



Study of gold and iron species in Au/Fe/zeolite system

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Abstract

In this research species of gold and iron in mixed Au/Fe/zeolite along with reference Au/zeolite and Fe/zeolite samples were studied. It was shown that calcinations temperature, type and cation of zeolite can significantly influence the iron and gold species. It was revealed that gold precursor is decomposed before temperature treatments with formation of reduced gold species in case of Au/zeolites. Reducibility of iron cations is higher for Fe-Y zeolites then for Fe-mordenites probably due to difference in their pore geometry. The addition of gold to iron-containing samples leads to modification of iron state in for Y- supported and NH₄-mordenite samples.

Keywords: gold states, gold nanoparticles, additive, iron, zeolite

Introduction

Last years gold attracts much attention in area of catalysis. Highly dispersed gold catalysts are very active in many reactions important for chemical industry such as: CO oxidation, NO reduction [1]. It was revealed that gold nanoparticles supported on Co₃O₄, Fe₂O₃, TiO₂, and MgO oxides have high activity for numerous reactions especially for low-temperature CO oxidation. The use of catalysts for carbon monoxide oxidation at room temperature is a substantial in a large number of industrial processes, in environmental protection and in special apparatus. It was reported that the amount of CO emitted into the atmosphere was the greatest among all of the air pollutants and exceeds the sum of all other air pollutants [2].

Bond et al. found correlation between support property, the preparation method of gold catalysts and the size of obtained Au nanoparticles. [3]. Since then many studies

have been devoted to preparation of ultra-fine gold particles on the surface of metal oxides [4-6] and zeolites [2, 7-11] for application in various reactions. It is accepted that the high catalytic activity of supported gold catalysts in low-temperature CO oxidation can be due to the presence of small gold particles which are stabilized by the support [12-15].

Nieuwenhus et al. [12] has reported influence of different metals oxides (MO_x) in the system Au-Al₂O₃. Influence of MO_x on the low-temperature CO oxidation activity and relationship between activity and average gold particle size were studied [16]. According to many studies the support for gold catalysts plays an important role [17-19]. It was revealed that zeolite is excellent matrix for clusters stabilization. The advantage of zeolite is due to its high surface area, ion exchange ability and the stabilization of small gold particles via inserting them into the small pores with regular and controlled size [9, 10, 20]. Diameter of gold nanoparti-

cles inside of zeolite can be controlled by pore size of zeolite.

It was revealed that iron additive can increase stability and activity of Au/Fe/Y-zeolite catalyst in CO oxidation [2, 7-11]. In the present research we study gold and iron species in zeolite matrices varying such parameters as sample calcinations temperature, pore size and cation type of zeolite. Regulation of the contribution of different gold and iron species in zeolite and the strength of their interaction with various parameters will permit to find out the active sites and develop the active zeolite-based catalyst.

Experimental

NaY and HY zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal 5 (Zeolyst Company, USA) and mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal 20 (TOSOH Corporation, Japan) were used for the samples preparation. Iron was introduced into zeolite by wet-impregnated method. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich Company, 99.99%) was used as a precursor. The samples were calcined at 500°C for

4 hours. Gold was exchanged on Fe/zeolites from aqueous solution of $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ complex prepared from HAuCl_4 and NH_4NO_3 [21] at pH 7. Gold exchange samples were washed with deionized water and dried at 60°C for 6 hours in air. Then as-prepared samples were calcined at selected temperature in range $100\text{--}500^\circ\text{C}$ for 1 h.

The prepared samples of Au/Fe/zeolites were studied by diffuse reflectance spectroscopy (DRS) in a CARY 300 SCAN (VARIAN) spectrophotometer. Optical spectra were obtained by subtraction of spectra of corresponding to Fe/zeolite from the spectra of Au/Fe/zeolite. Transmission electron microscopy (TEM) was carried out with a JEOL 2010 high resolution transmission electron microscope. X-ray diffraction was done with a Philips X-pert diffractometer equipped with a curved graphite monochromator applying $\text{CuK}\alpha$ ($\lambda=0.154$ nm) radiation. Thermo-programmed reduction with hydrogen (TPR) was measured in an AMI 1 Altamira-Instruments. Before TPR measurements samples were pretreated in argon at 100°C for 15 min. The chemical analysis was done with IPC.

Results and discussion

Temperature-programmed reduction

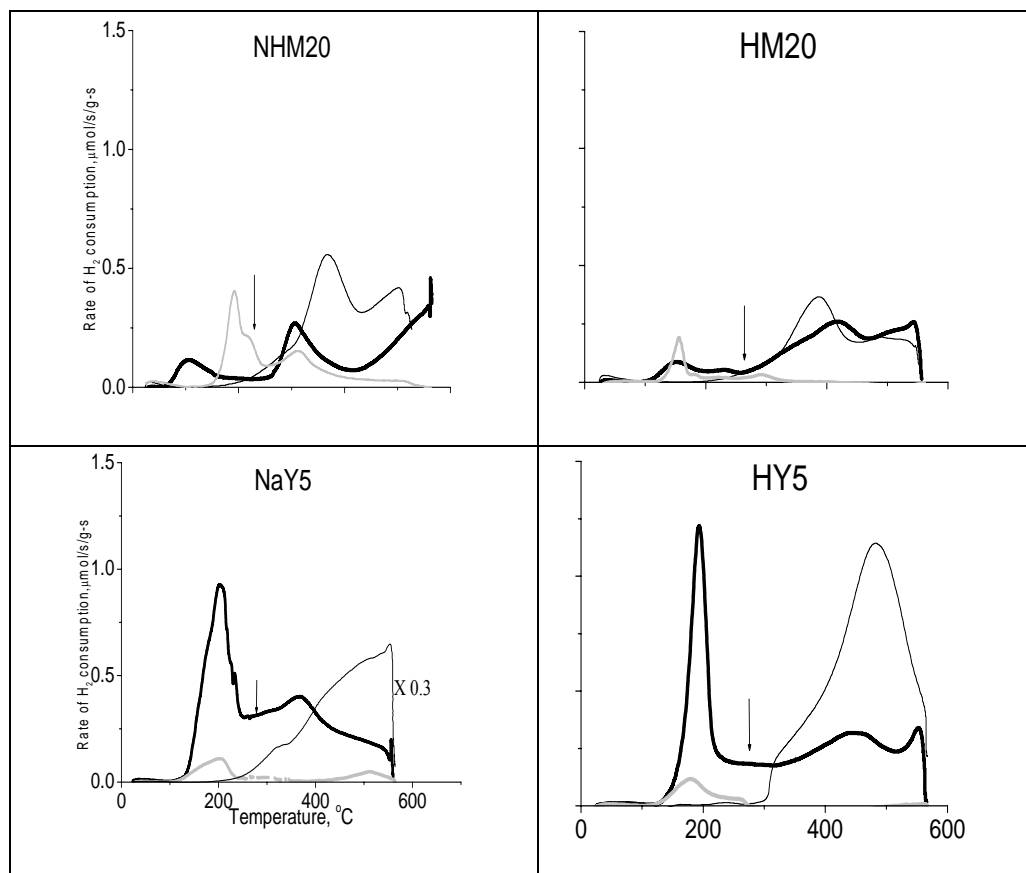


Fig. 1: TPR profiles of catalysts Fe/NHM20 (solid line), Au/Fe/NHM20 (bold line), Au/NHM20 (gray line); Fe/HM20, Au/Fe/HM20, Au/HM20; Fe/NaY5, Au/Fe/NaY5, Au/NaY5; Fe/HY5, Au/Fe/HY5, Au/HY5.

Table 1: Analysis of H₂ uptake according to TPR

Catalysts	Metal loading $\mu\text{mol/g}$ -sample		H ₂ uptake, $\mu\text{mol H}_2/\text{g}$ -sample		Part of metal reduced, %	
			Range of temperature (for Au/Fe/zeolite), °C			
	gold	iron	< 250	> 250	gold ²	iron ³
Au/NHM20	147.7 ¹	-	106.2	-	50	-
Fe/NHM20	-	731	-	311	-	28
Au/Fe/NHM20	6	729	30	120	-	-
Au/HM20	126.4 ¹	-	25	-	13	-
Fe/HM20	-	770.6	-	181	-	16
Au/Fe/HM20	62.6	691.7	26	166	-	-
Au/NaY5	97.5	-	31.2	-	21	-
Fe/NaY5	-	727.6	-	1024	-	90
Au/Fe/NaY5	117.7	759.2	215	253	-	-
Au/HY5	34.3	-	26	-	50	-
Fe/HY5	-	733	-	540	-	49
Au/Fe/HY5	101	704.3	176	215	-	-

¹Gold loading according to energy dispersive spectroscopy data obtained in a scanning electron microscopy JEOL (JSM 5300)

²Calculations made on suggestion of the reduction of gold (III) to gold metal

³Calculations made on suggestion of the reduction of iron (III) to iron metal

Fig.1 presents the TPR profile of as-prepared samples after drying at 60°C. There are three peaks with temperature maxima at 191°C, 222°C and 303°C in TPR profile for sample Au/NHM20. Note that two first peaks at temperature around 220°C are poorly resolved. In case of AuHM20 three peaks are also observed while first of them with maxima at 155°C is shifted to lower temperature. In contrast with mordenites just one wide poorly resolved peak is observed at temperature 200°C for NaY5 and 176°C and small shoulder at 250°C for HY5. Peak at temperature about 510°C is assigned to reduction of metal impurities presenting in zeolite that was proved by TPR blank experiment with sample of zeolite without gold. The profiles recorded are similar with to those published for mordenites and Y-zeolites [6, 10] as well. Comparison of hydrogen uptake during TPR runs with value of metal loading (Table 1) for the studied samples reveals that only part of gold presents in samples in ionic form because values of reduced gold are below 100% (Table 1). It implies that in as-prepared samples part of gold is in reduced form.

Reduction of iron in studied samples is displayed by broad peaks starting from ~200°C. The shape of peaks presented in profiles for iron-zeolite samples manifests obviously partial reduction of iron in the temperature range used. Indeed, the part of iron reduced (table 1) is less than 100% particular in case of mordenites. It seems to be determined by the difference in geometry of zeolites studied.

In case of Y-zeolite accessibility of iron could be higher due to larger dimensions of zeolite pores.

The TPR profiles for zeolites containing both iron and gold are more complicated. For sample Au/Fe/NHM20 there are resolved peaks with maxima at 100°C and 300°C and ascending reduction curve starting at temperature about 400°C. This profile differs from those for Au/NHM20 and Fe/NHM20. It is difficult to do definite assignment of peak at 300°C to reduction of either gold or iron because similar peak was observed for both Au/NHM20 and Fe/NHM20 samples. New peak at low temperature probably could be assigned to gold reduction. Let us consider once again data presented in Table 1. The content of gold in studied sample is essentially lower then value of hydrogen uptake corresponding to discuss peak. Simultaneous reduction of iron and gold at this temperature could be the simplest explanation of this fact. Probably, well dispersed gold formed during reduction can activate molecular hydrogen with formation of atomic one. It could be the reason of the iron reduction at so low temperature. This active state of gold seems to be non-stable and can exist only under at conditions described. However in the presence of gold only small part of iron was reduced in TPR run.

The profile of Au/Fe/HM20 is practically sum of profiles for Au/HM20 and Fe/HM20 as one can see in Fig 1. The amount of hydrogen consumed at temperature below 250°C corresponding to gold complete reduction is less then value of gold content Consequently in spite of the iron

presence gold in as-prepared sample presents ionic and partially reduced metallic species. On another hand the presence of gold does not increase the part of iron reduced.

The most dramatic changes in TPR profiles for Au/Fe/zeolites are observed in samples based on Y-zeolites. Intensive peak in range of gold reduction (100-220°C) appears while contribution of iron reduction (220-560°C) decreases. Calculation of hydrogen uptake reveals that amount of hydrogen consumed exceeds the content of gold reduced for both samples of Y-zeolites. As in case of Au/Fe/NHM20 sample joint reduction of gold and iron takes place in the low temperature range for Y-zeolites. Nevertheless, it is not possible to say exactly about contri-

bution of ionic and metallic gold species in as-prepared samples. As far as iron is concerned one could note the decrease of the total amount of iron reduced in spite of activated iron reduction at lower temperature in the presence of gold.

It was found significant influence of gold on the state of iron in Au/Fe/NHM20, Au/Fe/NaY5 and Au/Fe/HY5 samples. It consists in sharp change of reduction profile corresponding to iron reduction, decrease of amount of reducible iron and inactivated reduction of iron at lower temperature.

UV-Vis diffuse reflectance spectra

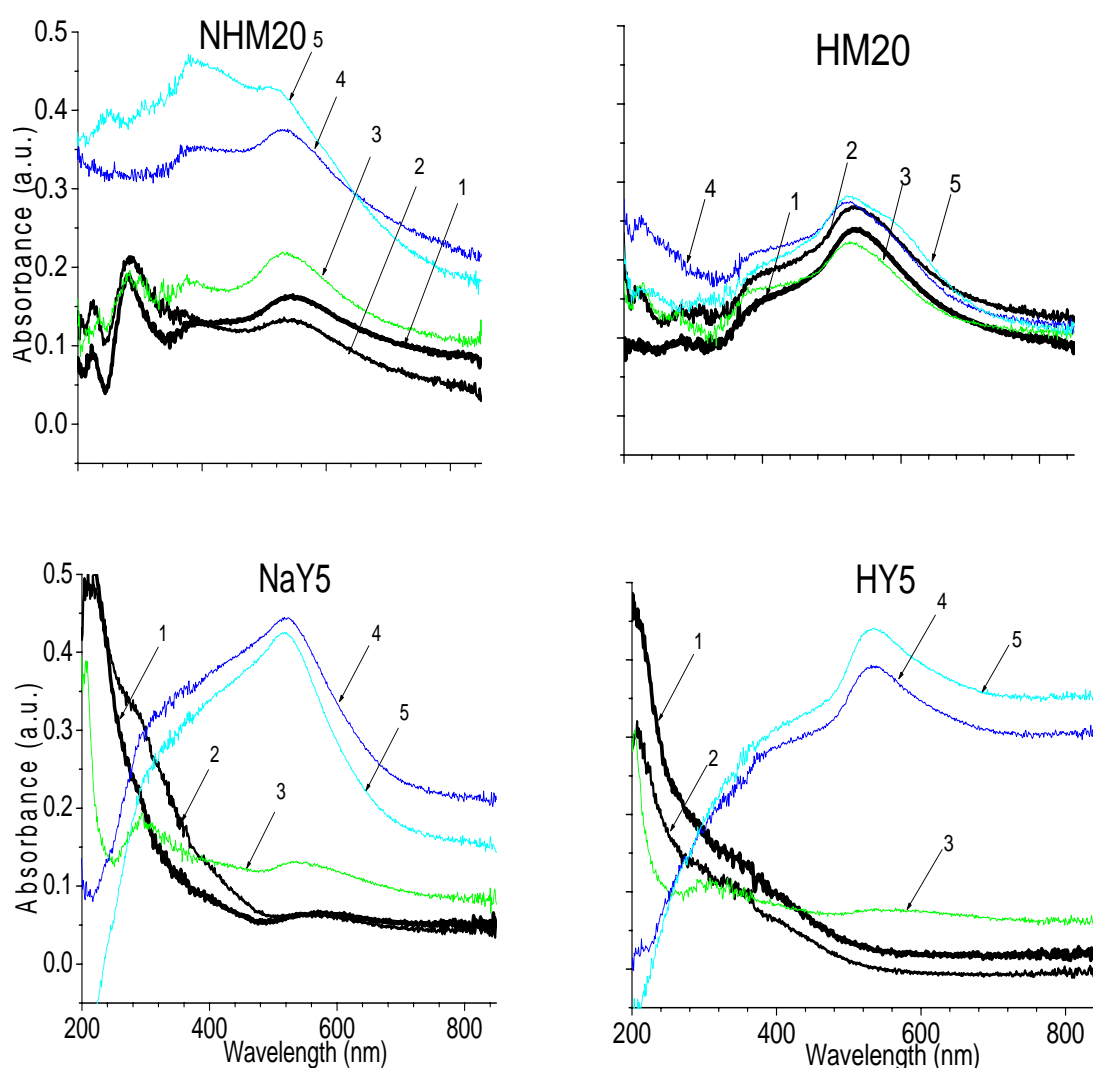


Fig. 2: UV-Visible spectra of Au-zeolite as-prepared and calcined at selected temperature: 1-as-prepared, 2-100°C, 3-200°C, 4-300°C, 5-500°C.

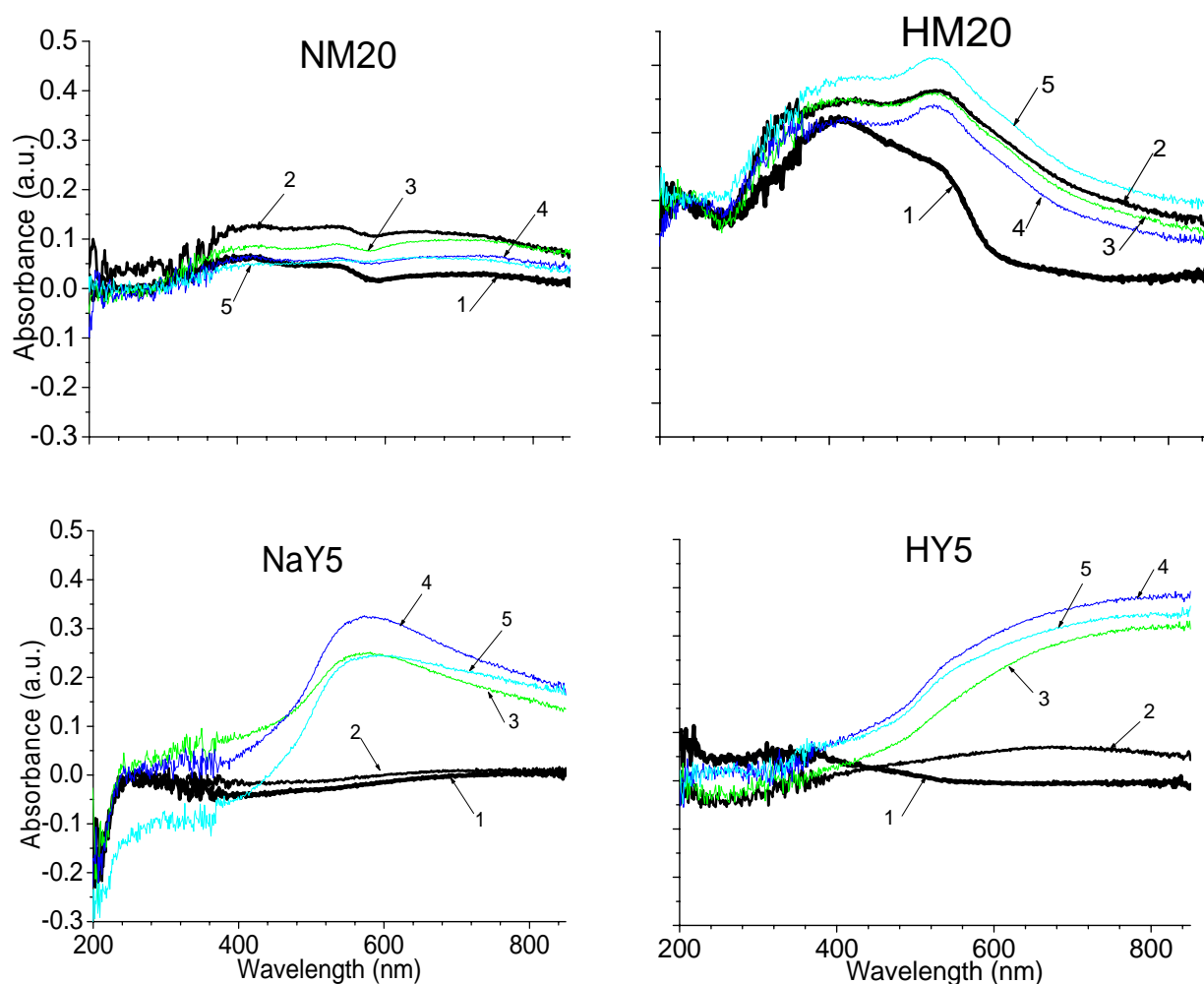


Fig.3: UV-Visible spectra of AuFe-zeolite as-prepared and calcined at selected temperature: 1-as-prepared, 2-100°C, 3-200°C, 4-300°C, 5-500°C.

Fig. 2 presents UV-visible spectra for Au-zeolites. In the spectrum of Au/NHM20 peaks are observed at 225 nm, 280 nm 390 nm and 550 nm. Peak at 225 is assigned to Au-cations, peaks at 280-390 nm to gold clusters and 550 nm to plasmon resonance adsorption of gold nanoparticles [22]. Temperature rise leads to decrease of relative intensity of peak at 280 nm and enhance of relative intensity of peak at 380 nm. Relative intensity of absorption band at 550 nm goes through maximum at temperature 200°C. It is clear that calcination temperature influences on the contribution of different gold species for mordenite NHM20.

Similar species is observed in the spectra for Au/HM20. In contrast with previous sample contribution of gold nanoparticles is higher while the contribution of gold cluster is lower then for Au/NHM20 sample.

The spectra for Au/NaY5 and Au/HY5 differ essentially from those for mordenite containing samples. The difference consists in very stable cationic gold species for Y based samples. Intensive peak assigned to gold cations (with maximum at <200 nm) is clearly observed up to 200°C. Profound peaks assigned to nanoparticles appear only after calcination at 300°C. Note that the spectra for Au/HY5 and Au/NaY5 are similar.

In Fig 3 the spectra of samples including both gold and iron are presented. The spectra for three samples (Au/Fe/NHM20, Au/Fe/NaY5 and Au/Fe/HY5) exhibit unusual optic features: i) negative values of absorption for NaY5; and ii) unusual shape of plasmon resonance peak for Au/Fe/NHM20 and for Au/Fe/HY5. Negative values testify incorrectness of the subtraction procedure used for spectra processing. Unusual shape of plasmon resonance consists in the dramatically shift of peak maximum to high wave length region (> 600 nm for Au/Fe/HNM20 and ≥ 800 nm for Au/Fe/HY5).

Comparison of the spectra for Au/HM20 and Au/Fe/HM20 shows that contribution of clusters is higher after iron addition. Moreover iron addition leads to wider plasmon peak which implies the smaller particles formation.

Two reasons for unusual shape of plasmon detected could be discussed. The first one is unusual shape of gold nanoparticles or their agglomerates. The second one could be incorrectness of spectra subtraction. The data of XRD and TEM permit to select the most probable explanation.

X-ray powder diffraction and TEM

XRD pattern for Au/Fe/HY5 and Au/Fe/NaY5 presented in Fig 4 and 5 indicate the presence of gold particles in samples calcined at 500°C. The analysis of XRD pattern with Rietveld procedure permits to estimate average diameter of gold nanoparticles corresponding to ~ 11 nm for both samples. Nevertheless the shape of plasmon resonance for these samples differs significantly that is another prove of incorrectness of subtraction procedure for them.

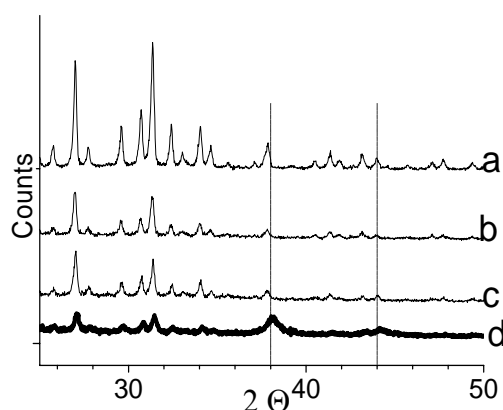


Fig. 4. The XRD patterns as-prepared NaY5 (a), Fe/NaY5 (b), Au/Fe/NaY5 (c), Au/Fe/NaY5 calcined at 500°C (d).

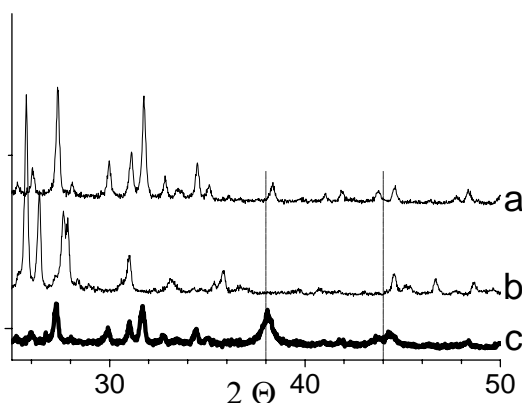


Fig. 5: The XRD patterns HY5 (a), Au/Fe/HY5 (b) and calcined at 500°C (c).

Typical TEM images for as-prepared Au/Fe/HY5 and calcined one demonstrate shape of gold particle close to sphere. Unusual shape for gold nanoparticles was not detected. Consequently, the reason of unusual optical feature for Au/Fe/NHM20 and Au/Fe/HY5 is incorrectness of spectra subtraction. Subtraction was not correct, but it permitted that Fe/zeolites sampler was changing after gold introduction.

According to TEM data the average size of gold particles is estimated as 5 nm in Au/Fe/HY5 before calcination. It can be observed that there is wide size distribution from 5 to 11 nm after calcinations at 500°C. This size agrees with average size calculated from XRD data.

Conclusions

The obtained data leads to the following conclusions:

- It was revealed that gold precursor is decomposed before temperature treatments with formation of reduced gold species in case of Au-zeolites studied.
- Reducibility of iron cations is higher for Fe/Y-zeolites then for Fe-mordenites probably due to difference in their pore geometry.
- It was shown that the addition of gold to iron-containing samples leads to change of iron state for Y- and NHM20 zeolites.
- It was shown the contribution of high dispersed gold is more pronounced for Au/Fe/HM20 than for Au/HM20.

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