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FTIR study of NO, C_3H_6 and O_2 adsorption and interaction on gold modified MCM-41 materials

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Abstract

This paper is devoted to the detailed FTIR study of the adsorption, co-adsorption, and interaction of all the reagents used in NO HC-SCR process addressed to lean-burn engines with the surface of new gold catalysts based on ordered mesoporous materials. Gold was introduced into silicate and niobiosilicate matrices by the impregnation (Au/MCM-41 and Au/NbMCM-41, respectively) and via co-precipitation with siliceous and niobium sources (AuNbMCM-41). The in situ FTIR study allowed the estimation of the possible chemisorption of the reagents and their interaction towards intermediates, depending on the chemical composition of the catalyst and the way of gold introduction. It has been found that propene is chemisorbed, but not, NO, on gold species at room temperature. Chemisorbed C_3H_6 interacts with NO only in the presence of oxygen excess. Oxygen oxidizes NO to NO_2, the latter interacts with chemisorbed propene towards carboxylates ($\sim$1570 cm^{-1}) 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. The co-precipitated AuNbMCM-41 exhibits higher NOx storage properties than the impregnated one.

Keywords: Au/MCM-41; Au/NbMCM-41; AuNbMCM-41; FTIR co-adsorption of NO; C_3H_6; O_2; NO-SCR

1. Introduction

Gold has been considered catalytically less active than other transition metals for many years. However, the last two decades have witnessed a renaissance of interest in using Au as catalyst component [1,2]. The catalytic applications of gold involve several processes [1,3]. One of them is the reduction of NOx by hydrocarbons such as propene in the presence of oxygen excess [1]. SCR of NOx in connection with exhaust-gas treatment for lean-burn gasoline engines and diesel engines remains as one of the major challenges in the environmental catalysis.

It has been reported that gold supported on ZnO, MgO, TiO_2, Al_2O_3, Fe_2O_3 [4,5] exhibits good activity in the reduction of NOx with propene between 473 and 773 K producing N_2 as the major product. In particular, Au/Al_2O_3 gives the highest conversion to N_2 among the supported gold catalysts tested; a gold loading 0.2 wt.% gave 72% conversion at 698 K [6]. It was suggested that NO reduction takes place trough the oxidation of NO to NO_2, which than reacts with propene to give nitrogen [1]. Moreover, Ueda and Haruta showed [7] that the addition of Mn_2O_3 enhance the activity of Au/Al_2O_3 in the SCR NOx, markedly improves the conversion of NO to N_2 even in the presence of oxygen and moisture at a wide range of temperatures (523–773 K). The reason of that behaviour is high activity of Mn_2O_3 in NO oxidation to NO_2.

Recently, mesoporous molecular sieves have been used as supports for gold [8,9], (e.g. MCM-41 materials, which exhibit a uniformly and hexagonally arranged mesopores, high surface area and large pore volumes). It has been found [8], that mesoporous MCM-41 support makes the high dispersion of gold nanoparticles, and the mesopores facilitate the transport of molecules.

In the literature there are only few reports concerning FTIR study of NO adsorbed on gold supported on oxides (e.g. [10]) and mesoporous materials (e.g. [9]), and, according to our knowledge, no reports about NO interactions with propene in the presence of oxygen on such kind of catalysts. It was found [10] that different adsorption modes exist for NO on gold

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catalysts depending on the calcination temperature. After NO adsorption on Au–TiO_2 unidentate nitrite (~1476 cm^{-1}) dominate in FTIR 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. The extended exposure of Au–TiO_2 to NO led to the transformation of nitrites to nitrates species. At elevated temperatures decomposition of NO_3^- into NO_2^- was observed. Bhargava and coworker [9] 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.

NO, C_3H_6 and O_2 take part in the HC SCR 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 FTIR 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 characterization of the surface properties. The aim of our study is located in this field. The new catalysts applied in this work were gold modified silicate and niobiosilicate (MCM-41 and NbMCM-41, respectively) ordered mesoporous materials. Gold was introduced into the catalysts by two methods, the impregnation (denoted by slash in the catalyst symbol) and by co-precipitation. The choice of NbMCM-41 matrix for gold was dictated by the earlier founding of NO storage properties of this material [11,12].

2. Experimental

MCM-41 mesoporous molecular sieves were synthesised by a hydrothermal method [13] and modified in the preparation of NbMCM-41 as in Ref. [14]. Sodium silicate (27% SiO_2 in 14% NaOH; Aldrich) was used as a silicon source and cetyltrimethylammonium chloride (25 wt.% in water, Aldrich) was applied as a surfactant. The formed gel from these components (molar gel ratios = 1 SiO_2:0.75 NaOH:6.5 CTMACl:0.075 H_2SO_4:103.75 H_2O) was stirred for about 0.5 h. For the preparation of NbMCM-41 catalyst Nb(V) oxalate was a source of Nb (Si/Nb molar ratio = 128 as assumed). The pH was adjusted to 11, 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. This reaction mixture was heated again to 373 K for 24 h to produce highly ordered samples. 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 Au/NbMCM-41 and Au/MCM-41 catalysts were prepared by the wetness impregnation of MCM-41 support with an aqueous solution of $HAuCl_4$ (49,39% Au, Johnson Matthey, UK–USA,) and a gold loading of 1 wt.%. Following the impregnation the catalysts were dried at 373 K for 5 h and calcined at 773 K for 3 h in air.

The alternative, direct synthesis of AuNbMCM-41 (co-precipitation) was performed in the same manner as conventional MCM-41 [13]. The only difference was the admission of $HAuCl_4$ and niobium oxalate (CBMM Brazil) as the sources of gold and niobium, respectively, into the gel-containing sodium silicate and the template (CTACl, cetyltrimethylammonium chloride, 25 wt.% in water, Aldrich). The Si/Au atomic ratio was 256 (corresponding to 1 wt.% of Au).

The prepared materials were characterized by XRD (TUR-62 diffractometer with CuKα radiation (λ = 0.154 nm), a step size 0.02° and 0.05° in the small-angle and high-angle range, respectively), nitrogen adsorption/desorption (at 77 K with a Micromeritics 2010 apparatus) and UV–vis (Cary 300 Scan Varian-spectrometer). Photoemission spectra (XPS) were collected by a VSW Scientific Instrument spectrometer, equipped with a standard Al Kα excitation source. The binding energy (BE) scale was calibrated by measuring C 1 s peak (BE = 285.1 eV).

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 723 K for 3 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 and 623 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

The studies performed within this work concentrated on the adsorption, co-adsorption and interaction between NO, propene, and oxygen estimated on the basis of FTIR spectra. The main goal was to answer the following questions: (i) whether all reagents are chemisorbed on the prepared catalysts, (ii) what is a role of niobium, (iii) what could be the reaction route, and (iv) what is the effect of oxygen. In order to answer these questions the adsorption of reagents was carried out in various sequences and it was followed by heating up to 623 K.

The nitrogen adsorption/desorption measurements confirmed that the impregnation and co-precipitation with gold source does not change significantly the texture parameters of both silicate and niobosilicate MCM-41 matrices (Fig. 1). XRD patterns and UV–vis spectra of Au-containing samples (not shown here) exhibit the presence of metallic gold particles characterized by the reflections at 2Θ = 38.2° from Au(1 1 1) and at 44.8° from Au(2 0 0) and ultraviolet–visible band at

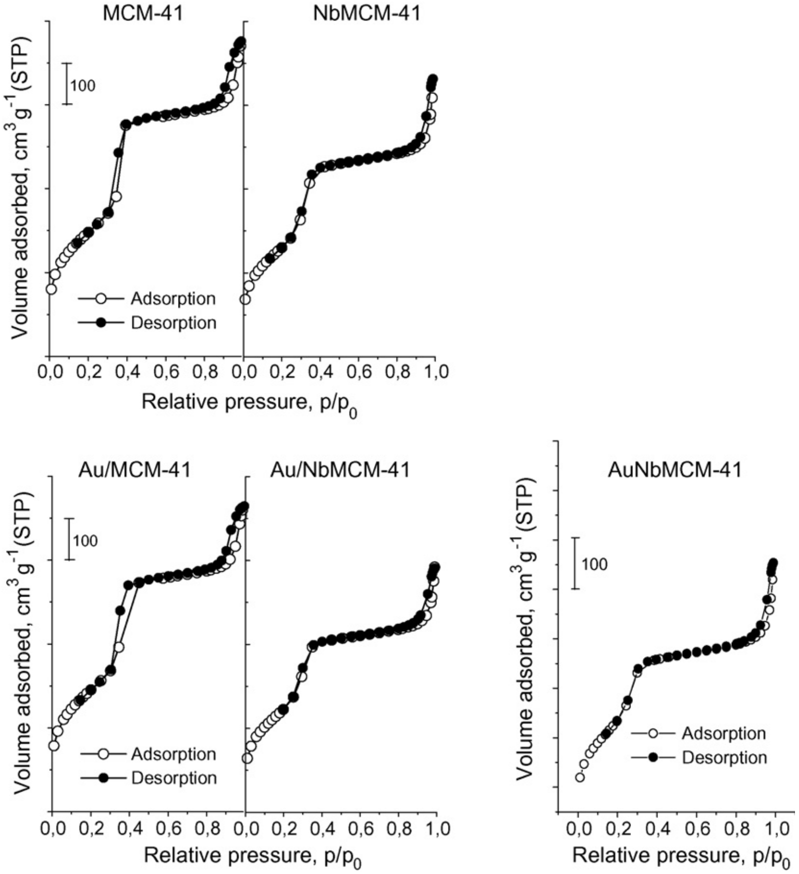

Fig. 1. N_2 adsorption/desorption isotherms of MCM-41 materials.

500 nm, respectively. Moreover, XPS results clearly indicate that only gold with the metallic state is present on the surface of gold-modified materials (in XPS spectra of Au 4f region peak cantered at about 84.5 eV is visible) [15–19].

Figs. 2 and 3 display the FTIR spectra after the admission of reagents in the following order: C_3H_6, O_2, NO into Au/NbMCM-41 (Fig. 2) and AuNbMCM-41 (Fig. 3) samples. Propene is weakly chemisorbed on the catalyst surface at RT

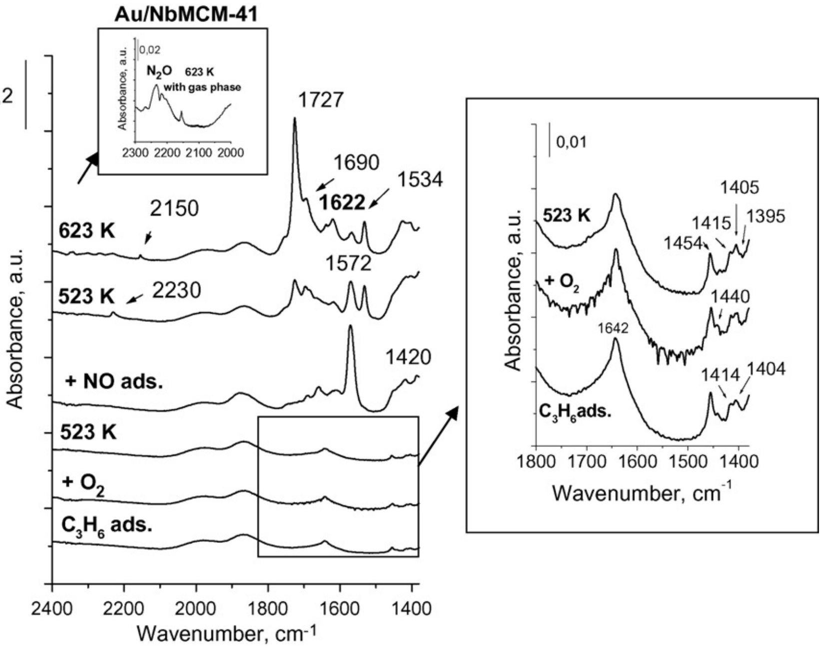

Fig. 2. FTIR spectra of Au/NbMCM-41 material after the admission of reagents at RT in the following order: C_3H_6, O_2, NO and heating at 523 and 623 K.

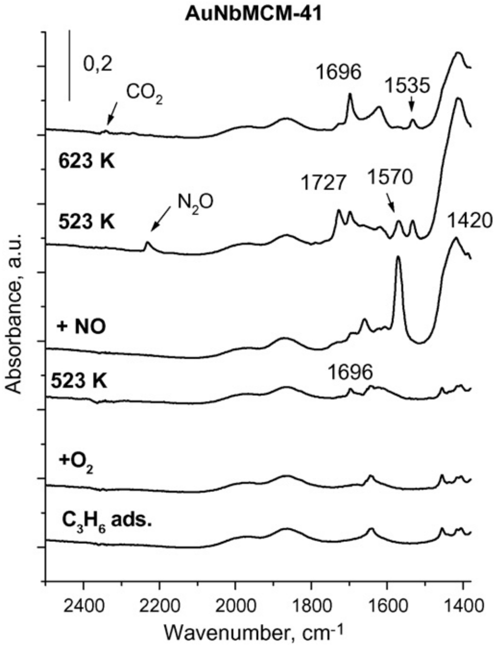

Fig. 3. FTIR spectra of AuNbMCM-41 material after the admission of reagents at RT in the following order: C_3H_6, O_2, NO and heating at 523 and 623 K.

(room temperature) as evidenced from the band at 1642 cm^{-1} (ν C=C; at 1647 cm^{-1} is a band of physisorbed propene) and the several bands in the 1450–1390 cm^{-1} range (ν =CH_2 and =CH physisorbed and weakly chemisorbed on various centres) [20]. The admission of O_2 and heating at 523 K do not change the FTIR spectra. It means that oxidation of C_3H_6 does not occur under these conditions. The same is true for Au/MCM-41 (the spectra not shown here). This behaviour completely changes after the next admission of NO at RT. One can clearly conclude the propene partial oxidation towards carboxylate species (the band at 1572 cm^{-1}, ν COO^- in acetate) [11,21–23] which transforms to carbonates (1534 cm^{-1}) [11,24,25] at 523 K and acetone (ν C=O at 1727 cm^{-1} from physisorbed acetone and a shoulder (Au/NbMCM-41) or a band (AuNbMCM-41) at 1696 cm^{-1} from acetone hydrogen bonded to hydroxyl groups [26]) at 523 K. The similar spectra in the discussed region were observed in Au/MCM-41. However, the role of Nb was evidenced in the formation of nitrite species after NO admission (the bands at ~1420 cm^{-1}) [11,21,27], which is especially visible for AuNbMCM-41 (prepared by co-precipitation) (Fig. 3). This species in case of Au/NbMCM-41 seems weakly interact with C_3H_6 and/or partially oxidized propene (oxygenates) contrary to Pt/NbMCM-41 [11] and AuNbMCM-41 co-precipitated. The interaction of nitrite species with oxygenates is especially evidenced on AuNbMCM-41 after heating at 623 K. After heating at this temperature the IR spectra differ depending on the method of Au introduction into NbMCM-41 matrix. On the impregnated material (Fig. 2) the band from physisorbed acetone dominates in the spectrum whereas on co-precipitated sample (Fig. 3) the hydrogen bonded acetone (1696 cm^{-1}) and nitrite (1420 cm^{-1}) are the main registered species. The Au/NbMCM-41 and AuNbMCM-41 materials are more active in the reaction between nitrogen oxides and partially oxidized propene than Au/MCM-41 sample as can be deduced from the appearance of the band at 2150 cm^{-1} (chemisorbed CO) [28,29], adsorbed N_2O (2230 cm^{-1}) [24,30] and CO_2 (~2300 cm^{-1}) [29] formation after heating at 523 and 623 K. The gas phase spectrum after heating at 623 K shows the presence of gaseous N_2O.

When the different sequence of the reagents admission onto Au/NbMCM-41 was applied (NO, next propene, next O_2) one did not observe NO chemisorbed species as well as the reaction products after the adsorption of NO and propene at RT and even after heating at 523 and 623 K (Fig. 4). The C_3H_6 weakly chemisorbed and physisorbed species can be

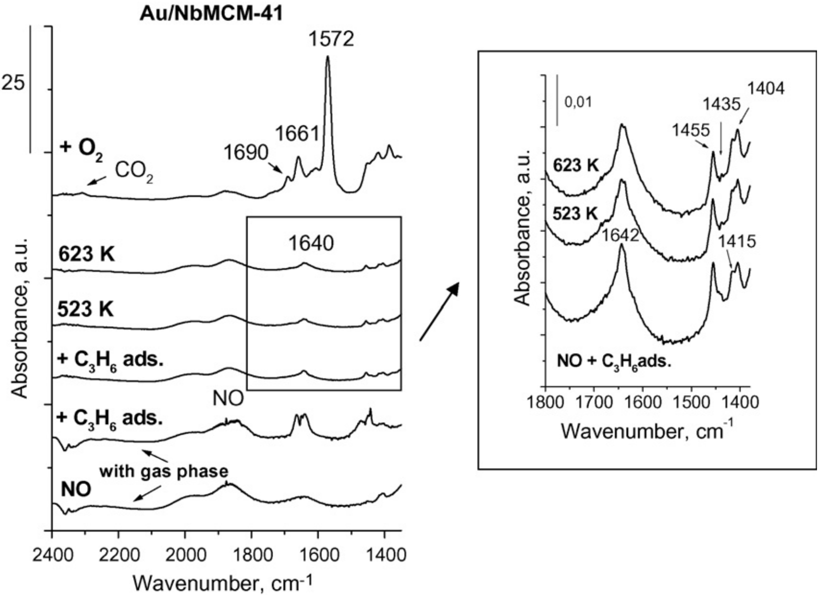

Fig. 4. FTIR spectra of Au/NbMCM-41 material after the admission of reagents at RT in the following order: NO, C_3H_6, heating at 523 and 623 K, and O_2 introduction.

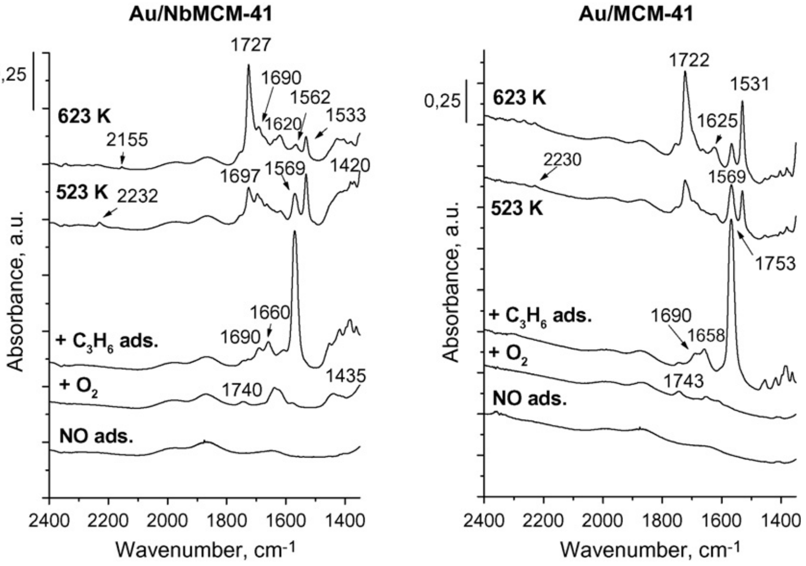

Fig. 5. FTIR spectra of Au/NbMCM-41 and Au/MCM-41 materials after the admission of reagents in the following order: NO, O_2, C_3H_6 and heating at 523 and 623 K.

found like in Fig. 2. Again the same behaviour is observed on Au/MCM-41. However, the latter sample is less active after the introduction of oxygen at RT. The partial oxidation of C_3H_6 occurs on both samples but the following interaction with nitrogen oxides towards CO_2 is observed only on Au/NbMCM-41.

To estimate whether NO interaction with oxygen towards NO_2 takes part in the following reaction with propene the experiments with the preadsorption of NO and O_2 prior to the propene admission were applied (Figs. 5 and 6). NO oxidation with oxygen leads to the formation of NO_2^- species chemisorbed on gold and characterized by ~1740 and ~1400 cm^{-1} [10,21] bands registered on all samples, but very weak on Au/MCM-41 (Figs. 5 and 6). Moreover, the chemisorbed NO_2 is observed at ca 1620 [27,30] and 1438 cm^{-1} mainly on the samples containing niobium. Thus, the presence of Nb in the matrix enhances the oxidation of NO towards NO_2. The latter interacts further with the admitted C_3H_6 towards partially oxidized products, and at higher temperatures to CO, CO_2, and N_2O. Carboxylate and carbonate species are less stable on Au/NbMCM-41 and AuNbMCM-41 than on Au/MCM-41 due to the strong Au–Nb interaction. The strong Au–Nb interaction makes the chemisorption of intermediates on Au weaker. Thanks to that their interaction with nitrogen oxide and nitrite species is more effective on Nb-containing catalysts. It is worthy of notice that, contrary to the behaviour of Pt/NbMCM-41 [11], in the case of Au-impregnated sample (Fig. 5) there is no clear evidence of NO_2^- participation in the reaction with propene. Contrary, nitrate/nitrite seems to be active species on AuNbMCM-41 prepared by co-precipitation method (Fig. 6).

The described results clearly indicate that without the presence of oxygen the reaction between propene and NO does not occur. Therefore, the final experiments were performed after the saturation of the impregnated catalysts with the oxygen atmosphere at RT (Fig. 7). Such pretreatment was especially effective in the case of Au/NbMCM-41 sample leading to the formation of nitrite (~1450 cm^{-1}) [27], only slightly visible on Nb free sample, and NO_2 chemisorbed (~1611 cm^{-1}) [27] species. The following admission of propene at RT causes the partial oxidation of olefin to carboxylate species (1573 cm^{-1}) only on Au/NbMCM-41. When oxygen is finally admitted to the samples the further reactions occur towards oxygenates and CO_2 (~2300 cm^{-1}), on Au/NbMCM-41. CO_2 was not detected on Au/MCM-41. Again the role of Nb in the increasing of the activity is evidenced.

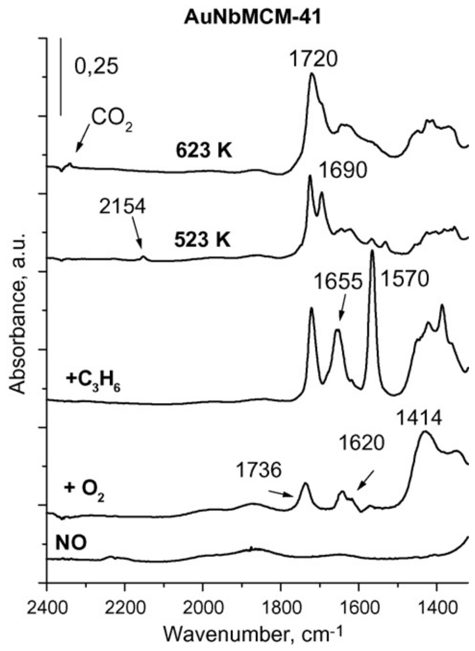

Fig. 6. FTIR spectra of AuNbMCM-41 material after the admission of reagents in the following order: NO, O_2, C_3H_6 and heating at 523 and 623 K.

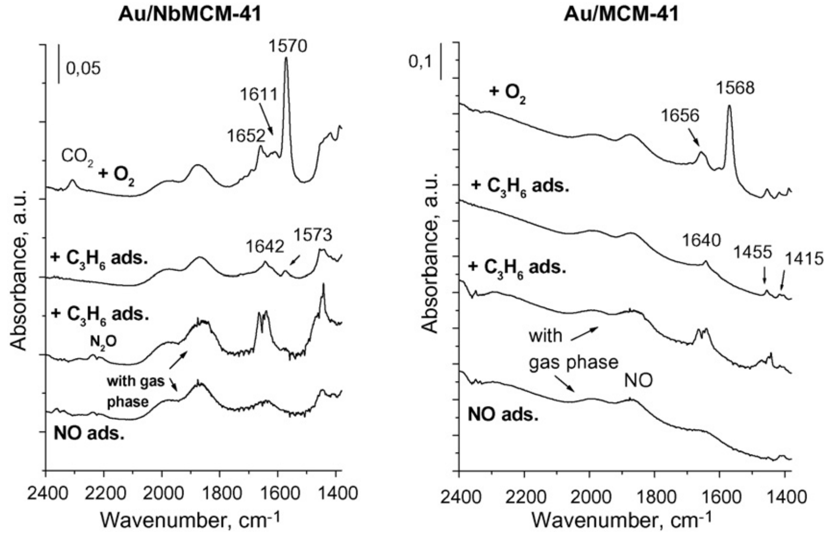

Fig. 7. FTIR spectra of Au/NbMCM-41 and Au/MCM-41 materials saturated with oxygen at RT before the admission of reagents at RT in the following order: NO, C_3H_6, O_2.

4. Conclusions

The presented results allowed us to estimate the chemisorbed species after the admission of NO HC-SCR reagents and their interaction on gold catalysts based on mesoporous MCM-41 matrices. 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 interacts with NO towards active NO_2. The latter oxidizes propene to carboxylate species ($1570\,cm^{-1}$) and it is reduced to N_2O at RT. At the higher reaction temperature (523 K) chemisorbed carboxylate species interacts with gaseous NO towards carbonate and N_2O and moreover at 623 K to acetone, CO and CO_2 formation. During the latter process oxygen is released and oxidizes the excess of NO to NO_2 causing the increase of IR band at $\sim1620\,cm^{-1}$. The presence of niobium in the NbMCM-41 matrix enhances the oxidative properties of the catalysts and as a consequence the activity in the NO_2 interaction with propene. This effect is especially high on the catalyst prepared by the co-precipitation (AuNbMCM-41). The latter sample exhibits higher NOx storage properties than the impregnated one.

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