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The role of niobium component in heterogeneous catalysts

Maria Ziolek*, Izabela Sobczak

Adam Mickiewicz University in Poznań, Faculty of Chemistry, Umultowska 89b, 61-614 Poznań, Poland

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ABSTRACT

This review article is devoted to the materials containing niobium and modified by the addition of different metals or thio- and amino-organosilanes towards the creation of new surface properties and enhancement of catalytic activity. The intention is to show and discuss the role of niobium supported on molecular sieves in the enhancement of the redox properties of transition metals (copper, silver, gold, platinum) and acidic or basic properties of the catalysts as well as to consider redox properties of pure and modified bulk niobium(V) oxide. This paper covers the contribution to the knowledge of this area brought over the last 15 years by our research team.

1. Introduction

Since the publication of review paper [1] dedicated to the niobium-containing catalysts, much effort has been devoted to the use of Nb (in different surroundings) as the catalytically active phase or promoter not only in the final material, but also in the process of catalyst preparation. Much progress has been achieved in the knowledge about the geometry, energetic, spectroscopic properties and molecular structures of supported niobium catalysts, which has permitted prediction of the optimal composition and structure of catalysts addressed to a desired catalytic process.

Below we present a short survey of the most characteristic papers (excluding the articles written by members of our research team, which are the basis of this review article) devoted to the discoveries made in the 21st century related to niobium catalysts, their characterization and application in different processes.

In the last years a few review papers have reported the use of niobium oxides as catalysts or supports in organic synthesis [2–4], the role of niobium as a promoter in different catalytic systems [5], the application of mesoporous molecular sieves containing niobium in the oxidation processes [6]. In addition to this, many research groups published results illustrating various catalytic applications of niobium compounds. Nb-based materials have been studied, among others, as catalysts in the esterification of fatty acids ($Nb_2O_5{\cdot}nH_2O$ and $NbOPO_4$) [7], levulinic acid esterification with ethanol to ethyl levulinate (SO_4/Nb_2O_5) [8], dehydration of glycerol to produce acrolein (Nb_2O_5) [9], dehydration of methanol to dimethyl ether (Nb_2O_5, $NbOPO_4$) [10], selective oxidation of cyclohexene to epoxide (niobium oxyhydroxides) [11], acetalization of glycerol to solketal [12] (niobium oxyhydroxides). The role of niobium as a promoter improving the activity and selectivity of catalysts is of a great importance. The promoting effect of niobium as an additive has been established for V_2O_5, NiO oxides used in oxidative dehydrogenation of lower alkanes [13,14], for Mo—V—O system applied in oxidation and ammoxidation of propane [15], for V—Sb—Al—O used in the ammoxidation of glycerol to acrylonitrile [16] and for Fe/CNT active in Ficher-Tropsch reaction [17].

Since the beginning of the 21st century the interest in niobium-containing mesoporous silica and other molecular sieves has systematically increased. The catalytic activity of NbMCM-41 has been studied e.g. in cyclohexanone oxime conversion to caprolactam [18,19], epoxidation of cyclohexene [20], in biodiesel production *via* methanolysis of sunflower oil [21]. NbSBA-15 has been used as a catalyst for epoxidation of *cis*-cyclooctene [22], whereas Nb-modified mesoporous SiO_2 in the liquid-phase epoxidation of limonene [23].

The aim of this paper is to show and discuss the effects of modification of zeolites and mesoporous molecular sieves with niobium, the role of niobium supported on molecular sieves on the enhancement of the redox properties of transition metals and acidic or basic properties of the catalysts as well as to consider redox properties of pure and modified bulk niobium(V) oxide. This paper covers the

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* Corresponding author.
E-mail address: ziolek@amu.edu.pl (M. Ziolek).

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contribution to the knowledge in this area developed in the last 15 years by our research team.

The first section of this paper (after Introduction) is devoted to the effectiveness of niobium introduction into zeolites and mesoporous molecular sieves. The following three sections are dedicated to the interaction of niobium species with functionalization agents (organosilanoamines and organosilanothiols), different transition metal species (copper, silver, gold, platinum), and oxidant (hydrogen peroxide). Finally, the catalytic activity of niobium catalysts is discussed in oxidation of methanol with molecular oxygen in the gas phase, oxidation of glycerol with molecular oxygen and hydrogen peroxide in the liquid phase, oxidation of cyclohexene with hydrogen peroxide in the liquid phase (a part of the fourth and the whole fifth section). Experimental and DFT calculation approach are described and the role of Nb species in the properties of modifiers and the reaction pathways is considered.

2. Isomorphous substitution of niobium in zeolites and ordered mesoporous molecular sieves

Modification of zeolites and ordered mesoporous silicas (OMS) with transition metals can be performed in two different ways: (i) by including the metal source into the reaction mixture from which zeolites and OMS are synthesized, (ii) by post synthesis loading of metal species via different methods (e.g. incipient wet or wetness impregnation). Both ways can result in the isomorphous substitution of metal into the skeleton of amorphous silica (in OMS) or the lattice of crystalline aluminosilicate (in zeolites) as well as in the extra framework location in the form of bulk metal oxide or reduced metal species. However, the isomorphous substitution is expected mainly if the metal source is included into the synthesis gel, in the so-called one pot synthesis. After modification of zeolites and OMS with transition metal species two features have to be considered, the effectiveness of metal incorporation and the location of metal species as both determine further surface and catalytic properties. Generally, the idea is to obtain catalysts containing exclusively isomorphously substituted metal atoms/ions located in the silicate skeleton or solely in the so-called extra framework positions. In this section the focus is on isomorphous substitution of niobium into mesoporous silicas and zeolites achieved in the one pot synthesis.

2.1. Niobium incorporation to ordered mesoporous silicas

Niobium introduced into the ordered mesoporous silicas during the synthesis is expected to occupy preferably the isolated position between silica tetrahedra inside the amorphous skeleton. The efficiency of such localization of niobium resulting from isomorphous substitution depends on the niobium source, conditions of the preparation procedure (pH of the reagent mixture, type of the template), and structure of the final OMS. For the same type of hexagonal arrangement of mesopores (MCM-41, SBA-15 and SBA-3 molecular sieves – Table 1) and the same niobium source (Nb(V) ammonium trisoxalate complex/Nb(V) oxalate) the combination of cationic surfactant, TEOS (tetraethoxysilane) and Nb source at pH of 1 (preparation of SBA-3) gives rise to the highest efficiency of isomorphous substitution of niobium [24], whereas in the preparation of NbMCM-41 (ionic surfactant; pH ~11) the yield of Nb incorporation is high, but a part of niobium is located in the extra framework position as niobium(V) oxide [25,26]. The lowest efficiency was found in the synthesis of NbSBA-15. However, the higher efficiency of Nb substitution into SBA-15 can be achieved by the replacement of Nb oxalate by Nb chloride as niobium source and elimination of hydrochloric acid [27] used in the standard procedure [28].

The role of Nb source on the effectiveness of Nb substitution has been considered e.g. for SBA-3 [24]. Table 2 shows that the efficiency of Nb isomorphous substitution significantly depends on the type of niobium precursor. A higher Nb content in the final material was obtained when Nb(V) chloride was used instead of Nb(V) ammonium trisoxalate complex in the synthesis. Another parameter considered was the character of the synthesis medium (basic or acidic). It has been documented that in both, NbMCM-41 (Nb oxalate used as a niobium source) [25,26] and in NbSBA-3 (Nb(V) chloride – a niobium precursor) [24] the amount of niobium incorporated during the synthesis was higher than the nominal one, estimated from the proportion of siliceous to niobium in the synthesis medium. The nominal atomic Si/Nb ratio was 32 in the synthesis gel of NbMCM-41 and NbSBA-3, the Si/Nb ratio in the final NbMCM-41 was 26, whereas in NbSBA-3 it was 24. Much lower Si/Nb ratio in the final material than in the gel, indicates that not all siliceous atoms used in the synthesis were incorporated in the final products. The reasons for the high niobium loadings in both types of materials are different. During the synthesis in a basic medium a significant part of niobium is located at the extra-framework positions in the form of niobium(V) oxide or $Na_3Nb_4O_{11}$, depending on niobium loading [25]. It has been proved that in basic media Nb_2O_5 and $Na_2Nb_4O_{11}$ are occluded in the walls as evidenced from ICP-OES and XPS results (Si/Nb ratio in bulk material was lower than on the surface). Such occlusion can lead to the formation of defects. In basic media, niobium oxide is precipitated before mesoporous silica is formed and therefore a part of niobium species is occluded in this form in the walls. In contrast, the synthesis in an acidic medium and by the use of ionic template towards NbSBA-3 formation allows the incorporation of niobium exclusively into the skeleton of silica [24] but to the limit of Si/Nb ratio ca. 30.

Not only pH of the synthesis medium but also the nature of template seems to play an important role in the niobium loading and location. Under the same acidic conditions both, NbSBA-3 and NbSBA-15 have been synthesized [28,29]. The use of non-ionic template, Pluronic 123, for the production of NbSBA-15 from Nb(V) ammonium trisoxalate complex did not allow the introduction of as high amount of niobium as into NbSBA-3 synthesized in the presence of cetyltrimethylammonium bromide (Table 2). Moreover, the non-ionic template favors the location of niobium not only in the framework but also at the extra-framework sites [30].

As follows from the above information concerning niobium loading and its location in the skeleton of niobiosilicate, the efficiency of isomorphous substitution of niobium into hexagonally ordered mesoporous silicas is determined by the appropriate selection of synthesis parameters such as the nature of template (ionic *vs* non-ionic), pH (acidic *vs* basic), Nb source (oxalate or ammonium oxalate complex *vs* niobium chloride). The effects of these features are illustrated in Fig. 1.

Niobium has been also incorporated to another structure of mesoporous silica, namely mesoporous cellular foams, NbMCF [e.g. 31,32]. The preparation procedure of MCF materials was similar to that applied for SBA-15 but additionally 1,3,5-trimethoxybenzene and NH_4F were added to the synthesis gel [33]. Such a change in the synthesis route did not influence significantly the effectiveness of niobium incorporation (the real atomic Si/Nb ratio was higher than the nominal one and only slightly lower than that obtained in NbSBA-15) but resulted in 100% isomorphous substitution of niobium into MCF silica.

The estimation of niobium location (in the silica skeleton or in the extra-framework positions) is not an easy task and several techniques have to be applied complementary. Table 3 summarizes different tools used for the assessment of niobium species in ordered mesoporous silicas. XRD patterns allow the identification of crystalline niobium oxides or niobiates located at the extra-framework sites as shown in Fig. S1A [25]. However, the lack of peaks in XRD pattern is an insufficient proof for the absence of extra framework niobium species. If the dispersion of niobium crystalline

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