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The properties of gold catalysts precursors adsorbed on the MCM-41 materials modified with Mn and Fe oxides

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Abstract Silica mesoporous materials modified with manganese and iron were obtained by the hydrothermal method. Gold was introduced to pure and modified silica materials by the direct hydrothermal and impregnation methods. Nitrogen adsorption/desorption studies evidenced formation of the materials with large total surface area and mesoporous structure. Unmodified silica materials showed regular pore arrangement. The uniform porous structure was distorted in the iron or manganese containing samples. XRD, UV-Vis/DRS spectroscopy and temperature programmed reduction studies revealed changes of the nature of transition metal oxide and gold species on the different preparation stages. The oxide species after drying were strongly dispersed and partially incorporated to the silica framework. High temperature treatment led to the formation of extraframework Mn and Fe oxide species. Complex processes of gold deposition were observed during hydrothermal synthesis and impregnation of modified silica materials. The increase of the size of gold species was observed during calcination. The presence of transition metal oxides decreased sintering of gold crystallites.

Keywords MCM-41 · Gold · Manganese · Iron · TEM · XRD · TPR · UV-Vis

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1 Introduction

Noble metals and transition metal oxides confined in the microporous supports have found wide interests in the area of new technologies. Gold for long time has been perceived as an expensive and inert metal. An exceptionally high catalytic activity of fine gold particles dispersed over the transition oxides, such as Fe_2O_3, MnO_x, Co_3O_4 or TiO_2 has been discovered in the end of the XX century (Haruta et al. 1987, 1993). The best activity for low temperature CO oxidation have been observed for supported or unsupported gold-iron and gold-manganese catalytic systems. Recently gold catalysts has been studied in wide range of oxidation and hydrogenation reactions, including CO oxidation, preferential CO oxidation in hydrogen stream, selective oxidation of alkenes, methanol synthesis, reduction of NO_x (Bond et al. 2006; Corti et al. 2005; Claus 2005; Hutchings 2002). It has been well documented that the activity of gold catalysts depends on the properties of the support, preparation methods and particularly the size of Au crystallites. The nature of gold species can be controlled in the synthesis conditions, using suitable pH of the solution, temperature, time, precipitating agents, washing procedures, and thermal treatment. On the other hand the properties of gold species can be modified by the application of different supports, with tailored surface or structural properties. It has been observed that small gold species can be located in the cavities of zeolites (Lin et al. 2002) or in the channels of the silica mesoporous materials

(Akolekar and Bhargava 2005). Gold has been introduced to the mesoporous materials by the different techniques, including the direct hydrothermal method (Lin et al. 2002; Bore et al. 2004; Glomm et al. 2005) or impregnation of the amine-functionalized silica matrices (Bore et al. 2004; Mukherjee et al. 2001; Lee et al. 2004).

The properties of noble metal catalysts are strongly related to the presence of reducible oxides. The oxides can increase oxygen mobility, induce electronic effects, increasing catalytic performance or decrease sintering, improving thermal stability (Grisel and Nieuwenhuys 2001). Noble metal–transition metal oxide systems supported on the silica mesoporous materials have not been widely studied. An excellent catalytic activity has been well documented for titania and gold or silver modified mesoporous silicas in the selective oxidation reactions, e.g. in the epoxidation of propylene (Uphade et al. 2001). General target of our studies was to obtain large surface area materials which could be used for CO and volatile organic compounds abatement. The aim of recent work was preparation and characterization of gold—manganese and iron oxides supported on the MCM-41 materials. To our knowledge such materials were not well described.

2 Experimental

2.1 Catalyst preparation

Silica mesoporous materials were obtained by the modified procedures described in the literature (Grün et al. 1997). Manganese and iron were introduced by the direct hydrothermal method (HT). Gold was introduced by the direct hydrothermal or the impregnation technique.

In the synthesis of pure silica material 2 g of hexadecyltrimethylammonium bromide (Aldrich) was dissolved in 90 cm^3 of distilled water. The mixture was stirred at the temperature of 40 °C, and then 8 cm^3 of tetraehylortosilicate (TEOS) (Aldrich) was introduced. Next 8 cm^3 of ammonium hydroxide (25 wt. %) was slowly introduced. The obtained white gel was stirred for 1 h, and next filtered and washed with distilled water. A sample was dried overnight at 90 °C, then initially calcined in the static air at 550 °C for 5 h, and then heated in the flow of oxygen for 8 h. In the preparation of gold materials 0.01 M solution of hydrogen tetrachloroaurate ($HAuCl_4$) was added to the surfactant containing mixture. In the preparation of silica modified with transition metal oxides small amounts of the aqueous solutions of iron nitrate or manganese acetate were introduced to the synthesis mixture containing surfactant or surfactant and gold compounds before TEOS addition. Then samples were prepared in the same way as pure silica materials.

The impregnated samples were prepared by dipping of pure and modified silica materials in the 0.001 M solution of $HAuCl_4$ for 22 h, then washed with distilled water, and dried at 50 °C for 3 h.

Samples were denoted according to the preparation method. The abbreviation "Imp" was used for the samples obtained by the impregnation method and "HT" for the samples prepared by the hydrothermal method.

2.2 Catalyst characterization

The catalysts composition was determined by applying the X-ray fluorescence method (ED-XRF Canberra 1510, USA).

Morphology and microstructure was investigated by TEM (Philips CM-20 SuperTwin, operating at 200 kV and providing 0.25 nm resolution). Analysis of TEM images and FFT (Fast Fourier Transform) patterns was made with ImageJ program (Rasband 1997). Specimens for TEM were prepared by dispersing some powder sample in methanol and putting a droplet of the suspension on a copper microscope grid covered with perforated carbon.

Nitrogen adsorption/desorption isotherms were determined volumetrically at −196 °C using ASAP 2405N analyzer (Micromeritics Corp., Norcross, GA). Before the measurements samples were degassed (10^{-2} mmHg) at 90 °C. The adsorption data were used to evaluate BET specific surface area, S_{BET} (from the linear BET plots) within $p/p_{\mathrm{o}} = 0.05$–0.25, the mesopore volume, V_{meso} (calculated from the isotherms at relative pressure $p/p_{\mathrm{o}} = 0.6$), total pore volume, V_{t} (from the adsorption at the relative pressure $p/p_{\mathrm{o}} = 0.98$) (Barett et al. 1951; Gregg and Sing 1982). Pore width (D) was estimated from the relation between pore width and condensation pressure reported for series of model adsorbents by Jaroniec and Kruk (Kruk and Jaroniec 2001). X-ray powder diffraction (XRD) measurements were conducted with the modified diffractometer DRON 3 (Russia) using CuK_{α} radiation. UV-Vis reflectance spectra were recorded on Specord M40 (Carl Zeiss, Jena, Germany) equipped with integration sphere. As the reference substance ZnO sample was used. The reflectance spectra were measured at 10 $nm\,s^{-1}$ rate over 200–900 nm range with slit spectral width 1 nm. Reducibility of the oxide species in catalysts was determined by the temperature programmed reduction method (TPR) performed in the Altamira AMI-1 system (Zeton Altamira). Reduction was performed in the mixture of 6.2% H_2 in Ar. The rate of temperature increase was 10 °C/min. Water evolved during reduction was removed from the carrier gas in a cold trap (at LN_2-methanol mixture temperature −98 °C) placed between reactor and thermal conductivity detector (TCD). Calibration of the TCD signal was done by injecting pulses of Ar to 6.2% H_2/Ar carrier gas.

3 Results and discussion

Table 1 shows composition, structural and surface properties of the studied materials. The amounts of iron or manganese oxides is relatively high, from 10 to 12 wt. %. Samples contain different amounts of gold, although the same quantities of $HAuCl_4$ have been added to the synthesis mixtures or introduced to the impregnation solution.

Figure 1 shows representative TEM images obtained for Au (Imp)-MCM-41 sample. Rounded grains of ordered MCM-41 support with the size from 50 to 200 nm are seen. Analysis of FFT pattern (see inset to Fig. 1b) reveals some compression of the lattice (positions of the spots correspond to 3.25 nm). The grains exhibit the ordered structure. The insets (Fig. 1b and Fig. 1c) show the presence of long parallel channels with the length corresponding to the size of the grains. However Fig. 1b indicate the occurrence of the regions of different arrangement of mesopores. Similar morphology has been observed for the samples prepared by the direct hydrothermal method. The samples with manganese or iron (not shown here) contained certain amount of an amorphous phase. In Fig. 1c an example of a 12 nm Au particle is presented. Taking account of its size, one can state that the crystallite is located on the outer surface of the grain.

Figure 2 shows nitrogen adsorption/desorption isotherms. The isotherms for unmodified silica materials display distinct step, which results from capillary condensation in mesopores of uniform sizes. Specific surface area (S_{BET}) of pure silica materials exceeds 1150 m^2/g. The effects of the changes of structural and surface properties caused by the impregnation of silica materials with small amounts of gold are not strongly manifested. The occurrence of the condensation step at similar relative pressures might indicate that gold species were dispersed in the silica channels, however deposition of gold species on the outer surface of the grains channels could not be ruled out. TEM studies confirmed formation of the large crystallites on the grains of silica support. Moreover total volume of gold crystallites or their surface area are relatively small in comparison with pore volume or specific surface area of silica materials. Larger decrease of the surface area of silica materials is observed for the samples prepared by the direct introduction of gold precursor to the synthesis mixture prior silica skeleton formation. The decrease can be rather ascribed to the different preparation conditions, resulted from the presence of gold precursors $HAuCl_4$, than physical decrease of the available surface silica sites. This method allows incorporating larger amounts of gold.

An introduction of iron and manganese decreases specific surface area and pore ordering. Modification of the silica mesoporous materials by the relatively large amount of manganese leads to the decrease of the surface area, slight decrease of mesopore volume (V_{meso}), as well as to increase of total pore volume (V_{t}). The characteristic increase of adsorption occurs in wider range of pressures. This indicates the broadening of pore size distribution. Similar changes of the surface area and mesopore volume are observed for iron modified materials. Manganese samples show strong

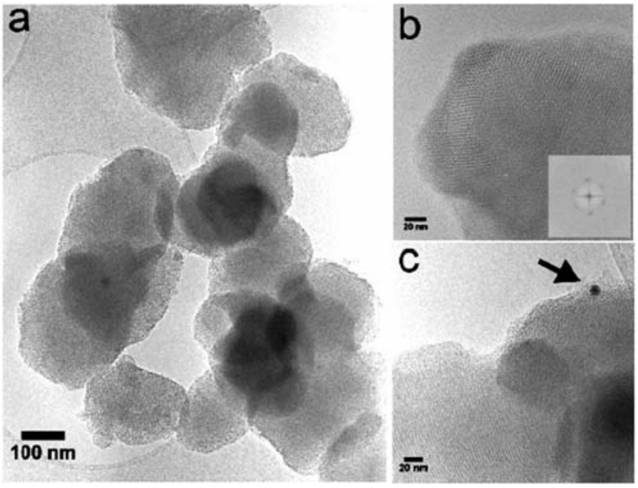

Fig. 1 TEM results for Au(Imp)-MCM-41 sample: general view (**a**), high resolution image of an ordered MCM-41 grain with FFT pattern (**b**) and Au particle (**c**)

Table 1 Composition, structural and surface properties of the samples

Sample	Composition (wt. %)		S_{BET} (m^2/g)	V_{mezo} (cm^3/g)	V_{t} (cm^3/g)	D (nm)
	Au	Mn or Fe				
MCM-41	–	–	1158	0.91	1.11	3.5
Au(Imp)-MCM-41	0.329	–	1124	0.87	1.05	3.5
Au(HT)-MCM-41	0.80	–	971	0.74	0.91	3.5
Mn-MCM-41	–	12.5	925	0.74	1.40	3.5
Au(Imp)-Mn-MCM-4	1.645	10.91	783	0.53	0.77	3.5
Au(HT)-Mn-MCM-41	0.079	12.14	913	0.71	1.59	3.5
Fe-MCM-41	–	10.11	888	0.60	0.92	3.5
Au(Imp)-Fe-MCM-41	0.157	9.86	799	0.53	0.87	3.5
Au(HT)-Fe-MCM-41	0.593	10.04	886	0.61	0.93	3.5

S_{BET}—specific surface area, V_{mezo}—mezopore volume, V_{t}—total pore volume, D—estimated mean pore diameter

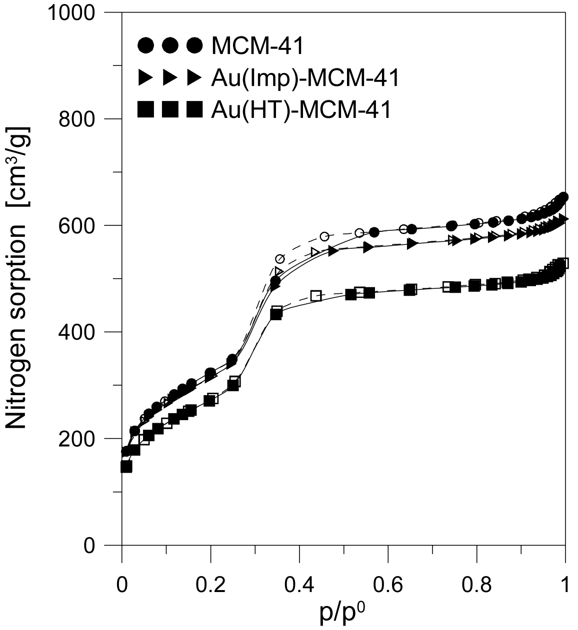

Fig. 2a Nitrogen adsorption/desorption isotherms for silica and gold-silica materials; *solid lines* (*filled symbols*)—adsorption, *dashed lines* (*open symbols*)—desorption

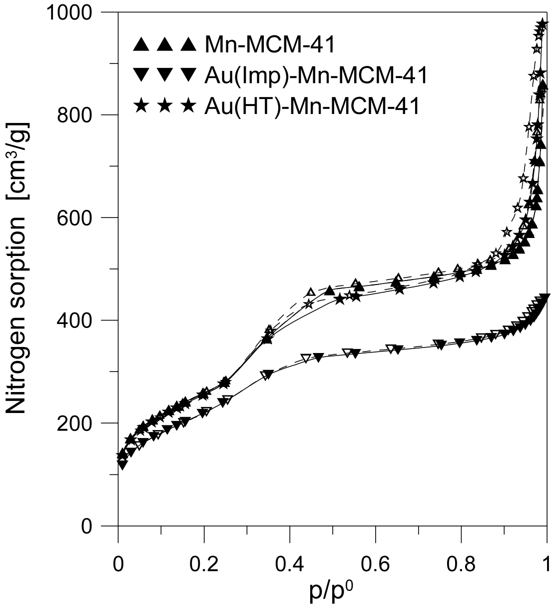

Fig. 2b Nitrogen adsorption/desorption isotherms for manganese containing samples; *solid lines* (*filled symbols*)—adsorption, *dashed lines* (*open symbols*)—desorption

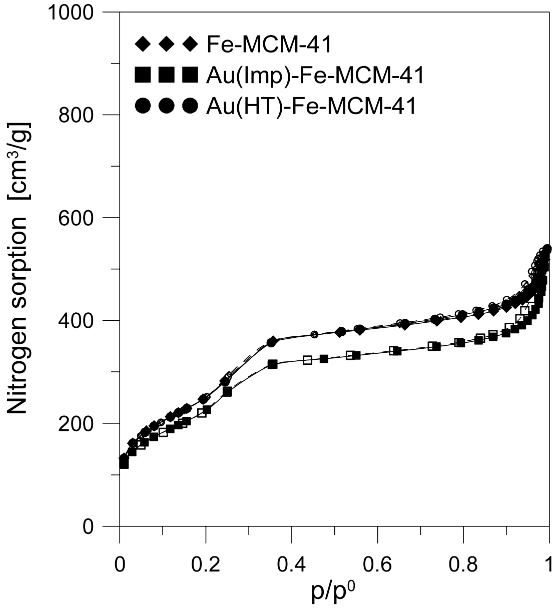

Fig. 2c Nitrogen adsorption/desorption isotherms for iron containing samples; *solid lines* (*filled symbols*)—adsorption, *dashed lines* (*open symbols*)—desorption

adsorption at high relative pressures, related with deterioration of structural ordering and formation of large mesopores. A series of MCM-41 materials modified with manganese was recently studied by Derylo-Marczewska et al. (2006). They observed gradual decrease pore ordering with an increase of manganese contents. Recent studies indicate that introduction of large amounts of modifiers (around 10 wt. %) by the hydrothermal method strongly influence the mechanism of formation of ordered silica mesoporous skeleton.

An introduction of gold by the impregnation method slightly decreases specific surface area of the samples. The decrease of mesopore and total pore volume is observed. The presence of manganese species increases gold loading, while an opposite direction is visible for iron containing samples. These changes may indicate different mechanism of sorption of gold complexes and their decomposition during preparation of the materials by the impregnation technique. The changes of the surface properties of the silica materials modified with manganese and iron, obtained by the direct introduction of gold precursor to the synthesis mixture before hydrothermal treatment are much weaker. Simultaneous deposition of gold and manganese in the direct hydrothermal method is less effective than in the impregnation method.

Figure 3a reveals an ordered arrangement of pores in the pure silica materials. Typical peaks, which correspond to the (100), (110) and (200) reflections, characteristic for hexagonal porous structure are clearly visible. An introduction of gold by the impregnation technique slightly moves the peaks to higher values of 2θ, indicating light shrinkage of the pores. Simultaneously, there is visible small decrease of the intensity of the peaks, which could be related to a partial distortion of the regular structure. However this effect could be also partially related to the changes of the optical density connected with the presence of gold crystallites

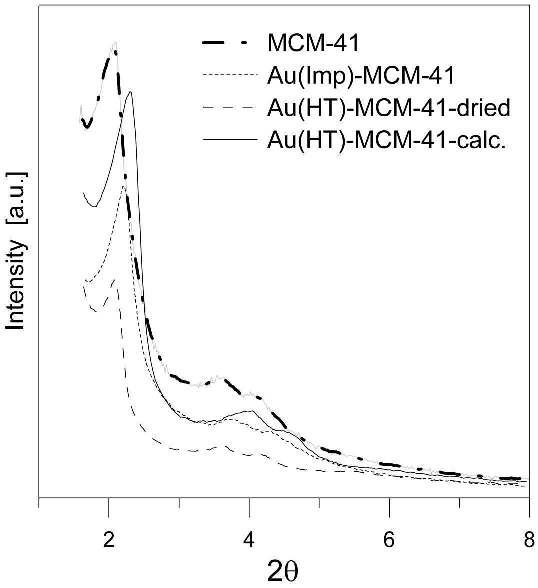

Fig. 3a XRD studies of pure and gold modified silica mesoporous materials at low angles

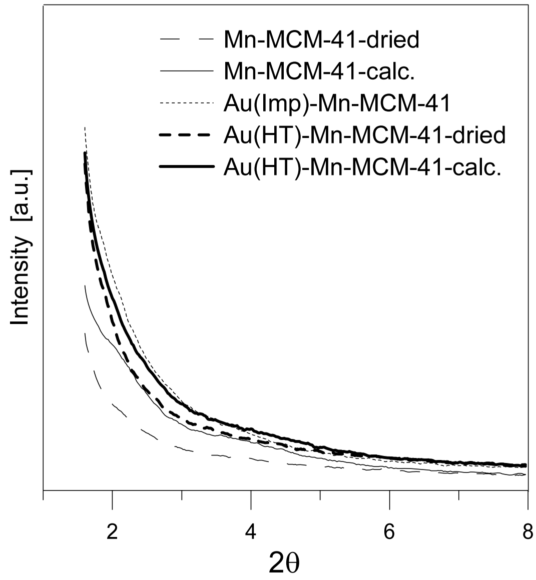

Fig. 3b XRD studies of manganese and gold containing silica mesoporous materials at low angles

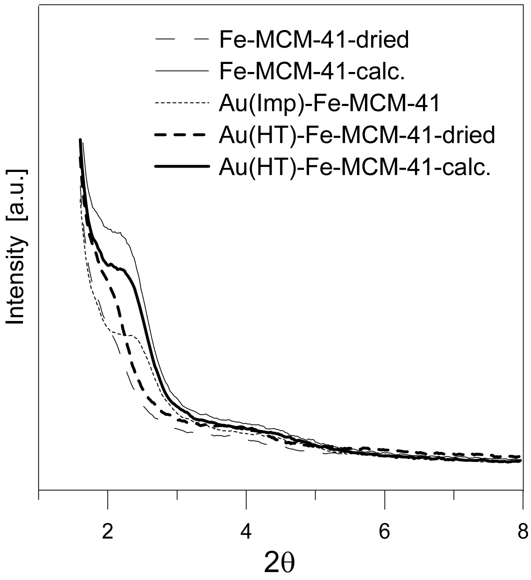

Fig. 3c XRD studies of iron and gold containing silica mesoporous materials at low angles

in the silica pores. An XRD data of gold samples prepared by the HT method illustrate the differences of the structure of materials before and after calcination. Final shaping of the materials occurs during calcination. The initial process in the calcination is desorption of water, then decomposition of the hexadycyltrimethylammonium cations via Hoffmann elimination reaction with production of unsaturated hydrocarbons and methylamines. Finally these products are desorbed or oxidized to nitrogen compounds, water, carbon oxides, and various partially oxygenated heavy hydrocarbons. High temperature causes partial removal of hydroxyl groups, and formation of more rigid structure with slightly smaller pores. Recently we have observed that the presence of gold or transition metal oxides can change the mechanism of template removal or partial modification of structural properties, without general variation of pore arrangement (Gac and Pasieczna-Patkowska unpublished results). Figures 3b and 3c show the changes of the structural properties of manganese and iron containing materials before and after calcination. Studies indicate less ordered structure of manganese materials. All samples before calcination show weak shoulder, which intensity increases after high temperature treatment. An introduction of gold to the modified silica materials decreases pore arrangement. The decrease is observed in the draying stage. This effect becomes more visible after calcination.

XRD spectra presented in the Fig. 4a reveal the presence of gold crystallites (PDF No 04-0784), with reflection lines of Au(111), Au(200), Au(220), and Au(311), respectively. An impregnation technique leads to the formation large crystallites of gold on the MCM-41 support. Broad peaks of gold for the dried samples, prepared by the HT method, indicate the presence of small crystallites (bellow detection limit of the XRD technique). Their size increases during calcination.

The studies of manganese containing materials reveal the presence of strongly dispersed manganese oxide species (Fig. 4b). Broad peaks for the dried samples can be related to the phases of hausmannite Mn_3O_4 (PDF No 80-0382) with tetragonal symmetry. These peaks become more visible for calcined samples. The characteristic reflections of gold are not detected in the materials obtained by the HT method due

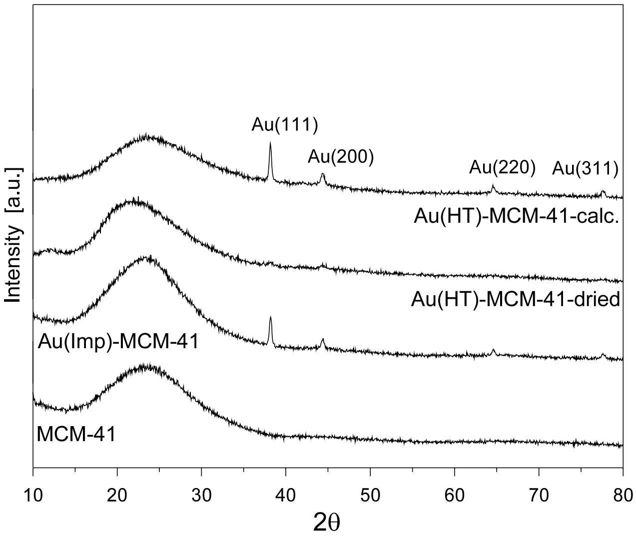

Fig. 4a XRD curves of silica and gold modified materials before and after calcination

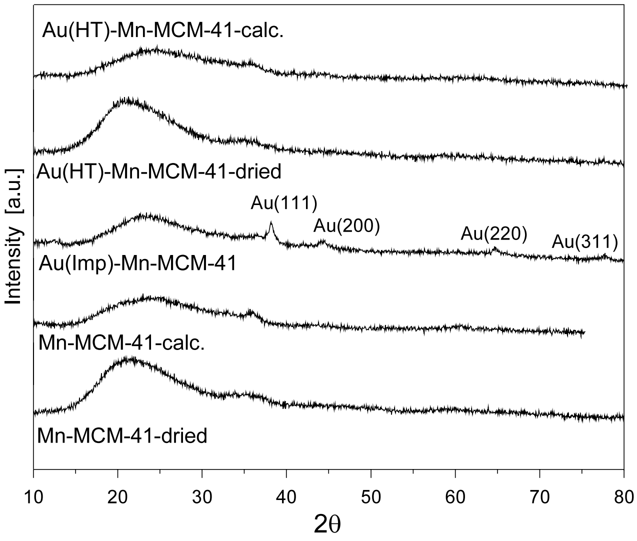

Fig. 4b XRD curves of manganese and gold containing materials before and after calcination

to low loading of gold. Samples prepared by the impregnation method contain relatively large amounts of gold; however the peaks are more broad than in the Au(Imp)-MCM-41 samples. This indicates stabilisation of small gold species by manganese oxides in the silica mesoporous materials. Similar effects are observed for iron containing materials (Fig. 4c). Iron oxide species before and after calcination are strongly dispersed. It is difficult to find any differences between them from the XRD results. Gold phases in the dried samples, obtained by the HT method are not observed, indicating that their size is below the detection limit of the XRD method. The size of gold particles increases during thermal treatment.

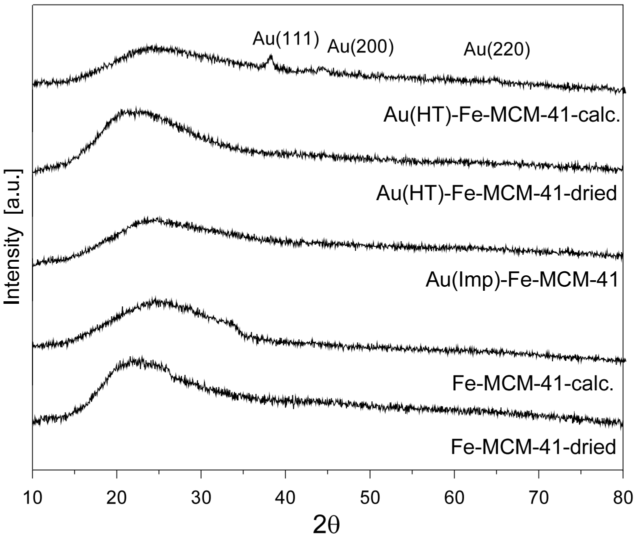

Fig. 4c XRD curves of iron and gold containing materials before and after calcination

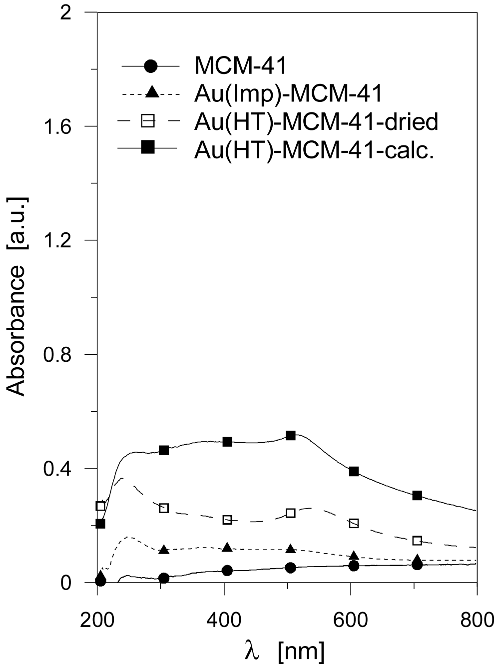

Fig. 5a UV-Vis spectra of the samples before and after calcination

The differences of the nature of the species in the materials before and after calcination are well visible in the UV-Vis/DRS spectra. Figure 5a reveals the presence of three different types of gold species in the samples. The absorption bands at low wavelength region (around 255 nm) indicate the presence of Au^+ cations. The peaks in the region 280–350 nm are considered as indication of $(Au)_n^{\delta+}$ clusters, while the absorption peaks at around 500–600 nm are ascribed to the gold nanoparticles, responsible for the striking violet or pink colors (Margitfalvi et al. 2002). The

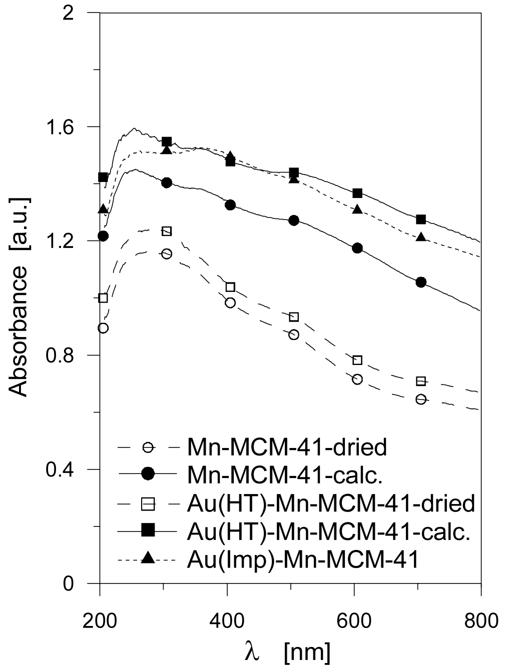

Fig. 5b UV-Vis spectra of manganese and gold containing materials before and after calcination

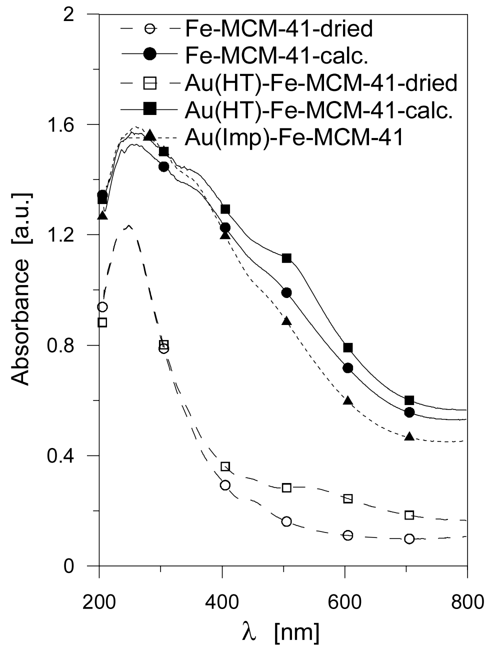

Fig. 5c UV-Vis spectra of the iron and gold containing materials before and after calcination

distribution of the species is changed during thermal treatment. It is observed an increase of the absorption peaks of gold clusters and metallic nanoparticles. The absorption bands for manganese containing samples indicate the presence of different forms of manganese species. Band at 270 nm have been ascribed by Takehira to the charge transition of $O^{2-} \rightarrow Mn^{3+}$ in tetrahedral coordination, indicating incorporation of manganese in the framework of MCM-41 (Zhang et al. 2002). The intensity of the bands at around 350 and 500 nm increases after calcination. These bands have been attributed to the charge transition of $O^{2-} \rightarrow Mn^{3+}$ in the Mn_3O_4 of octahedral coordination of Mn, and Mn^{2+} located on the surface (Selvaraj et al. 2005; Velu et al. 1999). The introduction of gold increases the intensity of absorption peaks. High intensity of the bands corresponding to the small gold clusters is observed for the impregnated sample. More pronounced changes of the nature of the oxide species are detectable for the iron samples. Samples before calcination exhibit strong absorption bands at low wavelength, indicating isolated Fe^{3+} species coordinated in the silica framework. After thermal treatment these samples show new absorption bands at 300 nm, 500 nm and the tail above 600 nm, which correspond to small oligonuclear iron species and extraframework oxide species, respectively (Pérez-Ramírez et al. 2003). An increased intensity of the bands in the range 500–600 nm for iron-gold samples indicates the presence of gold nanoparticles.

TPR curves presented in the Fig. 6 reveal direct interaction of gold and transition oxide phases in the silica materials. The multiple reduction course of oxides can result from the different oxidation state of Mn in the samples, various interaction of the species with silica or subsequent reduction $Mn^{4+} \rightarrow Mn^{3+} \rightarrow Mn^{2+}$. Usually first peak on the TPR curves is attributed to the consumption of hydrogen in the reduction of MnO_2 or Mn_2O_3, while the second peak to the reduction of M_3O_4 phases to MnO. Low-temperature peak indicate the presence of strongly dispersed manganese oxides on the higher oxidation state of Mn, which have not been detected by the XRD technique. An introduction of gold changes the shape of reduction curves. This effect is directly related to interaction of gold with manganese oxides, and confirms deposition or adsorption of gold species in the vicinity or directly within the phases of manganese oxides. An introduction of small amounts of gold by the HT method increases reducibility of manganese oxides. More visible changes are observed for impregnated sample. The presence of few semiimposed peaks can be connected with different location of gold species or their different properties. Similar changes ore observed for iron containing samples (Fig. 6b). The first peak in the Fe-MCM-41 sample is connected with reduction of F^{3+} to Fe^{2+} (Szegedia et al. 2001). Further reduction to metallic iron occurs above 800 °C. It is interesting that an introduction of gold by the hydrothermal method moves the reduction of Fe^{2+} to lower temperatures, without strong influence on the reduction of Fe^{3+} species. The comparison of the surface area of the peaks confirms, that calcined samples contain iron oxide species on the different oxidation state. Because gold influences only the reduction

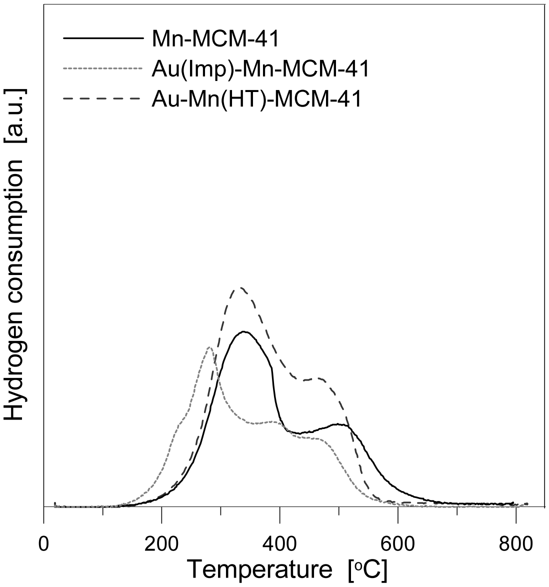

Fig. 6a TPR curves of manganese containing silica mesoporous materials

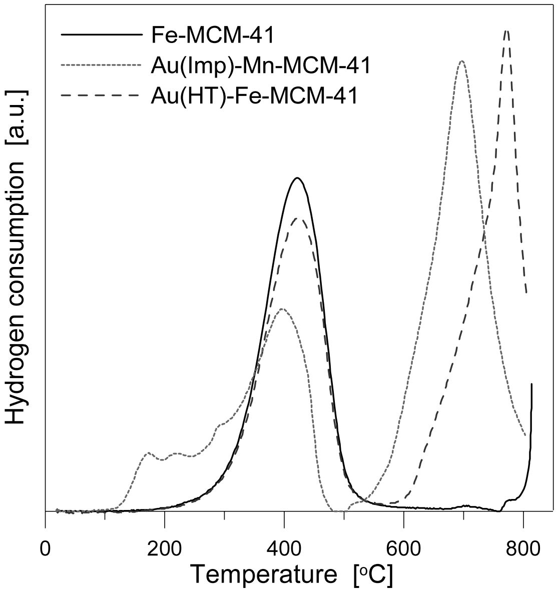

Fig. 6b TPR curves of iron containing silica mesoporous materials

of Fe^{2+} species, it seems to be probable that gold is located in the vicinity of that species. In the samples prepared by the impregnation technique, gold influences both reduction of Fe^{3+} and Fe^{2+} species. In this case the extent of reduction is more pronounced.

The changes of the composition of the samples reveal different mechanism of gold sorption influenced by the presence of iron or manganese species. Mesoporous silica materials are formed as results of polycondensation of silica source in the presence of large surfactant molecules, which develop an organized structure in the synthesis conditions. The surfactant molecules are removed from the materials by the extraction or calcintaion method, giving large surface area materials. The metal ions in the HT method are directly introduced to the synthesis mixture. The mechanism of the formation of modified silica materials is still under debate. The metal ions can induce changes of the properties of the water-surfactant systems, polymerisation of silica, or material structure shaping in the drying and calcination stages (Yuan et al. 2002). In the solution containing surfactant molecules, such as octadecyltrimethylammonium bromide, the inorganic species (I) can be located around organic micelles with positive charge on the nitrogen atom (S^+) as S^+I^- pairs or in $S^+X^-I^+$ arrangement with ions (X^-). The metal oxide species or metal crystallites in the HT method can by finely dispersed on the internal surface of the pores, or partially incorporated to the silica framework (Derylo-Marczewska et al. 2006; Ryczkowski et al. 2005). Gold catalysts are usually prepared by dissolution of $AuCl_3$ or direct introduction of $HAuCl_4$ solution. Thus gold in the acidic or neutral pH occurs mainly in the form of negatively charged complexes $[AuCl_4]^-$. Halogen ligands with increasing pH of the solution are replaced with hydroxyl groups, giving the dissolved complexes with general formula $[Au(OH)_nCl_{4-n}]^-$ ($n = 0$–4) or $Au(OH)_3$ precipitate (Chang et al. 1998). It has been stated that positive complexes of gold $[Au(NH_3)_4]^{3+}$ or $[Au(NH_3)_2(OH)_2]^+$ can exist in the solution of ammonia (Cotton 1997). pH of the solution in the hydrothermal synthesis method is gradually increased and leads to the formation of silica walls. Simultaneously, the adsorption of metal cations, precipitation of hydroxides of gold, manganese and iron, or formation of dissolved complexes can occur. Moreover the presence of amines in the channels of as prepared silica materials can stabilize gold species due to formation of N-donor complexes.

The UV-Vis spectra indicate that dried iron samples contain mainly Fe^{3+} species in the framework positions. This means that during synthesis iron could be incorporated into the silica framework of MCM-41, forming ≡Fe-OH-Si≡ entities. Their presence could change the charge of the silica surface and modify sorption of gold complexes. Studies of the manganese containing MCM-41 indicate that Mn^{2+} could be incorporated to the silica framework or located on the surface. Low gold loading might be explained by the mechanism of preferential sorption of manganese ions on the silica surface. However, determination of the detailed mechanism, need further studies. Metal ions in the impregnation technique are adsorbed on the surface of the materials. However this process depends on the properties of the silica surface and the nature of the ions. The isoelectric point (IEP) of pure silica materials is relatively low (1–2) (Brunelle 1978). Negatively charged surface can easily adsorb positive ions or complexes, e.g. iron or manganese species, whereas sorption of negatively charged species is hindered. It was found that complexes of $[Au(OH)_nCl_{4-n}]^-$ could be preferentially adsorbed on the Mn and Fe oxides (Ran et al. 2002). The specific adsorption of gold was proposed on the Mn oxide surface, whereas for iron oxides anion exchange process was considered. During impregnation stage the adsorbed gold complexes can be easily reduced to the metallic species and deposited as clusters or metallic nanoparticles in the channels of silica materials.

4 Conclusions

Silica mesoporous materials modified with manganese and iron were obtained by the hydrothermal method. Gold was introduced to pure and modified silica materials by the direct hydrothermal and impregnation methods. The changes of the composition of the samples indicated different mechanism of gold incorporation. The presence of manganese oxides increased gold sorption from the impregnation solution, however slight decrease was observed for iron containing materials. Complex processes of gold deposition were observed during synthesis of the materials by the hydrothermal method. XRD and UV-VIS techniques evidenced changes of the nature of gold and transition metal oxide species on the different preparation stages of the materials. Unmodified silica materials showed large surface area and well-ordered mesoporous structure. The introduction of relatively large amounts of manganese and iron deteriorates the structural ordering. The increase of the size of gold species was observed during calcination. The presence of transition metal oxides decreased sintering of gold crystallites. Redox properties of the materials were related to the amounts and the way of gold introduction.

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