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Gold, vanadium and niobium containing MCM-41 materials—Catalytic properties in methanol oxidation

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ABSTRACT

This work describes the syntheses, characterisation and catalytic application of silicate MCM-41 materials modified with gold, vanadium and niobium by their introduction during the synthesis (co-precipitation) performed with the use of HCl or H_2SO_4 as pH adjustment agent. The samples were characterised by XRD, N_2 adsorption and test reactions (2-propanol and acetonylacetone transformations). Moreover, they were applied in the methanol oxidation, studied in the flow system and in situ FTIR method. It is shown that the basicity of AuMCM-41 is diminished by the introduction of transition metal species (V, Nb). The materials prepared by the use of H_2SO_4 (for the adjustment of pH) reveals a higher acidity, better ordering of mesopores, and a lower activity in methanol oxidation than those prepared with the use of HCl. The latter exhibit high activity in methanol oxidation to CO_2. The presence of both, V and Nb, besides Au in MCM-41 makes the desorption of formaldehyde much easier increasing the selectivity.

1. Introduction

Mesoporous molecular sieves of the M41S family, introduced by the Mobil group in 1992 [1,2], are a promising new support for catalysts. This family includes hexagonal MCM-41 materials with a very high surface area (~1000 m^2/g) and a very narrow pore size distribution in the mesoporous range (2–10 nm).

Supported vanadia mesoporous catalysts (MCM-41, MCM-48, SBA-15) [e.g. 3–7] are nowadays intensively studied in the partial oxidation of methanol, especially towards formaldehyde—one of the most important intermediates used in industrial chemistry [8]. Moreover, the gas-phase partial oxidation of methanol is an important probe reaction, in which product selectivity depends on the concentration of redox, basic and acidic sites on the catalyst surface [8–12]. Redox sites are responsible for the production of formaldehyde and dimethoxymethane, whereas acidic and basic sites give rise to dimethyl ether and carbon oxides, respectively.

The mesoporous catalyst of MCM-41 type (V-MCM-41), with vanadium contents ranging from 0.56 to 1.86 wt.% have been successfully synthesized in the group of Haller [3–5] by the incorporation of vanadium into the silica framework. A formaldehyde selectivity of 59.4% in the methanol oxidation, using a 0.56 wt.% vanadium loaded V-MCM-41 catalyst, was achieved at a temperature of 873 K. The highest STY_{HCHO} (space time yield) with a high formaldehyde selectivity of 53.2% was obtained at 933 K with the V-MCM-41 catalyst containing 1.86 wt.% vanadium. The improved catalytic performance of the V-MCM-41 catalysts was related to the highly dispersed vanadium oxide species forming a high concentration of isolated active sites, which are crucial to minimize the consecutive oxidation of formaldehyde to carbon oxides.

The reactivity of vanadium oxide supported on mesoporous material in the methanol oxidation at 673 K was also studied on silica MCM-48 support [7]. The results showed increasing conversion and formaldehyde yields and selectivity with increasing vanadium loading (up to 3.5 wt.% V). Characterization by FTIR, Raman, and UV–vis diffuse reflectance spectroscopy revealed the presence of different *VOx* structures (monomers, polymers, and crystals) as a function of the vanadium loading (0–6.5 wt.% V). The major product as formaldehyde is produced on tetrahedral $(SiO)_3V{=}O$ redox sites. With increasing loadings (6.7 wt.% V), a small fraction of crystalline V_2O_5 is formed and causes the decrease of activity and formaldehyde selectivity as a result of loss accessible active sites in the V_2O_5 crystal lattice.

Recently, we have found [13] that gold-MCM-41 catalysts prepared by co-precipitation method (Au introduced during the synthesis) are active in the methanol oxidation at low temperature (473 K). Moreover, the most important finding from that work was

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the dependence of selectivity in methanol oxidation on the composition of mesoporous matrix. The introduction of Nb into MCM-41 significantly shifts the selectivity towards formaldehyde at 423–473 K. Au–Nb interaction diminishes the strength of aldehyde chemisorption and thanks to that decreases its further transformation to formate products.

The aim of our study is located in this field. The new catalysts applied in this work and studied in methanol oxidation were gold, vanadium and niobium modified silicate ordered mesoporous materials of MCM-41 type. We expected that vanadium introduced to MCM-41 structure instead of Nb or together with Nb will improve the activity and selectivity in methanol oxidation. It is known that Nb species generates defects in MCM-41 structure (plays a role of structure promoter) and vanadium enhances oxidative activity [14].

Gold, vanadium and niobium were introduced into the catalysts by co-precipitation method during the synthesis of mesoporous material. The MCM-41 synthesis procedure requires the adjustment of pH by acid. The idea is to use such acid which contains the same anion as the components applied for the synthesis. Therefore, we used H_2SO_4 (according to V-source) or HCl (related to template and Au-source) to study the effect of acid on the physicochemical and catalytic properties of the prepared materials.

2. Experimental

Mesoporous molecular sieves of MCM-41 type containing Au and V or Au, V and Nb were synthesised by the hydrothermal method in the same manner as conventional MCM-41 [1,2]. Sodium silicate (27% SiO_2 in 14% NaOH; Aldrich) was used as a silicon source and cetyltrimethylammonium chloride (Aldrich) was the surfactant template. The solutions of hydrogen tetrachloroaurate(III) hydrate (1.4×10^{-4} M) - ($HAuCl_4$—Johnson Matthey, UK-USA), vanadium(IV) oxide sulphate hydrate (3.4×10^{-3} M) - ($VOSO_4$—BDH) or ammonium niobate(V) oxalate hydrate (5.6×10^{-2} M) - ($C_4H_4NNbO_9$—Aldrich) as the sources of gold, vanadium or niobium, respectively, were next added into the formed gel (molar gel ratios = 1 SiO_2:0.75 NaOH:6.5 CTMACl:103.75 H_2O). The mixture was stirred for 0.5 h. The pH was decreased from 12.5 to 11 with H_2SO_4 (H_2SO_4:H_2O = 4:1) or HCl (HCl:H_2O = 3:1) acids, after which the distilled water was added. The gel was loaded into a stoppered polypropylene (PP) bottle and heated without stirring at 373 K for 24 h. The mixture was then cooled down to room temperature and the pH level was adjusted to 11 with H_2SO_4 or HCl. This reaction mixture was heated again to 373 K for 24 h. The Si/Au atom ratio was 256 (corresponding to 1 wt.% of Au). The Si/V and Si/Nb ratios were 128. The resulting precipitated product was washed with distilled water, dried in the air at ambient temperature, and the template in the catalysts was removed by calcination at 823 K, 2 h in helium flow and 14 h in the air under static conditions. The rate of heating was 55 K/min.

The XRD patterns were obtained on a D8 Advance diffractometer (Bruker) using Cu Kα radiation (λ = 0.154 nm), with a step size of 0.02° and 0.05° in the small-angle and high-angle range, respectively.

The surface area and pore volume of the samples were measured by nitrogen adsorption at 77 K, using the conventional procedure on a Micromeritics 2010 apparatus. Prior to the adsorption measurements, the samples were degassed in vacuum at 573 K for 2 h.

The catalysts were tested for acetonylacetone (AcAc) cyclisation and 2-propanol decomposition as the probe reactions.

A tubular, down-flow reactor was used in AcAc cyclisation reaction that was carried out at atmospheric pressure, using nitrogen as the carrier gas. The catalyst bed (0.05 g) was first activated for 2 h at 673 K under nitrogen flow (40 cm^3 min^{-1}). Subsequently, a 0.5 cm^3 of acetonylacetone (Fluka, GC grade) was passed continuously over the catalyst at 623 K. The substrate was delivered with a pump system and vaporized before being passed through the catalyst with the flow of nitrogen carrier gas (40 cm^3 min^{-1}). The reaction products were collected for 30 min downstream of the reactor in the cold trap (solid CO_2) and analysed by gas chromatography (CHROM-5, Silicone SE-30/Chromosorb column).

The 2-propanol conversion (dehydration and dehydrogenation) was performed, using a microcatalytic pulse reactor inserted between the sample inlet and the column of a CHROM-5 chromatograph. The catalyst bed (0.02 g) was first activated at 673 K for 2 h under helium flow (40 cm^3 min^{-1}). The 2-propanol (Aldrich) conversion was studied at 423, 473, 523 and 573 K using 3 μl pulses of alcohol under helium flow (40 cm^3 min^{-1}). The reactant and reaction products: propene, 2-propanone (acetone) and diisopropyl ether were analysed using CHROM-5 gas chromatograph on line with microreactor. The reaction mixture was separated on 2 m column filled with Carbowax 400 (80–100 mesh) at 338 K in helium flow (40 cm^3 min^{-1}) and detected by TCD.

Infrared spectra were recorded with the Vector 22 (Bruker) spectrometer. The pressed wafers of the materials (~5 mg cm^{-1}) were placed in the vacuum cell and activated at 673 K for 2 h (the heating rate 5 K/min). The experiments were carried out in two ways: (i) MeOH adsorption at room temperature (RT) and heating for 30 min at 573 K (the heating rate 10 K/min); (ii) MeOH adsorption at RT followed by O_2 admission and heating at 573 K for 30 min (the heating rate 10 K/min). After heating the sample was cooled to RT and few minutes after reaching this temperature spectra were recorded (at RT). The IR spectra of the activated samples were subtracted from those recorded after the adsorption of probe molecules followed by various treatments. The reported spectra are the results of this subtraction.

The methanol oxidation reaction was performed in a fixed-bed flow reactor. 0.02 g of the pure (not diluted) catalyst, with a size fraction of $0.5 < Ø < 1$ mm, was placed into the reactor. The samples were activated in helium flow (40 cm^3 min^{-1}) at 673 K for 2 h. The rate of heating was 15 K/min. Next the temperature decreased to the temperature of the reaction. A 40 ml/min He/O_2/MeOH (88/8/4 mol%) flow was used as a reactant mixture. The reactor effluent was analysed using an on line gas chromatograph (GC 8000 Top equipped with a capillary column of DB-1 -FID detector and Porapak Q and 5A molecular sieves columns-TCD detector). Helium was applied as a carrier gas.

3. Results

The catalysts prepared within this work (AuVMCM-41, AuVNbMCM-41) are characterized and the results are compared with those obtained for AuMCM-41 and AuNbMCM-41 published elsewhere [13,15].

3.1. Characterisation of the catalysts

3.1.1. X-ray diffraction

Both MCM-41 materials containing Au and V synthesised with the use of H_2SO_4 for the pH adjustment (AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4)) exhibit well-ordered hexagonal mesoporous structures of MCM-41 type deduced from the XRD patterns shown in Fig. 1. They reveal well-defined hexagonal XRD patterns with a main peak at $2\theta = 2.2°$ and up to three signals in the region 3–8°. These reflections are due to the ordered hexagonal array of

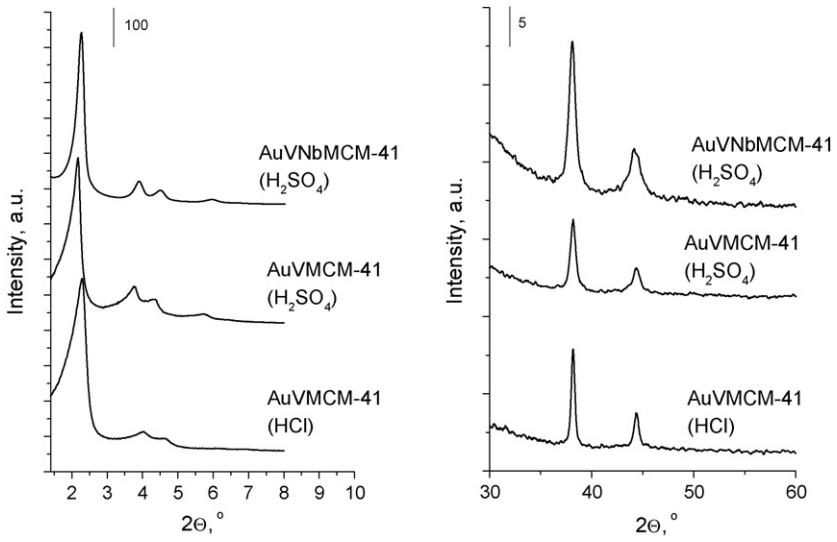

Fig. 1. XRD patterns of MCM-41 materials.

parallel silica tubes [1,2]. The XRD pattern of AuVMCM-41(HCl), in which HCl was used for pH adjustment during the synthesis, shows less pronounced reflections in the region 3–8°. It indicates the disordering of the hexagonal structure in the long-range. Moreover, AuVMCM-41(HCl) shows broader [1 0 0] interference than the sample prepared with the use of H_2SO_4, i.e. AuVMCM-41(H_2SO_4) and the shift of XRD signals towards higher 2θ values. The high-angle XRD patterns of all Au-containing samples indicate the presence of metallic gold particles characterized by the reflections at $2\Theta = 38.2°$ from Au(1 1 1) and at 44.8° from Au(2 0 0) [13,15–18]. Peaks from Au are sharper for AuVMCM-41(HCl) sample suggesting the bigger Au agglomerates on that surface than on the catalysts prepared with the use of H_2SO_4 (AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4)). TEM images (not shown here) confirmed this suggestion. It points out on the effect of the chemical composition of the MCM-41 and the synthesis conditions on the size and dispersion of gold particles.

3.1.2. Low temperature nitrogen adsorption

The N_2 adsorption/desorption isotherms (not shown here) are of type IV in the IUPAC classification, typical of MCM-41 materials [1,2]. Table 1 summarises textural data based on low-temperature nitrogen adsorption experiments. All MCM-41 materials studied are mesoporous with a high surface area (in the range 800–1100 $m^2\,g^{-1}$) and pore volume (ca. 1 $cm^3\,g^{-1}$). However, the use of HCl to adjust the pH during the synthesis leads to the catalyst with lower surface area and pore volume compared to the AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4) materials. Consequently, the wall thickness of these catalysts (designated (HCl)) is much higher. However, we cannot exclude that the detailed data in Table 1 can be effected by less crystallity of the materials prepared with the use of HCl.

Table 1
Texture parameters of the catalysts

Catalyst	Surface area BET, (ads.) ($m^2\,g^{-1}$)	Average pore volume BJH, (ads.) ($cm^3\,g^{-1}$)	Average pore diameter, BJH, (ads) (nm)	Wall thickness[a] (nm)
AuVMCM-41(HCl)	813	0.80	3.51	1.12
AuVMCM-41(H_2SO_4)	1055	1.34	4.27	0.59
AuVNbMCM-41(H_2SO_4)	1042	1.05	3.67	0.98
AuMCM-41(HCl)[b]	886	0.81	2.94	2.02
AuNbMCM-41(HCl)[b]	870	0.86	3.60	1.32

[a] $t = a_0 - w/1.05; a_0 = 2 \times d_{100}/1.732$; w – average pore diameter.
[b] Results described in Ref. [13,15].

3.2. Test reactions

3.2.1. 2-Propanol decomposition

The 2-propanol decomposition is a test reaction for the characterisation of acidic (Brønsted or Lewis) and/or basic properties of the solids [19]. Dehydration of alcohol to propene and/or diisopropyl ether requires acidic centres (Lewis or BrØnsted), whereas the dehydrogenation to acetone occurs on the Lewis basic sites. It is noteworthy that ether production requires the presence of pairs Lewis acid–base centres. Some authors [e.g. 20] have stated that acetone formation takes place on redox centres. The conversion of 2-propanol is much higher in the presence of acidic centres on the catalyst surface than that noted on basic catalysts.

Table 2 exhibits the results of 2-propanol decomposition on the selected MCM-41 samples. The conversion of 2-propanol and products distribution depend on the composition of the catalyst and the synthesis conditions (HCl or H_2SO_4 used for pH adjustment). AuVMCM-41(HCl) is almost inactive, whereas AuVMCM-41(H_2SO_4) exhibits much higher conversion in the 2-propanol decomposition at 523 and 573 K. The introduction of

Table 2
The results of 2-PrOH decomposition

Catalyst	Temperature (K)	2-PrOH conversion (%)	Propene selectivity (%)	Ether selectivity (%)	Acetone selectivity (%)
AuVMCM-41 (HCl)	423	0.1	100	–	–
	473	0.6	100	–	–
	523	0.4	31	–	69
	573	0.4	16	–	84
AuVMCM-41 (H_2SO_4)	423	0.1	100	–	–
	473	0.1	100	–	–
	523	2.8	90	5	5
	573	17.6	98	1.5	0.5
AuVNbMCM-41 (H_2SO_4)	423	0.1	46	–	54
	473	1.6	13	69	18
	523	12.4	96	1	3
	573	36.3	98	1	1

niobium into MCM-41 leads to the significant increase of activity. For AuVNbMCM-41 (H_2SO_4) the highest conversion of alcohol (ca. 36% at 573 K) was observed. At lower temperatures, i.e. 423 and 473 K, propene was the only product formed on gold-vanadium MCM-41 material. At higher temperatures, 523 and 573 K, the main reaction product on AuVMCM-41(HCl) was acetone, indicating the presence of Lewis basic centres on the surface of this catalyst. The drastically change in acetone selectivity with the increasing temperature can be caused by the modification of vanadium species with water formed at lower temperature during 2-propanol dehydration. Contrary, on AuVMCM-41(H_2SO_4) at 523 and 573 K the main reaction product was still propene, but a small amount of diisopropyl ether and acetone was also registered in the reaction products, indicating the presence of Lewis acid–base pairs beside acidic centres. The Lewis-acid centres are also present on the surface of niobium containing AuVNbMCM-41(H_2SO_4) (high selectivity to diisopropyl ether and acetone at 473 K), but the high selectivity to propene at 523 and 573 K indicates the domination of acidic properties of the sample.

3.2.2. Acetonylacetone cyclisation

The cyclisation of acetonylacetone has been used as a test reaction for basicity/acidity properties. This reaction was proposed by Dessau [21] as BrØnsted acid–base test. The formation of 2,5-dimethylfuran (DMF) occurs on acidic centres, whereas in the production of 3-methyl-2-cyclopentenone (MCP) basic centres take part. On the basis of the ratio of selectivity to MCP/selectivity to DMF, the sequence of the basicity of the prepared catalysts can be estimated. According to the literature [21,22] the basicity of the catalyst is stated if MCP/DMF $\gg 1$. When MCP/DMF $\ll 1$ the catalyst exhibits acidic properties, while for MCP/DMF ≈ 1 the acid–base character of catalysts is postulated.

The data in Table 3 demonstrate a significant influence of the catalyst composition on the activity in AcAc cyclisation and dehydration. The conversion is higher on AuVMCM-41 materials than on AuVNbMCM-41 sample. The sequence of conversion differs from that of 2-propanol reaction. However, one should remember that the mechanisms of both processes are different. In 2-propanol conversion a large variety of reaction pathways is possible involving both types of acid (BrØnsted and Lewis) and Lewis base centres. In acetonylacetone cyclisation BrØnsted acid and/or base centres are required. It is worthy of notice a significant influence of the nature of acid used during the preparation of MCM-41 on the properties of the catalyst. AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4) materials exhibit acidic properties (MCP/DMF $\ll 1$). The application of HCl during the synthesis (AuVMCM-41 (HCl)) significantly increases the basicity of the material, documented by MCP/DMF $\gg 1$. There is no doubt that the presence of chlorine near Au species is responsible for a very high basicity of AuVMCM-41(HCl), as was indicated earlier for AuMCM-41(HCl) [15].

Interestingly, introduction of vanadium besides gold into MCM-41 material does not change significantly the conversion of AcAc (see Table 3: AuMCM-41—38%; AuVMCM-41 (HCl)—31%; AuVMCM-41 (H_2SO_4)—37%) but dramatically changes the MCM/DMF ratio, reducing basicity of the material. This effect is much higher when H_2SO_4 is applied as the pH adjustment medium.

Table 3
The results of acetonylacetone cyclisation, 623 K

Catalyst	AcAc conversion (%)	MCP/DMF
AuVMCM-41(HCl)	31	22
AuVMCM-41(H_2SO_4)	37	0.19
AuVNbMCM-41(H_2SO_4)	11	0.05
AuMCM-41(HCl)[a]	38	104
AuNbMCM-41(HCl)[a]	19	9

[a] Results described in Ref. [13,15].

Among vanadium containing samples AuVMCM-41(HCl) shows the highest MCP/DMF ratio which is in line with the highest basicity registered in 2-propanol reaction at higher temperatures.

3.3. Methanol oxidation

3.3.1. FTIR spectroscopy study

Fig. 2 reveals the effect of methanol adsorption on the surface of MCM-41 catalysts at room temperature (RT) and the subsequent heating at various temperatures. Methanol is chemisorbed on both AuVMCM-41 materials in two forms: methoxy species characterized by an IR band at ~1445 cm^{-1} and formate species giving rise to a band at ca. 1597 cm^{-1} (νCOO^-) [23,24].

The wavenumber range of 2700–3100 cm^{-1} is less informative than 1300–1800 cm^{-1} one because of low intensity of bands. Nevertheless, IR bands characteristic of methoxy species adsorbed on vanadium and gold are visible: a $\nu_{as}(CH_3)$ band at 2969 cm^{-1} and a $\nu_s(CH_3)$ band at 2929 cm^{-1} [23,25]. The other observed band at 2857 cm^{-1} can be assigned to associatively chemisorbed CH_3OH [25,26]. Moreover, a $\nu_s(CH)$ band at 2882 cm^{-1} confirms the presence of formate species on the surface of MCM-41 after MeOH adsorption.

Heating of chemisorbed methanol decreases the intensity of IR bands (1445 and 1597 cm^{-1}). Additionally, in the case of AuVMCM-41(HCl) heating of MeOH at 573 K leads to the formation of adsorbed formaldehyde ($\nu C{=}O$ at 1625 cm^{-1}, $\nu_{as}(CH_2)$ at 2876 cm^{-1}). Such transformation requires the oxidizing route and indicates the higher oxidation properties of the AuVMCM-41 sample prepared with HCl than H_2SO_4. The oxidizing effect is higher when oxygen is added and the system is heated at 573 K. In both cases the IR band from adsorbed formaldehyde becomes very intense. However, in the spectra of AuVMCM-41(HCl) methoxy and formate species are still present on the surface, whereas for AuVMCM-41(H_2SO_4) these species almost disappear under the same conditions. It suggests that acidity of the latter sample makes the chemisorption of methoxy and formate species much weaker.

The higher acidity of AuVNbMCM-41(H_2SO_4) than the other catalysts, results in the absence of IR band from chemisorbed formate species (at 1597 cm^{-1}). Instead of that the IR band at 1611 cm^{-1} appeared. This band is accompanied by the other one at 3089 cm^{-1} in the $\nu(CH)$ range (not shown here) and therefore, one can assign it to C–H vibrations in olefins (H–C=C). It is clear from the IR spectra (Fig. 2C) that olefins are relatively strongly held on the catalyst surface even upon heating at 573 K.

Interestingly, when methanol was adsorbed on AuVNbMCM-41(H_2SO_4) activated in the presence of oxygen at 673 K both, formate and H–C=C, species appeared in IR spectra (Fig. 2D) at 1597 and 1611 cm^{-1}, respectively. It means that oxidized surface enhances the chemisorption of formate species.

The comparison of Fig. 2A with Fig. 3A and B led us to the conclusion that methanol chemisorption at room temperature on gold catalysts (prepared with the use of HCl) give rise to the same main species, indicated by 1445 (methoxy) and 1596 cm^{-1} (formate) bands, on all three samples, independently of the presence or absence of vanadium or niobium. Thus, it seems to be characteristic for gold centres. The role of V or Nb in the material is visible after admission of oxygen at 573 K. The activity in the formation and chemisorption of formaldehyde upon O_2 admission changes in the following order: AuNbMCM-41(HCl) > AuVMCM-41(HCl) > AuMCM-41(HCl).

However, one should stress that the discussed IR spectra describe the strength of intermediates or products chemisorption which does not indicate directly the selectivity of the reaction

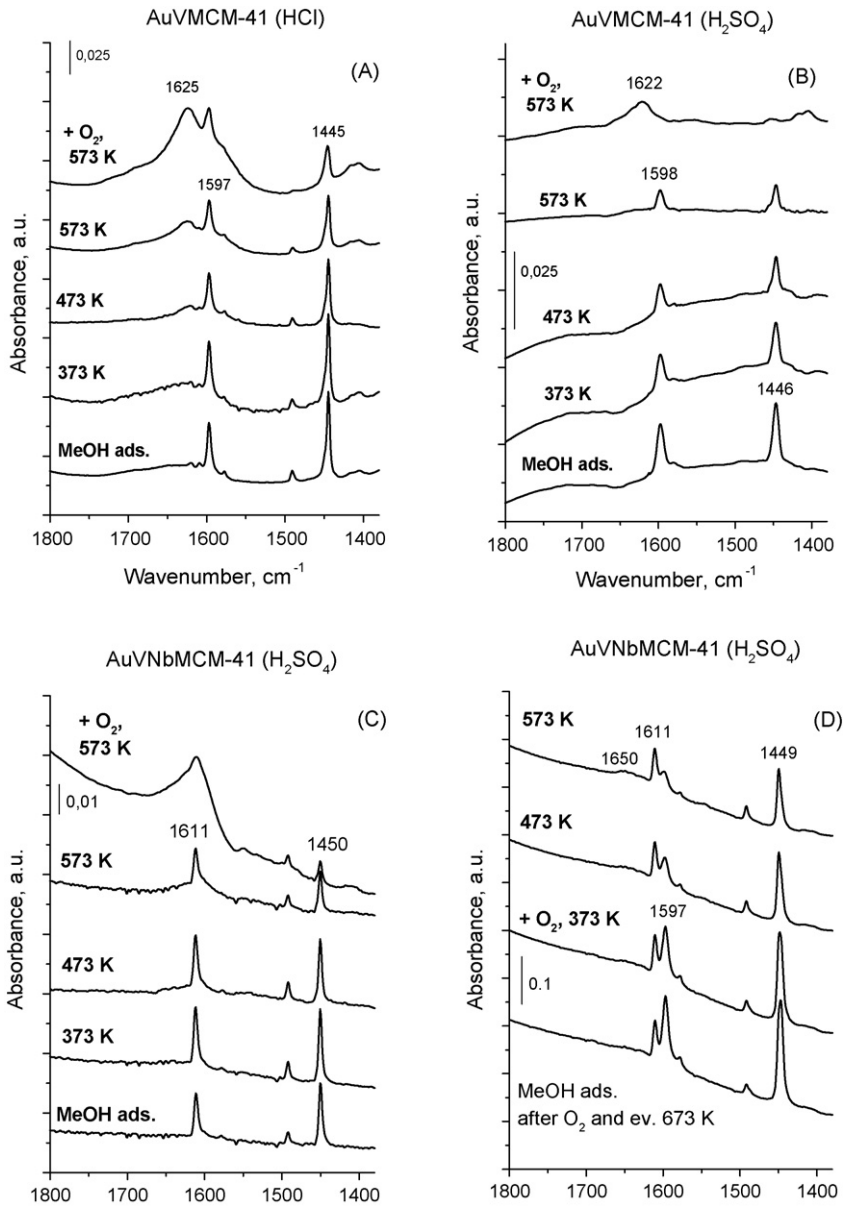

Fig. 2. FTIR spectra of Au, V, Nb-containing MCM-41 catalysts after MeOH adsorption.

carried out in the flow system. The results of methanol oxidation in the flow reactor are shown below.

3.3.2. Activity

The results of methanol oxidation in the flow system at 523 K and 473 K are displayed in Table 4. One can divided the catalysts on two groups: (i) prepared with the use of HCl as the pH adjustment medium and (ii) prepared with the use of H_2SO_4 for that purpose. For the first group of catalysts it can be considered the change in activity after the modification of MCM-41 with V or Nb besides gold introduction. It is clear that niobium and vanadium increase the activity of gold containing MCM-41 (Nb slightly and much more vanadium), but dramatically enhance the total oxidation toward CO_2 from 20% selectivity on AuMCM-41(HCl) to 44% and 59% selectivity on AuNbMCM-41(HCl) and AuVMCM-41(HCl), respectively. This behaviour indicates that the introduction of Nb or V into the MCM-41 framework enhances the basicity responsible for CO_2 selectivity. Total oxidation to CO_2 occurs according to the radical mechanism which requires easy electron transfer [27]. The disordering of the bimetallic materials (AuNbMCM-41 and AuVMCM-41) prepared by the use of HCl for pH adjustment (see XRD results) favours the defect formation and due to that the possibility of electron transfer, like it was found earlier [14]. AuMCM-41(HCl) activates the reaction mainly towards methyl formate.

The second group of catalysts, prepared with the use of H_2SO_4, is a few times less active but the total oxidation of methanol is diminished and the selectivity toward formaldehyde is enhanced. The highest formaldehyde selectivity (52%) is reached on AuVNbMCM-41 (H_2SO_4). This catalyst is the most acidic among all the materials studied in this work. It confirms the role of acidity in methanol oxidation discussed in the literature [e.g. 8,23].

The selectivity to dimethyl ether on both catalysts (prepared with the use of H_2SO_4) is low and towards ethene it is negligible. The acidic centres in these catalysts enhance the redox properties of the surface involved in the formaldehyde production. Small amounts of dimethoxymethane are also formed on these catalysts.

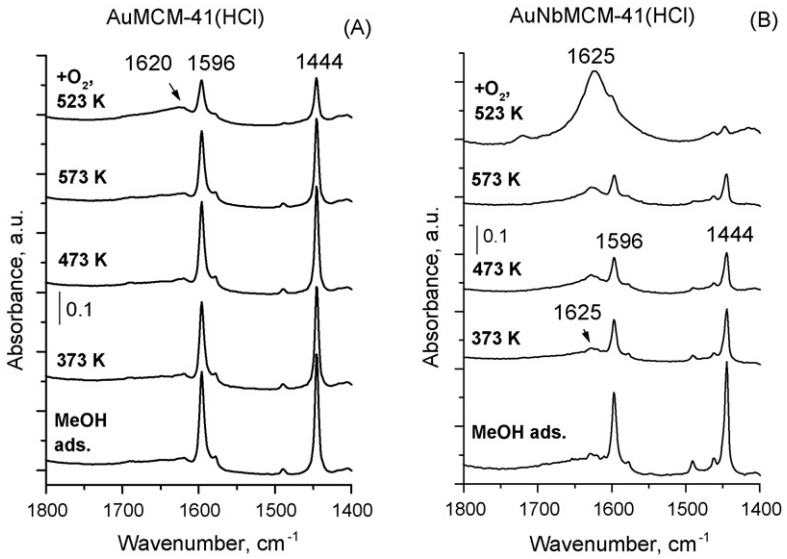

Fig. 3. FTIR spectra of Au, Nb-containing MCM-41 catalysts after MeOH adsorption [13].

Table 4
Catalytic activity in MeOH + O_2 reaction (stationary state – average values)

Catalyst	Temperature (K)	MeOH conversion (%)	Selectivity (%)					
			HCHO	$HCOOCH_3$	CH_3OCH_3	$(CH_3O)_2CH_2$	C_2H_2	CO_2
AuVMCM-41(HCl)	473	24	3	78	–	Traces	–	19
AuVMCM-41(HCl)	523	62	10	31	–	Traces	–	59
AuVMCM-41(H_2SO_4)	523	13	37	48	1	2	Traces	12
AuVNbMCM-41(H_2SO_4)	523	10	52	34	3	2	Traces	9
AuMCM-41(HCl)	523	52	10	70	–	Traces	–	20
AuNbMCM-41(HCl)	523	55	6	50	–	Traces	–	44

The question arises whether the increase of selectivity towards formaldehyde is due to the lower methanol conversion. The experiment performed at lower temperature, 473 K, on AuVMCM-41(HCl) excluded such a suggestion (Table 4). After the decrease of methanol conversion from 62 to 24% (at 523 and 473 K, respectively) the formaldehyde selectivity decreased from 10 to 3% and that of methyl formate increased from 31 to 78%. So, the level of methanol conversion does not simply determine the formaldehyde formation.

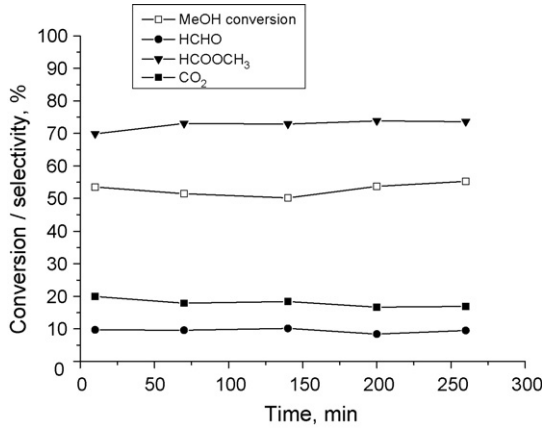

Fig. 4. MeOH conversion and selectivity in the methanol oxidation reaction on AuMCM-41(HCl).

The important feature is the stability of the catalyst. Fig. 4 shows the plot of activity and selectivity vs. the reaction time on AuMCM-41(HCl). It is well visible that during ca. 5 h of the reaction the methanol conversion and products selectivity are stable.

4. Discussion

The main task of this work was to apply gold catalysts based on MCM-41 mesoporous materials with various chemical compositions in the oxidation of methanol. Early transition metals, vanadium and niobium, were used as modificators for gold-silicate mesoporous catalysts.

Methanol oxidation is not only the target process (e.g. for the production of formaldehyde) but also the test reaction for acidic–basic and redox centres studied in many laboratories (e.g. [8–12,23]). Therefore, the consideration of the reaction products (appeared in the process carried out in flow system) and the chemisorption of intermediates and/or products (FTIR study) allow the determination of the surface properties of the catalysts. In this work these properties are related to the texture/structure parameters and basicity–acidity, evaluated by the test reactions (2-propanol decomposition and acetonylacetone cyclisation and dehydration).

Two main behaviours in the preparation of gold containing MCM-41 materials were considered in this work: (i) the composition of the gel used in the syntheses (vanadium and/or niobium besides gold and siliceous sources) and (ii) the nature of acid applied for the pH adjustment (HCl or H_2SO_4).

Summarizing texture/structure properties one has to state that the use of HCl as pH adjustment medium causes the disordering in hexagonal arrangement of mesopores, gives rise to the smaller pore size, bigger wall thickness and bigger Au particle size if compared with the samples prepared with H_2SO_4. It is known from the literature that the sulphuric acid or sulphates used during the preparation of catalysts generate acidity [25,28]. Therefore, the materials prepared with the use of HCl are more basic. AuMCM-41 reveals the highest basicity. The introduction of vanadium and/or niobium into MCM-41 together with gold diminishes the basicity of the materials (much more when Nb is introduced) observed in 2-propanol and acetonylacetone test reactions. One should answer how do changes in the surface properties of AuMCM-41, resulted from V or/and Nb introduction, influence on the activity and selectivity in methanol oxidation.

The mechanism of methanol oxidation can be considered on the basis of literature [8,23,24,29–31]. Catalytic oxidation of methanol requires the formation of chemisorbed methoxy groups, which are further transformed to formaldehyde species resulted from the extraction of hydrogen from methoxy species. If formaldehyde is enough strongly chemisorbed on nucleophilic species it can interact with the next methanol molecule and form methyl formate. Methanol can be also chemisorbed on pairs of active centres giving rise to formate species, which further interacts with methanol to methyl formate. Of course, the total oxidation of methanol to CO_2, which usually involves the radical mechanism, is also possible. The observed reaction products depend on the possibility of the formation and the strength of chemisorption of the intermediates. They are determined by the surface properties of the catalysts.

It is clear that the surface properties of the materials containing transition metals and gold depend on the activation conditions. If the samples were activated under vacuum (for FTIR experiments) the surface was much more reduced than after heating in the presence of oxygen. Such dependence is well illustrated by the FTIR study of AuVNbMCM-41(H_2SO_4) after vacuum and oxygen activation (Fig. 2C and D). The activation in the vacuum or in the flow of helium gives rise to the reduced surface in which oxygen is released and the oxygen hole on the metal cation is generated. Such centre plays a role of Lewis acid site which presence was indicated by the formation of diisopropyl ether in 2-propanol dehydration. The adsorption of methanol on such a surface (Fig. 2C) leads to its transformation to olefin detected by FTIR spectra as bands at 1611 and 3089 cm^{-1}. This species is strongly held even at 573 K. However, when the surface is more oxidised one could observe less olefin and more formate species after methanol adsorption (Fig. 2D). The consideration of olefin formation (related to the presence of Lewis acid sites) basing on the 1611 cm^{-1} IR band (Fig. 2A–D) leads to the conclusion that the presence of both, Nb and V, besides Au makes the release of oxygen from the surface much easier. There is no doubt that this feature should be related to niobium–vanadium interaction in the sample and makes AuVNbMCM-41(H_2SO_4) catalyst much more selective to formaldehyde in the methanol oxidation (Table 4).

The disordering of the mesoporous materials prepared by the use of HCl as the pH adjustment agent and their basic character (2-propanol and AcAc reactions) seems to be responsible for the high total oxidation of methanol to CO_2 (Table 4). The presence of vanadium or niobium besides gold in MCM-41 makes this process more effective (the highest selectivity to CO_2 on AuNbMCM-41 and AuVMCM-41) showing that Au–Nb(V) interactions enhance the electron transfer. The more acidic catalysts (prepared by the use of H_2SO_4 during the synthesis) exhibit much lower total oxidation activity.

The methyl formate genesis requires the concurrence of two kinds of active centres on the catalyst surface, in line with the reaction pathway proposed by Busca et al. [23]. The partially poisoning of active centres by the strong chemisorption of olefin on AuVNbMCM-41(H_2SO_4) (see Fig. 2C) results in the lowering of $HCOOCH_3$ formation in the flow system (Table 4) if one compares with the selectivity on AuVMCM-41(H_2SO_4).

The above considerations of the selectivity in methanol oxidation process shows that the catalytic phenomenon in this reaction is complex. One can prepare the catalyst required for the desired activity and selectivity applying not only the special components for the catalyst but also by the choice of the synthesis procedure.

5. Conclusions

1. The introduction of V and/or Nb together with Au into MCM-41 diminishes basicity of AuMCM-41.
2. The preparation of metals (Au, V, Nb) containing MCM-41 by the use of H_2SO_4 as a pH adjusting agent leads to the materials which reveal the higher acidity than those prepared with the application of HCl for that purpose. That determines the catalytic properties.
3. The composition of the catalyst and the preparation route strongly influence the catalytic activity and selectivity in the methanol oxidation.
4. The interaction between Au, V and Nb in AuVNbMCM-41(H_2SO_4) results in the highest selectivity to formaldehyde in methanol oxidation due to the weaker chemisorption of HCHO. The same feature causes the lowest activity of this catalyst.
5. Bimetallic catalysts (AuVMCM-41(HCl) and AuNbMCM-41(HCl)) are the most active in the oxidation of methanol to CO_2 because of their disordering and basicity which assist in the electron transfer required in the radical mechanism of methanol total oxidation.

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