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Gold-vanadium-niobium catalysts in environmental protection—adsorption and interaction of NO, C_3H_6 and O_2—FT-IR study

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Abstract FT-IR study of NO and C_3H_6 adsorption, co-adsorption and interaction in the presence of oxygen were performed in order to estimate the catalytic behaviour of Au and V-containing MCM-41 materials in NO-SCR with propene. MCM-41 were modified with gold, vanadium and niobium by their introduction during the synthesis (co-precipitation) carried out with the use of HCl or H_2SO_4 as pH adjustment agent. The texture/structure properties of the prepared samples were investigated by N_2 adsorption, XRD, XPS and TEM techniques. It has been found that the nature of acid used for the pH adjustment during the synthesis determines the gold particles size and dispersion and influences the interaction of $NO + O_2 + C_3H_6$ with the catalyst surfaces. In both types of AuVMCM-41 catalysts, the SCR reaction route occurs via NO_2 formation. In the case of AuVMCM-41(HCl) and AuVNbMCM-41(HCl) nitrites are formed and stored, and upon heating NO_2 is released. These kinds of nitrites are not formed on AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4). Instead of that NO_2 is chemisorbed on metallic gold, niobium and vanadium species and reacts with propene and/or oxygenates.

Keywords AuVMCM-41 · AuVNbMCM-41 · FT-IR co-adsorption of NO, C_3H_6, O_2

1 Introduction

In recent years, a growing amount of attention has been paid to noble metals-supported catalysts due to their potential applications in industrially important chemical reactions and environmental protection. Gold supported on various matrices is in the focus of this attention (Bond et al. 2006; Heiz and Landman 2007).

The catalytic applications of gold to preserve the quality of the earth' environmental involve several processes. Among them is the reduction of NOx by hydrocarbons such as propene in the presence of oxygen excess (Bond et al. 2006; Bond and Thompson 1999).

Studies with Au-based catalysts for their application in NOx removal have focused on SCR of NO with propene (Ueda et al. 1997; Ueda and Haruta 1998; Mihut et al. 2002). Haruta and co-workers first reported the effectiveness of supported Au-catalysts for this reaction (Ueda et al. 1997). It was shown that gold supported on ZnO, Fe_2O_3 and ZrO_2 is active at lower temperatures for HC-SCR-NOx. Moreover, the important advantage of Au-catalysts is their apparent greater selectivity for N_2 over N_2O formation. On $Au/Al_2O_3 \sim 100\%$ selectivity for N_2 have been observed (Ueda et al. 1997; Kung et al. 1997; Seker and Gulari 2002).

NO, C_3H_6 and O_2 take part in the HC-SCR (Selective Catalytic Reduction with Hydrocarbons) of nitrogen oxides addressed to lean burn engines. Before the use of new catalysts in this process it is important to know whether all reagents are chemisorbed on the catalyst surface and which kind of intermediate products could be formed. For that purpose the use of in-situ FT-IR (Fourier Transform Infrared Spectroscopy) study of the adsorption and co-adsorption of the reagents followed by their interaction at various temperatures is a useful tool for both, the prediction of the reaction route and for the characterisation of the surface properties. In the literature there are only few reports concerning FT-IR study of NO adsorbed on gold supported on oxides (e.g. Debeila et al. 2005) and mesoporous materials (e.g. Akolekar and Bhargava 2005) and NO interactions with

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propene in the presence of oxygen on such kind of catalysts (e.g. Sobczak et al. 2008). It was found (Debeila et al. 2005) that different adsorption modes exist for NO on gold catalysts depending on the calcination temperature. After NO adsorption on Au-TiO_2 unidentate nitrite ($\sim$1476 cm^{-1}) dominate in FT-IR spectra for uncalcined Au-TiO_2 and for Au-TiO_2 calcined at 973 K. In addition, bridging nitrite (1540 cm^{-1}) was one of the dominant species seen on Dry-Au-TiO_2. At elevated temperatures decomposition of NO_3^- into NO_2^- was observed. Akolekar and Bhargava (2005) reported that NO adsorbed on AuAlMCM-41 (Au introduced during the synthesis) leads to the formation of adsorbed nitrous oxide, chemisorbed nitrogen dioxide, nitrite, mononitrosyl and dinitrosyl complexes. The distribution and formation of these NO complexes was influenced by the nano gold particles concentration, reaction temperature, and pressure of NO.

Our recent FT-IR study of the adsorption and co-adsorption of NO, C_3H_6 and O_2 presented in (Sobczak et al. 2008) allowed to estimate the chemisorbed species and their interaction towards intermediates on gold catalysts based on mesoporous MCM-41 matrices. Gold was introduced into silicate and niobiosilicate matrices by the impregnation and via co-precipitation. It has been found that propene is chemisorbed on metallic gold species, but does not interact with NO which is not chemisorbed on gold centres. The presence of oxygen is absolutely necessary for this reaction. Oxygen oxidises NO to NO_2, the latter interacts with chemisorbed propene towards carboxylates and NO_2 is reduced to N_2O. At higher temperatures carboxylates interact with gaseous NO to carbonate, N_2O, CO and CO_2. The presence of niobium in the NbMCM-41 matrix enhances the oxidative properties of the catalysts and as a consequence the interaction between intermediates in NO reduction with propene in the oxygen excess. This effect is especially high on the catalyst prepared by the co-precipitation. The latter sample exhibits the higher NOx storage properties than the impregnated one.

It is well known that the properties and the activity of the supported Au catalysts strongly depend on the method of preparation (Bond et al. 2006; Heiz and Landman 2007). The use of a careful procedure is crucial in order to obtain small gold crystallites well dispersed on the support. It has been found that an optimal Au particle size to obtain a good catalyst activity is between 2 and 5 nm. However, larger particles ($\geq$10 nm) have also been shown to have activity and play a significant role (Bond et al. 2006; Heiz and Landman 2007; Mellor et al. 2002). It is in case of SCR-NOx reaction. It has been reported (Kung et al. 1997) that maximum activity of Au/Al_2O_3 was observed in the 15 to 30 nm particle range. Smaller Au particles appear to favour the combustion of propene, lowering the NOx activity (Kung et al. 1996).

The supported Au catalysts are generally prepared from chloride-containing Au precursors. The residual chloride can affect the activity, because it facilitates the agglomeration of Au particles during heat treatment and poison the active sites (Heiz and Landman 2007). On the other hand, the role of chloride anions localised in AuMCM-41 as promoters in HC-SCR reaction has been demonstrated (Sobczak et al. 2007).

The aim of this work is to study the effect of synthesis conditions (the role of HCl and H_2SO_4 used during the synthesis for adjustment of pH) and the addition of vanadium besides gold on the properties of AuVMCM-41 and AuVNbMCM-41 catalysts and their behaviour in SCR-NOx process. For the latter purpose we studied the NO + C_3H_6 + O_2 adsorption, co-adsorption and interaction on MCM-41 modified with Au and V or Au, V and Nb by in situ FT-IR spectroscopy.

2 Experimental

2.1 Preparation of mesoporous catalysts

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 (Beck et al. 1992). 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 ($HAuCl_4$—Johnson Matthey, UK-USA), vanadium(IV) oxide sulphate hydrate ($VOSO_4$—BDH) or ammonium niobate(V) oxalate hydrate ($C_4H_4NNbO_9$—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 or HCl 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 from the catalysts was removed by calcination at 823 K, 2 h in helium flow and 14 h in the air under static conditions.

2.2 Samples characterization

The X-ray Diffraction (XRD) patterns were obtained on a D8 Advance diffractometer (Bruker) using CuK_α radiation

($\lambda = 0.154$ 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.

For transmission electron microscopy (TEM) measurements powders were deposited on a grid with a holey carbon film and transferred to JEOL 2000 electron microscope operating at 80 kV.

Photoemission spectra (XPS) were collected by a VSW Scientific Instrument spectrometer, equipped with a standard Al K_α excitation source. The binding energy (BE) scale was calibrated by measuring C 1s peak (BE = 285.1 eV).

A Bruker FT-IR Vector 22 spectrometer was used to detect infrared spectra of the solid state powder MCM-41 samples. The resolution was selected to be 2 cm^{-1} and the number of scans was 64. The samples were dispersed in KBr pellet (1 mg of the sample and 200 mg of KBr) with slight grinding. FT-IR measurements were performed at room temperature.

2.3 Adsorption and co-adsorption of NO, C_3H_6 and O_2—FT-IR study

Infrared spectra were recorded with the Vector 22 (Bruker) spectrometer (resolution 4 cm^{-1}, number of scans = 64). 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 experiments were carried out in various ways including different sequences of the reagents admission (propene ≥99%, Aldrich, nitric oxide 99%, Merck, oxygen Messer Poland) and heating treatment at 523, 623 and 723 K. The spectra were registered at room temperature (RT). The spectrum without any sample ("background spectrum") was subtracted from all recorded spectra. The IR spectra of the activated samples were subtracted from those registered after the adsorption of probe molecules followed by various treatments. The reported spectra are the results of this subtraction.

3 Results and discussion

3.1 Characterisation

The texture/structure of the AuVMCM-41 and AuVNb-MCM-41 catalysts prepared within this work (gold, vanadium and niobium introduced by co-precipitation method during the synthesis of MCM-41) was characterized by N_2 adsorption, XRD, XPS, FT-IR, and TEM measurements.

The N_2 adsorption/desorption isotherms of all catalysts studied are of type IV according to the IUPAC classification, typical of MCM-41 materials (Beck et al. 1992) (Fig. 1). They exhibit a steep condensation step at a relative pressure of ~0.35 characteristic for nitrogen condensation in mesopores. The sharp condensation step for materials prepared by the use of sulphuric acid (for the pH adjustment) reflects high uniformity of mesopores. This step is less distinct on isotherms of the samples prepared with the application of HCl. For the later materials plateau indicating the saturation of mesopores is observed at a lower value of adsorbed volume (at ca. 350 $cm^3\,g^{-1}$ (STP)) than that for the other samples (ca. 600 $cm^3\,g^{-1}$ (STP)). Interestingly at $p/p_0 = 0.9$–1.0 a high increase of the adsorbed volume is noticed indicating a considerable macroporosity or intergranular porosity.

Table 1 summarises textural data based on low-temperature nitrogen adsorption experiments and clearly indicates that these features significantly depend on the conditions of synthesis. All MCM-41 materials posses high surface areas (in the range 800–1100 $m^2\,g^{-1}$) and average pore volumes between 0.8 to 1.34 $cm^3\,g^{-1}$. The mesopore volumes are lower because of the participation of macropores in the calculation of average volume. The use of HCl to adjust the pH during the synthesis leads to the catalyst

Table 1 Texture parameters of the catalysts

Catalyst	Surface area BET[a] (ads.) $m^2\,g^{-1}$	Average pore volume BJH[b] (ads.) $cm^3\,g^{-1}$	Mesopore volume BJH[b] (ads.) $cm^3\,g^{-1}$	Average pore diameter BJH[b] (ads) nm	Mesopore diameter (PSD)[c] nm
AuVMCM-41(HCl)	813	0.80	0.60	3.51	2.40
AuVNbMCM-41(HCl)	851	1.08	0.66	5.10	2.53
AuVMCM-41(H_2SO_4)	1055	1.34	1.02	4.27	3.33
AuVNbMCM-41(H_2SO_4)	1042	1.22	1.06	3.67	2.74

[a] Surface area calculated on the basis of Brunauer-Emmett-Teller (BET) theory

[b] Average pore volume and diameter calculated on the basis of Barrett-Joiner-Halenda (BJH) method

[c] Pore size distribution

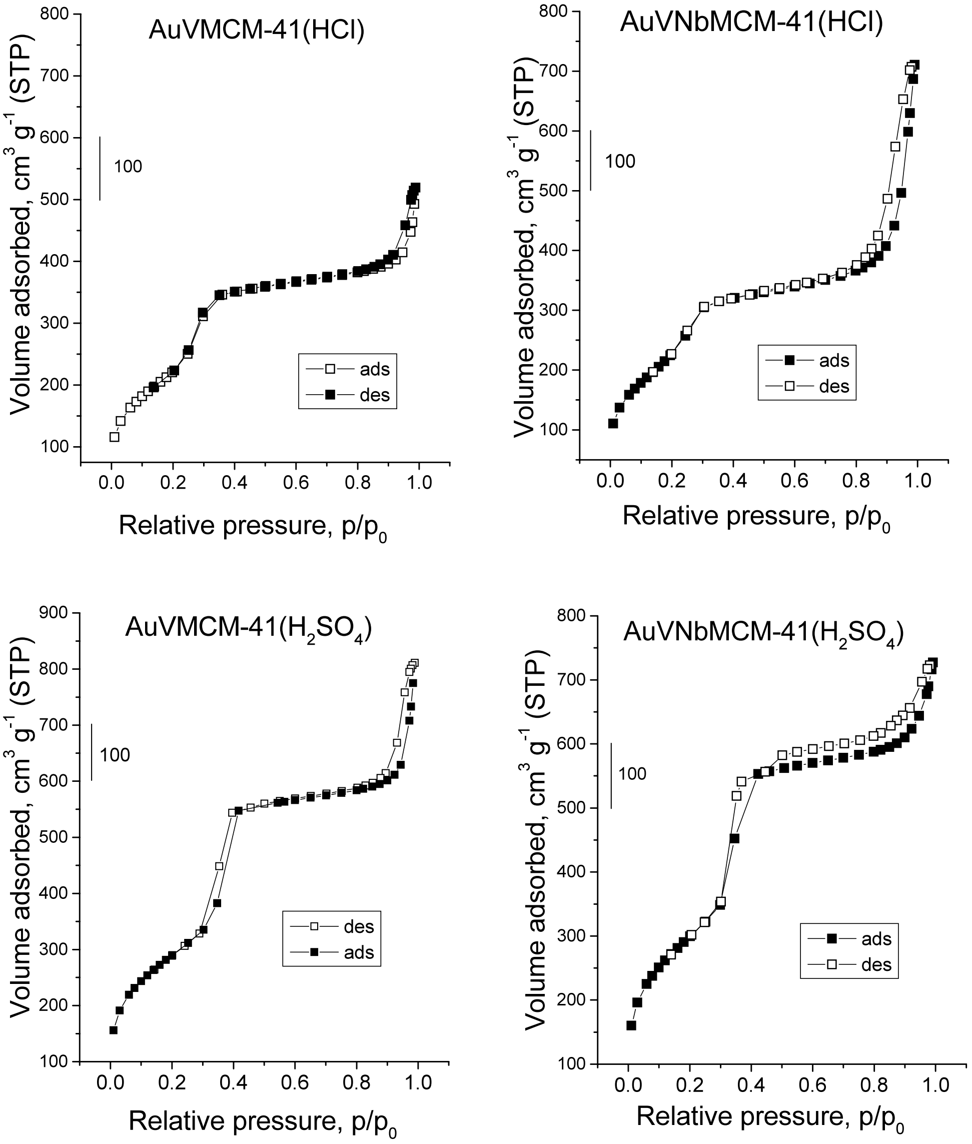


Fig. 1 N_2 adsorption/desorption isotherms of MCM-41 materials

with lower surface area and pore volume compared to the AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4) materials.

In addition to the nitrogen adsorption/desorption measurements, which are commonly used to evaluate the mesostructured materials the X-ray diffractions technique is a method of choice for evaluation of the structure ordering of mesoporous solids. Figure 2A shows the X-ray diffraction patterns at a low-angle range of MCM-41 materials. XRD patterns of MCM-41 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)) are characteristic of the mesostructured materials with highly ordered hexagonal arrangement (Beck et al. 1992). They are characterised by a narrow single Bragg peak (100) at $2\theta \sim 2°$ and up to three peaks in the region of $2\theta \sim 3$–8°. These reflections are due to the ordered hexagonal array of parallel silica tubes (Beck et al. 1992). Contrarily, the XRD patterns of AuVMCM-41(HCl) and AuVNbMCM-41(HCl) (Fig. 2A), in which HCl was used for pH adjustment during the synthesis, shows less pronounced reflections in the region 3–8° (the most visible for sample containing niobium). It indicates the disordering of the hexagonal structure in the long-range.

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(111) and at 44.8° from Au(200) (Okumura et al. 2003; Lü et al. 2005) (Fig. 2B). Peaks from Au are sharper for AuVMCM-41(HCl) and AuVNbMCM-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)). Moreover, it is worth of notice that niobium species located in MCM-41 samples

Fig. 2 XRD patterns of MCM-41 materials

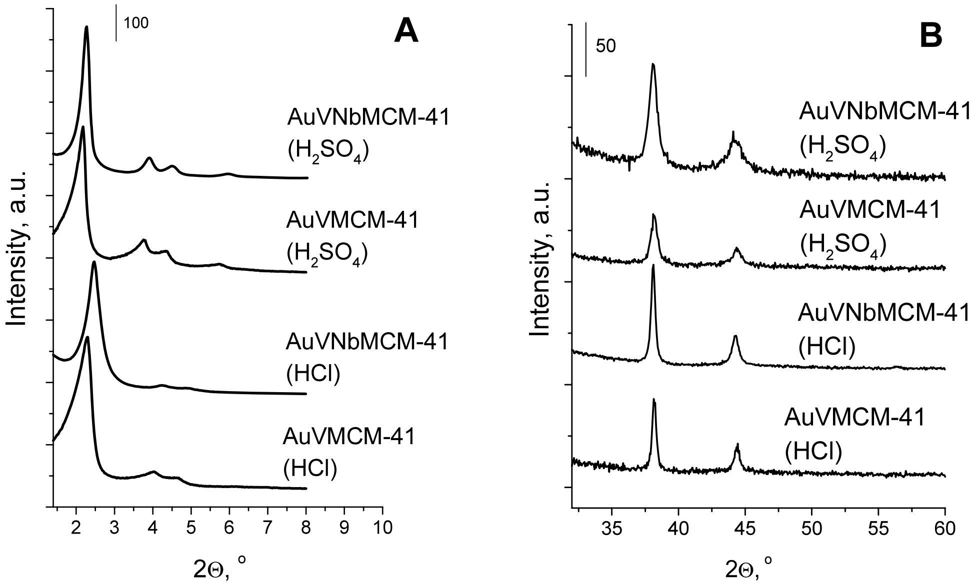
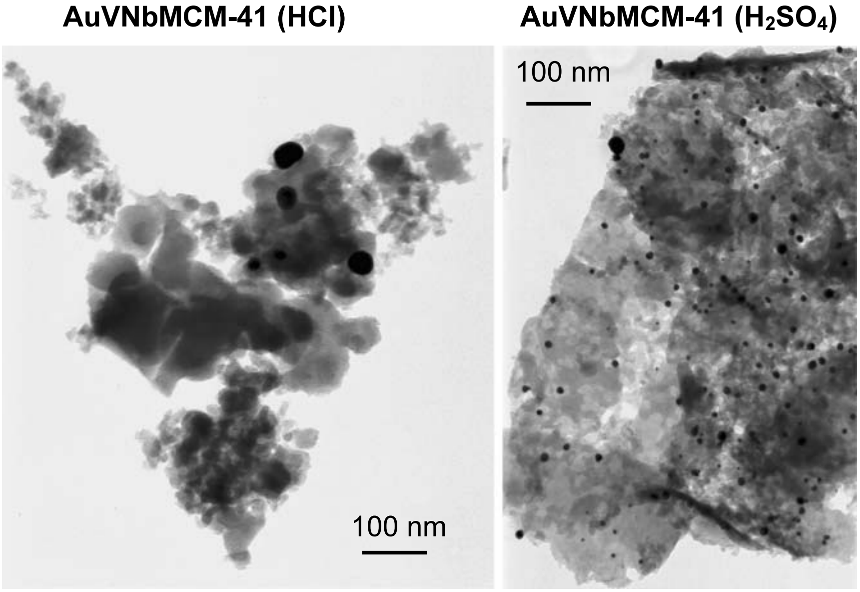


Fig. 3 TEM micrographs of AuVNbMCM-41(HCl) and AuVNbMCM-41(H_2SO_4) catalysts



play the role of a structural promoter that decreases the agglomeration of gold (peaks from Au are sharper for AuVMCM-41 than AuVNbMCM-41 samples). TEM images (Fig. 3) confirm above suggestions. The average size of Au crystallites in AuVMCM-41(HCl) and AuVNbMCM-41(HCl) estimated on the basis of the TEM images was as 50 nm. The application of H_2SO_4 to adjust the pH during the synthesis leads to much lower gold particles (average size ∼20 nm) and higher gold dispersion (Fig. 3 for AuVNbMCM-41(H_2SO_4)). However, the size of Au particles is not uniform and it ranges between 15 and 60 nm for AuVNbMCM-41(HCl) and between 2 and 40 nm for AuVNbMCM-41(H_2SO_4). 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. However, we cannot exclude that the texture/structure characteristic of the MCM-41 materials (Table 1) has a very high impact on the gold dispersion. The highest surface area and mesopore diameter noted for AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4) result in the highest (among the studied samples) gold dispersion seen in TEM images (Fig. 3).

Beside XRD and TEM techniques, also XPS results clearly indicate that only gold with the metallic state is present on the surface of all gold-vanadium modified materials (in XPS spectra of Au 4f region peak cantered at about 84 eV is visible—Table 2). Moreover, in the O1s XPS region one can observe the intense peak at ca. 533 eV with a tail at lower binding energy. The deconvolution allows the distinguish of two components, one at ca. 533 eV and the

Table 2 XPS results of the Au4f, Nb3d, O1s regions

Catalyst	Au4f BE/eV	Nb3d BE/eV	O1s BE/eV
AuVMCM-41(H_2SO_4)	83.9	–	532.9 530.2
AuVMCM-41(HCl)	84.3	–	532.6 530.8
AuVNbMCM-41(H_2SO_4)	84.1	208.1	533.0 530.2
AuVNbMCM-41(HCl)	83.9	208.2	533.3 530.6
Nb_2O_5	–	207.3	–

Table 3 Structural properties of the MCM-41 samples estimated by infrared measurements

Catalyst	$R = I_{960}\ cm^{-1}/I_{480}\ cm^{-1}$
AuVMCM-41(HCl)	0.32
AuVMCM-41(H_2SO_4)	0.36
AuVNbMCM-41(H_2SO_4)	0.40
MCM-41	0.25

second (very low intense) at ca. 530 eV (Table 2). This behaviour can be assigned to the existence of two various surrounding of oxygen, namely Si-O-Si (BE = ~533 eV) and Me(Nb, V)-O-Si (BE = ~530 eV). Therefore, it confirms the introduction of Nb (V) into the framework of MCM-41. It is worth of notice, that the BE of Nb3d in the materials studied is higher than that of Nb_2O_5. It suggests the incorporation of niobium into the skeleton of the samples and the interaction of Nb with Au loaded in MCM-41.

The additional proofs for the introduction of Nb and V into the framework of MCM-41 are results of FT-IR in the skeleton region (tablets with KBr). The IR spectra of all samples show bands characteristic of MCM-41 in the region of 1500–400 cm^{-1} (Rana and Viswanathan 1998). Beside the bands form Si-O-Si vibrations (1235, 1082, 795 and 460 cm^{-1}) the band at ~960 cm^{-1} is observed. It can be assigned to Si-O-Si-OH vibrations in pure siliceous MCM-41 or Si-O-Me vibrations in the framework of metallosilicate MeMCM-41 (AuVMCM-41, AuVNbMCM-41). The ratio (R) between the absorbance of a band which could be assigned to the polarized $Si\text{-}O^{\delta-}\cdots Nb^{\delta+}$ or $Si\text{-}O\cdots V$ bond (960 cm^{-1}) and a structure band (480 cm^{-1}) should give information about the position of niobium or vanadium (Nowak 2002). As one can see from Table 3 this ratio is bigger for samples prepared with addition of V or Nb than for pure silicate MCM-41. It confirms the incorporation of V and Nb into the framework of the mesoporous molecular sieves.

3.2 Adsorption and co-adsorption of NO, C_3H_6 and O_2—FT-IR study

In order to estimate the adsorption and catalytic behaviour of the prepared materials AuVMCM-41(H_2SO_4), AuVNbMCM-41(H_2SO_4), AuVMCM-41(HCl) and AuVNbMCM-41(HCl) in the NO reduction with propene FT-IR investigations were performed. The experiments were carried out in a vacuum cell, in which pressed wafers of the sample were placed and NO, O_2, and C_3H_6 were added in various sequences and compositions. The obtained results are shown in Figs. 4–6.

The difference in the adsorption and interaction between NO and C_3H_6 in the presence of oxygen is observed, depending on the chemical composition of the catalyst and the way of MCM-41 preparation determining the structure and surface properties as indicated above. Upon NO adsorption at room temperature (RT) one did not observe NO chemisorbed species on the surface of all catalysts studied. NO is present only in gas phase (1875 cm^{-1}) (Fig. 4). The following admission of oxygen leads to formation of nitrite, nitrate species or chemisorbed NO_2 depending on the catalyst. Exposure of AuVMCM-41(HCl) to $NO + O_2$ produces nitrite species (NO_2^-) characterized by the intense IR bands at ~1740, 1417 and 1354 cm^{-1} (Fig. 4) (Hadjiivanov 2000; Debeila et al. 2005; Sazama et al. 2005). For its formation the gaseous oxygen is used and electron transfer from the solid to NO_2 molecule must occur. The introduction of Nb (AuVNbMCM-41(HCl)) does not change significantly the behaviour of the catalyst in this matter. The source of transferred electron can be chloride ions in the surrounding of gold centres as it was shown earlier for AuMCM-41(HCl) catalyst (Sobczak et al. 2007). The band at 1417 cm^{-1} is still present after heating at 523 K. This feature indicates that AuVMCM-41(HCl) and AuVNbMCM-41(HCl) materials contain sites which can play the role of NOx traps. Such sites are not observed on AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4) exhibiting a higher Au dispersion than that of AuVMCM-41(HCl) and AuVNbMCM-

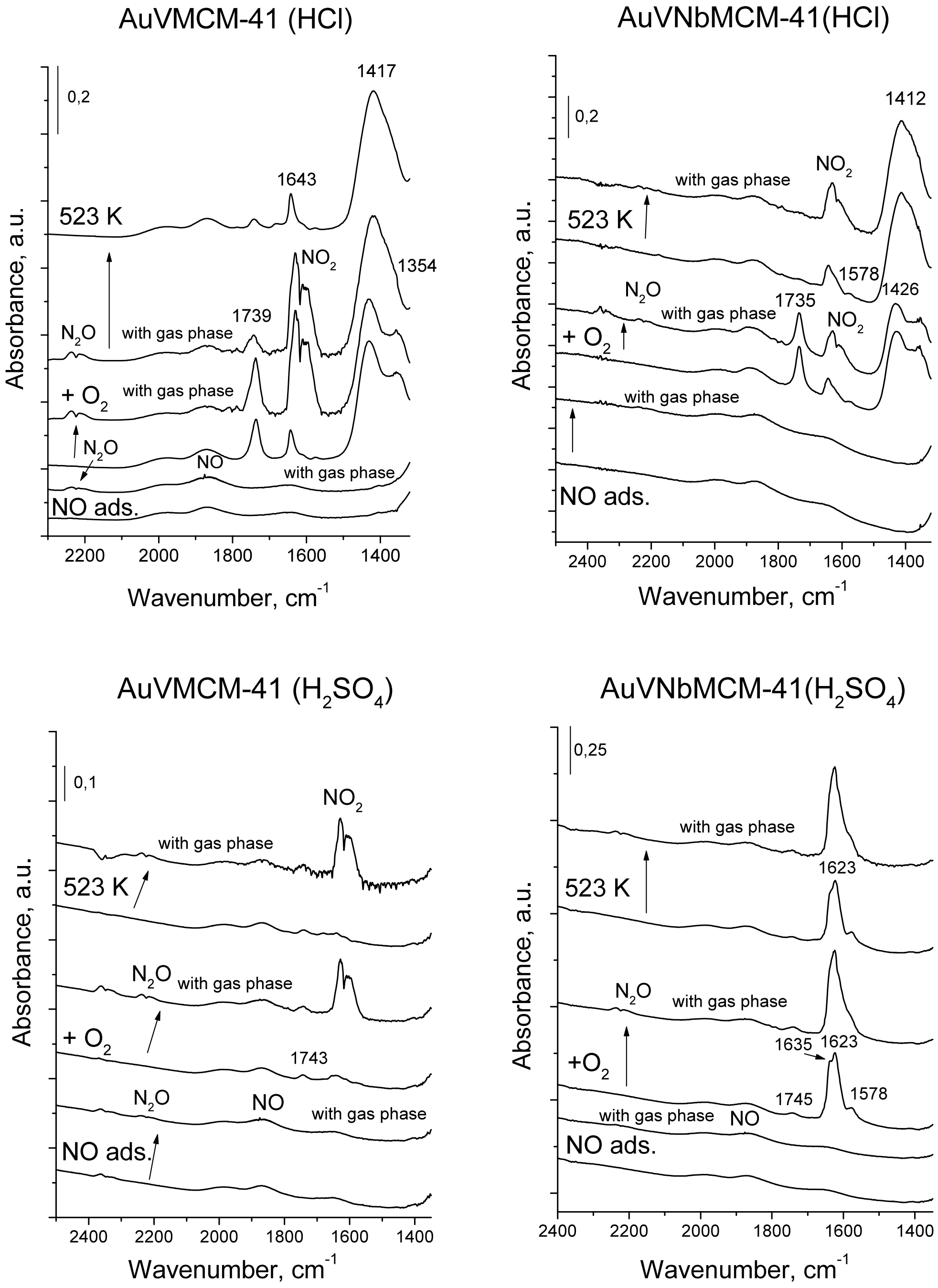


Fig. 4 FTIR spectra of MCM-41 materials after NO adsorption at RT, O_2 admission and heating at 523 K

41(HCl). The admission of NO + oxygen to these samples results in the band at 1745 cm^{-1}, which could be assigned to N_2O_4 (Hadjiivanov and Dimitrov 1999) or NO_2^- chemisorbed on gold species (per analogy to Pt^0-NO_2^- Goscianska et al. 2008), the other bands from nitrites in the region 1300–1500 cm^{-1} are not visible. NO adsorption in the presence of oxygen gives also the bands at ~1630 and 1578 cm^{-1} from bridging and bidentate nitrates (chemisorbed on vanadium/niobium species), respectively (Hadjiivanov 2000; Sazama et al. 2005). These last two bands are much more pronounced in the spectrum of AuVNbMCM-41(H_2SO_4) (two kinds of nitrates at 1635 and 1623 cm^{-1} chemisorbed on V and Nb). It indicates that the presence of Nb in the MCM-41 synthesised with the use of H_2SO_4 enhances the oxidation of NO towards NO_2. It was indicated elsewhere (Ziolek et al. 2000, 2001) that NO_3^- species is formed on NbO^- centres generated after dehydroxylation of Nb-containing MCM-41 materials. The formation of nitrates requires the oxidation of NO to NO_2. The latter is chemisorbed on NbO^- building NO_3^- species.

Oxidation of NO in the disproportionate process is accompanied by its reduction to N_2O ($3NO \rightarrow N_2O + NO_2$).

N_2O is observed in the gas phase of all MCM-41 catalysts (Fig. 4). Moreover, it is worth of notice that for the samples containing gold and vanadium (AuVMCM-41(H_2SO_4), AuVMCM-41(HCl)) the transformation of NO to N_2O is deduced from the FT-IR spectra (a band at 2223 cm^{-1} from N_2O) after NO adsorption at room temperature, before admission of oxygen. N_2O is less visible in case of AuVNbMCM-41(H_2SO_4) and AuVNbMCM-41(HCl) ma-

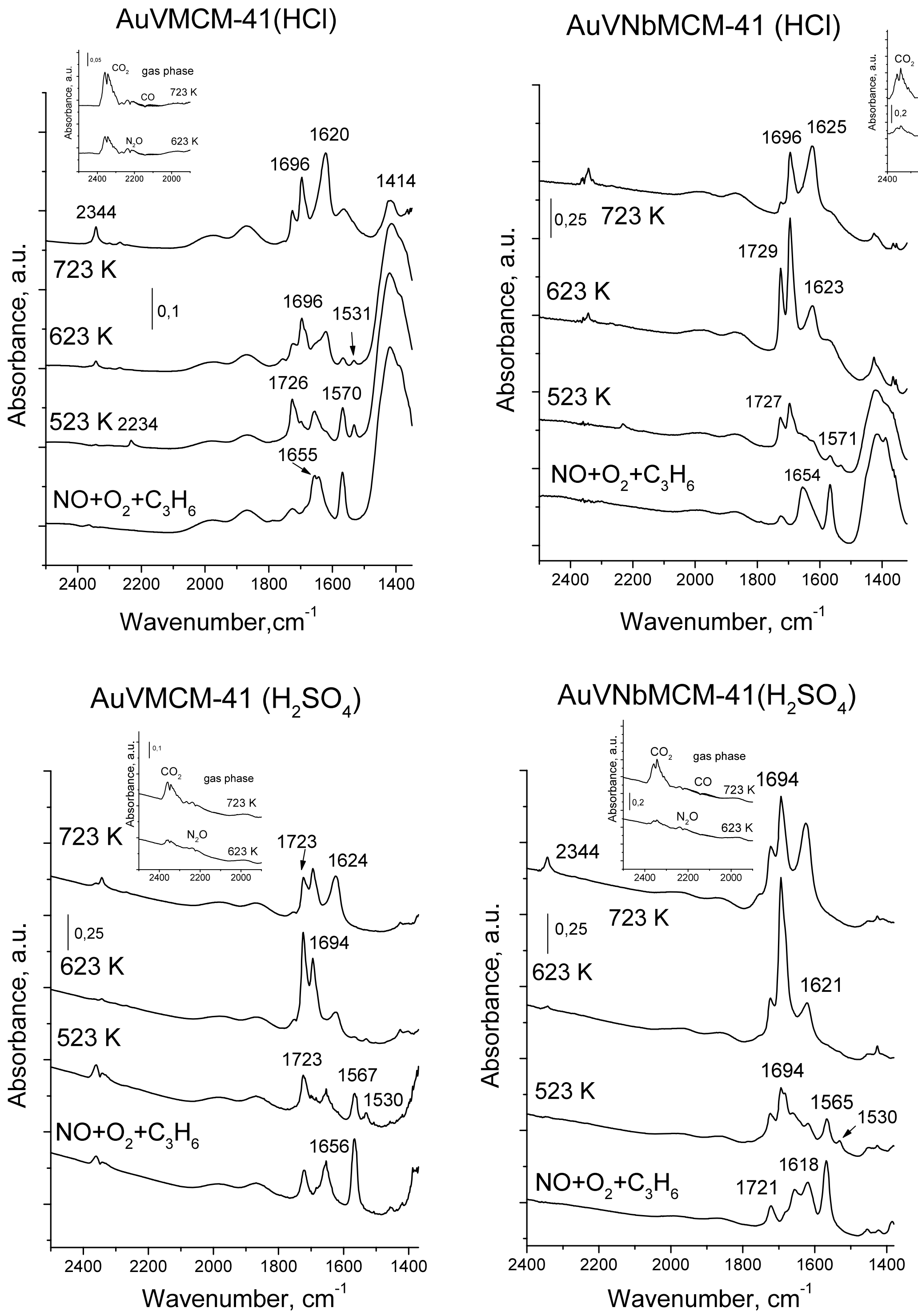


Fig. 5 FT-IR spectra of MCM-41 materials after the admission of reagents in the following order: NO, O_2, C_3H_6 and heating at 523, 623 and 723 K

terials. Formation of N_2O from NO can be assigned to the redox mechanism like it was noted on Pt/V/MCM-41 or on the support (V/MCM-41) (Jeon et al. 2003a, 2003b). Such redox properties of AuVMCM-41 can be also responsible for the NO oxidation to NO_2 after oxygen admission.

The introduction of propene after the adsorption of NO followed by O_2 admission creates three main IR bands in the range 1500–1750 cm^{-1} in case of all MCM-41 samples (Fig. 5). There are bands at ∼1570 cm^{-1} assigned to acetates (Schießer et al. 2001; Sazama et al. 2005; Sobczak et al. 2005), ∼1655 cm^{-1}—to organic nitrito compound (C_3H_7–ONO) (Chi and Chuang 2000), and at ∼1725 cm^{-1}—to C=O in acetone (Hoost et al. 1995; Sobczak et al. 2005). The formation of these bands indicates the partial oxidation of propene. Heating of the catalysts with the adsorbed species (523–723 K) causes the transformation of carboxylate species (the band at 1570 cm^{-1}, ν COO^- in acetate) to carbonates (1534 cm^{-1}) at 523 K and acetone (ν C=O at ∼1725 cm^{-1} from physisorbed acetone and at 1696 cm^{-1} from acetone hydrogen bonded to hydroxyl groups (Datka et al. 2005) at 623 and 723 K. Such transformations are typical of noble metals containing MCM-41 as was shown earlier for Pt/MCM-41 (Sobczak et al. 2005) and Au/MCM-41 (Sobczak et al. 2008) catalysts. The difference between catalysts synthesised with the use of H_2SO_4 and HCl appears in the region characteristic of NO adsorption. In case of AuVMCM-41(HCl) and AuVNbMCM-41(HCl) (Fig. 5) the IR band from nitrite species (ca. 1420 cm^{-1}) disappears after heating indicating the desorption of NO_2 from the surface. Nitrite species are decomposed much easier and at lower temperature (623 K) on the catalysts containing niobium (AuVNbMCM-41(HCl) due to the strong Au-Nb interaction which makes the chemisorption of NO_2^- weaker. Thanks to that propene interaction with nitrite species is more effective on Nb-containing catalyst. Simultaneously, it indicates that Nb species in the framework of MCM-41 reveals good storage properties (better than vanadium one).

Nitrite species in the region 1300–1500 cm^{-1} is not formed on the surface of the AuVMCM-41(H_2SO_4) exhibiting a higher gold dispersion. In case of AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4) chemisorbed NO_2 interacts with the admitted C_3H_6 towards partially oxidized products (the intensity of the band at ∼1620 cm^{-1} decreases at 523 and 623 K and increases at 723 K).

The AuVMCM-41(HCl) and AuVNbMCM-41(HCl) catalysts are more active in the reaction between nitrogen oxides and partially oxidized propene than AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4) samples as can be deduced from the appearance of the more pronounced bands from adsorbed N_2O (2230 cm^{-1}) (Hoost et al. 1995; Sobczak et al. 2005) and CO_2 (∼2300 cm^{-1}) (Manzoli et al. 2007) formed after heating at 523–723 K. The gas phase spectrum after heating at 623 K shows the presence of gaseous N_2O, CO_2 and CO at 723 K.

Figure 6 displays the FT-IR spectra after the admission of C_3H_6 and $C_3H_6 + O_2$ on AuVMCM-41 samples. Propene is weakly chemisorbed on the catalysts surface at RT (room temperature) as evidenced from the band at ∼1640 cm^{-1} (ν C=C; at 1640 cm^{-1} is a band of physisorbed propene) and ∼1450 cm^{-1} ($\nu = CH_2$ and $= CH$ physisorbed and weakly chemisorbed on various centres) (Datka and Kukulska-Zajac

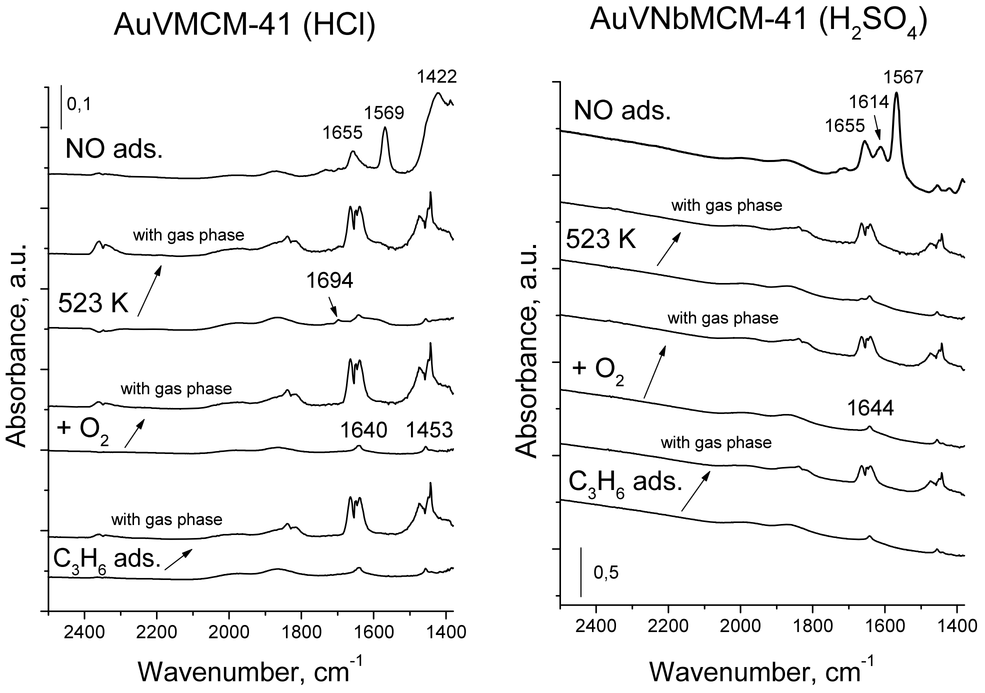


Fig. 6 FT-IR spectra of MCM-41 materials after the admission of reagents at RT in the following order: C_3H_6, O_2 and NO

2004). The admission of O_2 and heating at 523 K do not change the FT-IR spectra of the AuVMCM-41(H_2SO_4), AuVNbMCM-41(H_2SO_4) and AuVNbMCM-41(HCl) materials (Fig. 6 for AuVNbMCM-41(H_2SO_4)). It means that the oxidation of C_3H_6 does not occur under these conditions. In contrast, the same treatment of AuVMCM-41(HCl) (Fig. 6) leads to both, partial oxidation of propene to acetone (small intensity band at 1694 cm^{-1} from acetone hydrogen bonded to hydroxyl groups) and complete oxidation to CO_2 (evidenced by the bands at $\sim$2360 cm^{-1} in the gas phase). After the admission of NO at RT onto the MCM-41 samples one can clearly conclude transformation of propene towards partial oxidation products (bands in the range 1500–1750 cm^{-1}). It means that on AuVMCM-41(H_2SO_4), AuVNbMCM-41(H_2SO_4) and AuVNbMCM-41(HCl) catalyst NO molecule promotes partial oxidation of propene. The activity of AuVMCM-41(HCl) material in the oxidation of C_3H_6 with O_2 (without the presence of NO) results from the described above redox character of this catalyst.

4 Conclusions

FT-IR studies of the NO interaction with propene in the presence of oxygen allow determining the reaction pathway of SCR NOx. In both types of AuVMCM-41 catalysts, synthesized with the use of HCl and H_2SO_4 for pH adjustment, the reaction pathway is via NO_2 formation. However, the main difference between both types of samples is that on AuVMCM-41(HCl) and AuVNbMCM-41(HCl) nitrites are formed and stored, and upon heating NO_2 is released. These kinds of nitrites are not formed on the materials prepared with the use H_2SO_4(AuVMCM-41(H_2SO_4) and AuVNbMCM-41(H_2SO_4)). Instead of that NO_2 is chemisorbed on metallic gold, niobium and vanadium species in the form of nitrites/nitrates and reacts with propene and/or oxygenates. All catalysts (with an exception of AuVMCM-41(HCl)) are not active in the direct oxidation of propene by oxygen. Propene oxidation requires the presence of NO in the gaseous mixture.

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