] M. Ziolek, I. Nowak, H. Poltorak, A. Lewandowska, I. Sobczak, Stud. Surf. Sci. Catal. 125 (1999) 691.
[100] J. Xin, J. Suo, X. Zhang, Z. Zhang, New J. Chem. 24 (2000) 569.
[101] M.P. Kapoor, A. Raj, Stud. Surf. Sci. Catal. 129 (2000) 327.
[102] H. Kokusen, S. Matsuhara, Y. Nishino, S. Hasegawa, K. Kubono, Catal. Today 28 (1996) 191.
[103] M. Che, E. Giamello, Stud. Surf. Sci. Catal. B 57 (1990) 265.
[104] M. Ziolek, I. Nowak, I. Sobczak, H. Poltorak, Stud. Surf. Sci. Catal. 130 (2000) 3047.
[105] A. Lewandowska, S. Monteverdi, M. Bettahar, M. Ziolek, J. Mol. Catal. A 188 (2002) 85.
[106] P. Decyk, M. Trejda, M. Ziolek, A. Lewandowska, Stud. Surf. Sci. Catal. 142 (2002) 1785.
[107] F.B. Noronha, D.A.G. Aranda, A.P. Ordine, M. Schmal, Catal. Today 57 (2000) 275.
[108] T. Armaroli, G. Busca, C. Carlini, M. Giuttari, A.M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A 151 (2000) 233.
[109] C. Carlini, M. Giuttari, A.M. Raspolli Galletti, G. Sbrana, T. Armaroli, G. Busca, Appl. Catal. A 183 (1999) 295.
[110] P.G. Pries de Oliveira, J.G. Eon, M. Chavant, A.S. Riche, V. Martin, S. Cardarelli, J.C. Volta, Catal. Today 57 (2000) 177.
[111] A.M. Duarte de Farias, W. de A. Gonzales, P.G. Pries de Oliveira, J.G. Eon, J.M. Herrmann, M. Aouine, S. Loridant, J.C. Volta, J. Catal. 208 (2002) 238.
[112] R. Brayner, J.A.J. Rodrigues, G.M. Cruz, Catal. Today 57 (2000) 219.
[113] A.G. Aleksanyan, S.K. Dolukhanyan, Int. J. Hydrogen Energy 26 (2001) 429.
[114] D.S. Yang, P.A. Hackett, J. Electr. Spectr. Related Phenom. 106 (2000) 153.
[115] R. Brayner, G. Djega-Mariadassou, G.M. da Cruz, J.A.J. Rodrigues, Catal. Today 57 (2000) 225.
[116] H.S. Kim, G. Bugli, G. Djéga-Mariadassou, J. Solid State Chem. 142 (1999) 100.
[117] P. Ettmayer, W. Lengauer, in: R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, Wiley, Chichester, 1994, p. 519.

[118] C.Ch. Yu, S. Ramanathan, B. Dhandapani, J.G. Chen, S.T. Oyama, J. Phys. Chem. B 101 (1997) 512.
[119] V. Gaborit, N. Allali, C. Geantet, M. Breysse, M. Vrinat, M. Danot, Catal. Today 57 (2000) 267.
[120] N. Allali, A. Yacoubi, A. Nadiri, Ch. Geanted, M. Danot, Ann. Chim. Sci. Mater. 23 (1998) 209.
[121] N. Allali, A. Leblanc, M. Danot, Ch. Geantet, M. Vrinat, M. Breysse, Catal. Today 27 (1996) 137.
[122] Ch. Geantet, J. Afonso, M. Breysse, N. Allali, M. Danot, Catal. Today 28 (1996) 23.
[123] N. Allali, E. Prouzet, A. Michalowicz, V. Gaborir, A. Nadiri, M. Danot, Appl. Catal. A 159 (1997) 333.
[124] R. Berg, Coord. Chem. Rev. 113 (1992) 1.
[125] P. Jackson, K.J. Fisher, G.D. Willett, Int. J. Mass Spectr. 197 (2000) 95.
[126] P. Jackson, K.J. Fisher, G.D. Willett, Chem. Phys. 262 (2000) 179.
[127] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A 212 (2001) 175.
[128] I. Nowak, B. Kilos, M. Ziolek, A. Lewandowska, Catal. Today, this issue.
[129] G. Busca, E. Finocchio, G. Ramis, G. Ricchardi, Catal. Today 32 (1996) 133.
[130] D. Wei, W.-T. Chueh, G.L. Haller, Catal. Today 51 (1999) 501.
[131] I. Nowak, Stud. Surf. Sci. Catal. 142 (2002) 1363.