

CHARACTERIZATION OF Pd-Cu/ γ -Al₂O₃ CATALYSTS BY XPS AND CATALYTIC MEASUREMENTS

KARAKTERIZACIJA Pd-Cu/ γ -Al₂O₃ KATALIZATORJEV Z XPS METODO IN KINETIČNIMI TESTI

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Liquid-phase hydrogenation using a solid catalyst provides a potential technique for the removal of nitrates from waters. Various Pd-Cu bimetallic catalysts were prepared according to different impregnation sequences of γ -Al₂O₃ support, and tested for the selective hydrogenation of aqueous nitrate solutions to nitrogen. Measurements were performed in a semi-batch slurry reactor at T=293 K. The results show that the nitrate-to-nitrite reduction step undergoes a structure-insensitive hydrogenation with a heterolytic electron transfer. The most suitable distribution of metallic copper and palladium phases, which results in the minimum formation of ammonium ions, was obtained for the catalyst preparation procedures, in which the alumina is impregnated first by copper salt. XPS examination of mono- and bimetallic catalysts revealed that in all examined samples Pd is present in the metallic form. On the other hand, in a Cu/ γ -Al₂O₃ sample previously reduced at T=773 K in hydrogen atmosphere, copper is found in +1 and +2 oxidation states. In the presence of both elements on the catalyst surface, copper is detected in low oxidation states (i.e., 0 and +1).

Key words: catalytic liquid-phase hydrogenation, drinking water purification, nitrate removal, Pd-Cu catalysts, catalyst characterization, XPS

Heterogeno katalizirana hidrogenacija vodnih raztopin nitratnih ionov predstavlja potencialno metodo za čiščenje z nitratnim ionom kontaminirane pitne vode. Pd-Cu bimetalni katalizatorji, pripravljeni z različnimi impregnacijskimi nanosi kovinskih prekurzorjev na γ -Al₂O₃ kot nosilec, so bili testirani na selektivno pretvorbo v vodi raztopljenega nitrata v dušik. Poskusi so bili opravljeni v semišaržnem reaktorju z goščo, obratujočem pri T=293 K in atmosferskem tlaku. Rezultati meritev kažejo, da je redukcija nitrata v nitritni ion strukturno neselektivna reakcija s heterolitskim prenosom elektronov. Za minimalno produkcijo amonijevega iona kot stranskega produkta procesa katalitske redukcije vodnih raztopin nitrata je prednostna tista prostorska porazdelitev Pd in Cu specij, pri kateri se na zunanji strani delca katalizatorja nahaja kovinska faza, na kateri se vodik adsorbira disociativno. Rezultati XPS analize monometalnih in bimetalnih katalizatorjev kažejo, da se Pd v vseh testiranih vzorcih nahaja v kovinskem stanju. Baker je v Cu/ γ -Al₂O₃ katalizatorju prisoten v oksidacijskih stanjih +1 in +2, medtem ko se v Pd-Cu bimetalnih katalizatorjih nahaja bodisi v kovinskem stanju bodisi v +1 oksidacijski obliki.

Ključne besede: katalitska hidrogenacija, čiščenje pitnih voda, odstranjevanje nitrata, Pd-Cu katalizatorji, karakterizacija katalizatorjev, XPS

1 INTRODUCTION

One of the most promising processes for removing nitrate both from drinking water streams and industrial effluents is liquid-phase hydrogenation with noble metal catalysts¹. The reaction obeys a consecutive reaction scheme in which nitrite appears as an intermediate, while nitrogen and ammonia are the final products. To maintain the electroneutrality of the aqueous phase, consumed nitrates are replaced by hydroxide ions. Supported Pd-Cu bimetallic catalysts promote the nitrate reduction in spite of an inadequate selectivity towards nitrogen production^{1,2}. Since the described method is in a stage of development, further kinetic and mechanistic studies with different systems in aqueous solutions are needed.

Relatively few investigations have been published concerning the characterization of Pd-Cu bimetallic catalysts. The structure of these solids has so far been studied by means of EXAFS, XANES, CO adsorption and FTIR analyses³⁻⁵. Skoda et al.⁵ used also two test reac-

tions in order to characterize the nature of the active surface sites, i.e., gas-phase toluene hydrogenation and decomposition of ethanol. It is demonstrated by these authors that the preparation procedure was found to exhibit remarkable effects on the surface properties of these solids; more or less separated phases, alloys or one of the phases being coated or partially covered by the other one could be formed. The potential of various Pd-Cu/ γ -Al₂O₃ catalysts, which had been prepared according to different impregnation sequences of alumina, was recently evaluated in the process of liquid-phase nitrate hydrogenation^{6,7}. It was tentatively concluded that the nitrate-to-nitrite reduction step is a structure-insensitive reaction, catalyzed only by metal ensembles consisting of Pd and Cu atoms. On the other hand, the nitrite ion can be simultaneously reduced on both Pd clusters and Pd-Cu contacts, the former being more selective. The behaviour of various Pd-Cu solids was found to be different only in the amount of accumulated nitrite ions; its higher production results in a lower reaction selectivity. How-

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ever, the oxidation states of Pd and Cu phases deposited on alumina support have not been determined yet. Correspondingly, the present paper reports a XPS examination of Pd-Cu/ γ -Al₂O₃ catalysts with the aim to characterize the palladium and copper species involved in the process of liquid-phase nitrate reduction.

2 EXPERIMENTAL

2.1 Catalyst preparation

Pd-Cu bimetallic catalysts (labelled as CAT-A and CAT-B) were prepared by impregnation of the powdered alumina support (γ -Al₂O₃ of high purity from Nikki-Universal; NST-3H type; S_{BET} : 154 m²/g; average particle diameter: 25 μ m; pore diameter: 10-25 nm) with aqueous solutions of copper and palladium nitrate. The monometallic Pd/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ were labelled as CAT-C and CAT-D, while a physical mixture of the Pd/ γ -Al₂O₃ and powdered copper particles as CAT-C + Cu. After every alumina impregnation step, the resulting solids were dried at 423 K. The catalyst preparation procedures were carried out as follows:

CAT-A: impregnation by copper nitrate, drying, calcination (1 h, 773 K in air), impregnation by palladium nitrate, drying, calcination (3 h, 773 K in air), reduction (1 h, 773 K in H₂).

CAT-B: impregnation by palladium nitrate, drying, reduction (1 h, 773 K in H₂), impregnation by copper nitrate, drying, calcination (3 h, 773 K in air), reduction (1 h, 773 K in H₂).

CAT-C: impregnation by palladium nitrate, drying, calcination (3 h, 773 K in air), reduction (1 h, 773 K in H₂).

CAT-D: impregnation by copper nitrate, drying, calcination (3 h, 773 K in air), reduction (1 h, 773 K in H₂).

The concentrations of metallic palladium and copper phases (ICP-AES analysis), the surface area (BET method), the isoelectric point (iep), and reaction selectivities of bimetallic samples obtained in the process of liquid-phase nitrate reduction are listed in **Table 1**. It should be noted that the alumina support as well as CAT-C and CAT-D samples exhibit no activity for nitrate reduction.

Table 1: Properties of the support and catalysts

Material	Metal loading wt. %	S_{BET} m ² /g	iep /	Selectivity ^a mol. %
γ -Al ₂ O ₃ support	-	154	8.5	-
CAT-A	4.7%Pd, 1.4%Cu	142	8.8	91
CAT-B	4.9%Pd, 1.5%Cu	141	8.7	82
CAT-C	5.0%Pd	146	8.6	-
CAT-D	1.5%Cu	143	-	-
(CAT-C+Cu) ^b	5.0%Pd; 100%Cu	-	-	82

^aMeasured in the process of catalytic liquid-phase nitrate reduction ^bPhysical mixture

2.2 Catalyst characterization

Bulk palladium and copper elemental compositions were determined by inductively coupled plasma - atomic emission spectroscopy on a Thermo Jarell Ash instrument. For ICP-AES measurements, the sample was fused with KHSO₄ and dissolved with a diluted HCl solution. The zeta potential of catalyst suspensions (0.07 wt.% in distilled water) was measured by means of a laser zee meter (Pen Chem, model 501) at 293 K and different pH values, adjusted by adding 0.1 M HCl or 0.1 M NaOH solutions. The XRD patterns were recorded on a Philips PW 1710 diffractometer with Cu K α radiation (λ =1.5406 Å) in the 2 θ range of 10 to 95°.

The XPS measurements were performed with a VG 310F Microlab system, using a monochromated Mg K α radiation (1253.6 eV) and a hemispherical energy analyzer. The pressure inside the analysis chamber was below 10⁻⁹ torr. Binding energies in the XPS spectra were referenced to an internal standard, the C 1s line of adventitious carbon contamination (284.6 eV). O 1s, C 1s, Al 2p, Cu 2p, Pd 3d X-ray photoelectron spectra, and Pd MVV and Cu LMM Auger spectra were obtained. The electronic state of Pd was characterized by core electron BEs for Pd 3d_{3/2} and Pd 3d_{5/2} photoelectrons. To study the influence of the catalyst treatments on the state of Cu species, the Cu 2p_{3/2} electronic transition and the Cu LMM Auger transition were monitored. The error in binding energy measurements was $\pm$ 0.2 eV whatever the sample. The BE and KE values were obtained by using the Peakfit program implemented in the control software of the spectrometer.

The activity and selectivity tests of the liquid-phase hydrogenation of aqueous nitrate solution were performed in an isothermal semi-batch slurry reactor at the operating conditions given in the caption of **Figure 1**, for which both intraparticle and interfacial mass-transfer resistances are negligible. The apparatus, the procedure for these measurements, and the analysis (concentrations of nitrate, nitrite, and ammonium ions) of the representative aqueous samples are described in detail elsewhere^{6,7}.

3 RESULTS AND DISCUSSION

The results of kinetics measurements obtained in an isothermal semi-batch slurry reactor demonstrate that differently prepared Pd-Cu/ γ -Al₂O₃ catalysts, and the physical mixture containing Pd/ γ -Al₂O₃ (CAT-C) and metallic copper particles exhibit a very similar activity. In the latter case, the Pd-Cu active sites that promote liquid-phase nitrate reduction were formed in situ by collision of particles; however, at the given reaction conditions the nitrate disappearance rate was found to be independent of the collision probability⁶. The nitrite ions concentration vs. time dependencies obtained during the catalytic nitrate reduction are illustrated in **Figure 1a**. It can be seen that the lowest nitrite amounts are determined for the CAT-A sample. Appropriate concentra-

tions, as a function of time for ammonium ions formed during the nitrate reduction, are presented in **Figure 1b**. The reaction selectivities (defined as the molar percentage of initial nitrate content converted to nitrogen at complete conversion of nitrates and nitrites) of the Pd-Cu systems used in this study are given in **Table 1**. The minimum concentrations of ammonium ions produced were observed again for the CAT-A sample. The comparison of ammonium ions concentration vs. time dependencies and the values listed in **Table 1** show that the reaction selectivity obtained in the presence of CAT-B equals to that evaluated for the physical mixture consisting of CAT-C and metallic copper particles. This finding and the above discussion allude that dispersion of Pd and Cu atoms on the alumina support has no influence on the observed activity and selectivity. Furthermore, the results of EXAFS examination³, and the fact that the physical mixture exhibits the same nitrate disappearance rate as it was observed in the presence of CAT-A and CAT-B samples, confirm that the nitrate-to-nitrite reduction step is a structure-insensitive reaction, as proposed already in the previous paper⁶.

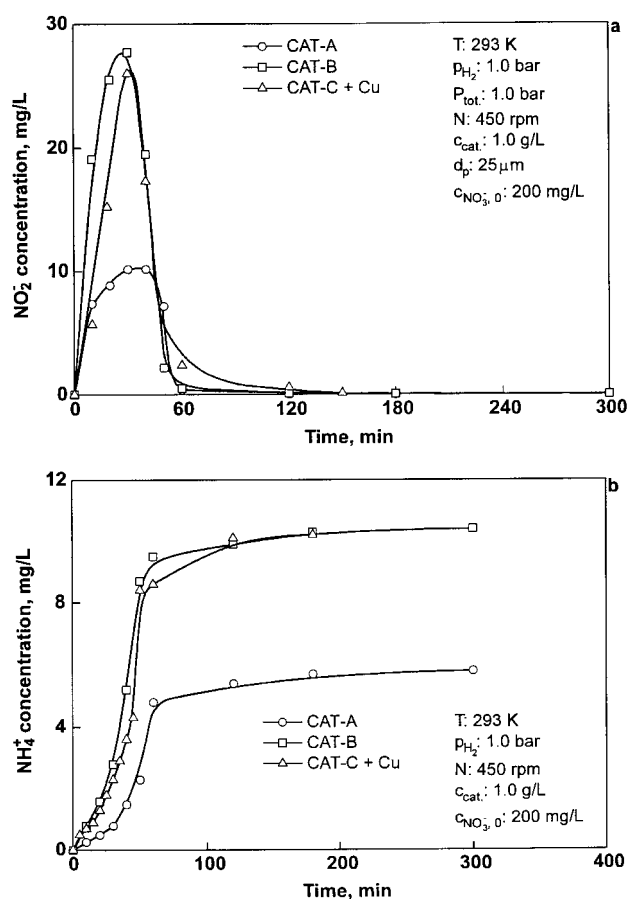


Figure 1: Nitrite (a) and ammonium (b) ions concentrations vs. time dependencies obtained in the slurry reactor over different bimetallic systems

Slika 1: Koncentracija nitritnih (a) in amonijevih (b) ionov kot funkcija časa, izmerjena v procesu katalitske redukcije vodne raztopine nitratnega iona v semišaržnem reaktorju z goščo, ob uporabi različnih Pd-Cu bimetalnih katalizatorjev

Data illustrated in **Figure 1** clearly demonstrate that the reaction selectivity is related to the amount of free (i.e., in the aqueous solution accumulated) nitrite. As observed, the catalyst preparation procedure in which the alumina was first impregnated by copper salt followed by the deposition of palladium salt (CAT-A), enhances the nitrogen production yield. The reaction selectivity can be explained by taking into account the results of AES examinations⁸. It was reported by Batista et al.⁸ that in the case of CAT-A sample, the very first surface sublayers are enriched with Pd atoms. On the other hand, in CAT-B and (CAT-C + Cu) catalytic systems the relative concentration of Pd-Cu active sites on the catalyst surface is higher, which results in nonselective transformation of intermediate nitrites to ammonium ions. This is also confirmed by the unsymmetrical concentration-time profiles for nitrites in **Figure 1a**.

The XRD patterns of the prepared catalysts show all the main characteristic peaks of the γ -Al₂O₃ support. No reflections for Pd- or Cu-containing phases were recorded. The particle of Pd and Cu metallic phases in the catalysts were either too small to be detected or in the amorphous phase. However, the catalyst preparation procedures mainly influence the peak position at 2θ close to 40° , which could be attributed to the preferred diffusion of Cu and Pd atoms into the γ -Al₂O₃ lattice⁹. The EXAFS investigation confirms no significant structural differences among CAT-A and CAT-B catalyst samples synthesized, which results into an identical activity for the nitrate removal³. The EXAFS analysis further provides an evidence that clusters with fcc crystal structure of Pd metal are formed, which consist of about 20 atoms in a tentative shape of an octahedron with a diameter of 0.56 nm. In bimetallic catalysts, the Cu atoms are situated either on the surface of the Pd cluster or attached elsewhere in the matrix; the EXAFS evidence is provided by the Cu-O correlation, which is almost twice as strong as Pd-O correlation. The shape of K-edges of both Pd and Cu, however, strongly resembles those of bulk metals, therefore the zero-valence state is definite for Pd and prevailing for Cu. The presence of a copper-aluminium spinel formed by a reaction with the substrate, is not supported by EXAFS data. To resolve oxidation states of Pd and Cu species deposited on the alumina support, XPS examination of CAT A-D samples was performed.

The preliminary XPS results of Pd/ γ -Al₂O₃, Cu/ γ -Al₂O₃ and Pd-Cu/ γ -Al₂O₃ are summarized in **Tables 2 and 3**. Pd 3d XPS spectra of CAT A-C samples are shown in **Figure 2**. As the Pd 3d level splitting is unchanged (≈ 5.1 eV, **Figure 2**) for the catalyst samples in the reduced state, we shall thereafter only report the values of the 3d_{5/2} level in attempt to identify the chemical state of palladium. The measured binding energy (BE) for the Pd 3d_{5/2} photoelectrons are given in **Table 2** together with published results¹⁰. Palladium reduced in hydrogen and subsequently exposed to ambient air (under

mild conditions) is not reoxidized and shows the Pd 3d_{5/2} BE level at 335.6-335.8 eV, which is in good agreement with values reported for Pd⁰ on alumina and for metallic palladium¹⁰. To try to measure the extra-atomic relaxation energy, the Auger electron kinetic energy (KE) of Pd (Auger Pd MVV), in addition to Al 2p and O 1s transitions of the support, were also recorded. Unfortunately, the Auger Pd-MVV peak is ill defined and an Auger parameter α , variations of which are directly related to the variations of the relaxation energy, was not determined. Although the Pd-MVV Auger lines are poorly resolved, it is possible to detect a slight modification in the line shape comparing mono- and bimetallic samples (not shown here). To study the influence of catalyst preparation procedures on the state of Cu species, the Cu 2p_{3/2} electron transition and the Cu-LMM Auger transition were recorded. Since the Cu 2p_{3/2} transition does not permit us to distinguish the oxidation states of copper, these were characterized by taking into account both Cu 2p_{3/2} and Cu-LMM transitions, the modified Auger parameter (α), and the shake-up satellite associated to the Cu 2p_{3/2} transition. Namely, Cu²⁺ species shows a shake-up satellite at about 10 eV higher than the Cu 2p_{3/2} transition that is not shown by Cu¹⁺ or Cu⁰ species; this characteristic is used to differentiate between Cu²⁺ and Cu¹⁺ or Cu⁰. The Cu 2p core level spectra and Cu-LMM Auger spectra of the reduced CAT-D sample are displayed in **Figure 3**. The Cu 2p_{3/2} BE, Cu-LMM Auger kinetic energy (KE) and modified Auger parameter (α) of CAT-A, CAT-B and CAT-D reduced samples are compiled in **Table 3**. In CAT-D sample, where the reduction was carried out by heating for 1 h in H₂ at 773 K, the Cu 2p_{3/2} peak at 932.9 eV is accompanied by the characteristic Cu²⁺ shake-up satellite peak at 943.4 eV (**Figure 3a**). Both the measured α value (1846.8 eV) for the reduced CAT-D sample and the spectrum shown in **Figure 3b** indicate that the major copper species present on the surface of this sample is Cu¹⁺; however, it cannot be excluded that a small portion of Cu⁰ species is also present. It is reported by Alejandro et al.¹² that γ -Al₂O₃ supported CuO catalysts calcined at temperatures lower than 973 K, are completely reduced in hydrogen atmosphere at 600 K. Although in this work the CAT-D sample was reduced at 773 K, no further reduction of Cu¹⁺ ions to Cu⁰ occurred. It seems that there exists a very strong metal-support interaction (SMSI), which prohibits the formation of metallic copper phase in the given preparation conditions. In reduced CAT-A and CAT-B bimetallic samples, the intensity of the shake-up satellite is substantially reduced (**Figure 4a**) and practically disappears. This reflects the reduction of Cu²⁺ to Cu¹⁺ and Cu⁰ species (**Table 3**). It can be seen in **Figure 4b** that each of Cu-LMM signals exhibits two maxima. BE peaks at 335.6 and 335.8 eV (which correspond to α values of 1851.0 and 1850.9 eV, respectively) reflect the presence of Cu⁰ in the investigated samples. Furthermore, BE maxima located at 340.9 and 341.0 eV (corresponding α values are equal to

1845.7 eV) are attributed to Cu¹⁺ species. By means of deconvolution of spectra plotted in **Figure 4b**, it was discovered that for the employed catalyst preparation procedures about one-half of the deposited copper content is present in zero-valent state. Based on the results of XPS analysis shown in **Figures 3 and 4**, it is concluded that due to a strong SMSI effect, the presence of Pd atoms on the catalyst surface strongly assists the transformation of Cu¹⁺ and Cu²⁺ species into the metallic state.

Table 2: Pd 3d_{5/2} binding energy value (BE) of Pd/ γ -Al₂O₃ and Pd-Cu/ γ -Al₂O₃ catalysts

Sample	Treatment History	BE (eV) Pd 3d _{5/2}	Assignment
CAT-A	Reduced(H ₂),773K	335.6	Pd ⁰
CAT-B	Reduced(H ₂),773K	335.8	Pd ⁰
CAT-C	Reduced(H ₂),773K	335.6	Pd ⁰
6.8wt.%Pd/ γ -Al ₂ O ₃	Calcined,1073K	337.1 ^a	Pd ²⁺
6.8wt.%Pd/ γ -Al ₂ O ₃	Calcined,1073K, Reduced(H ₂),773K	334.9 ^a	Pd ⁰

Note: BE referenced to C 1s (284.6 eV). The error in BE determination is ± 0.2 eV

^aData taken from Ref. 10

Table 3: Cu 2p_{3/2} binding energy (BE), Cu-LMM Auger kinetic energy (KE) and modified Auger parameter (α) of reduced Cu/ γ -Al₂O₃ and Pd-Cu/ γ -Al₂O₃ catalysts

Sample	BE Cu 2p _{3/2} (eV) (+satellites)	Cu-LMM (eV) KE	α (eV) ^a	Assignment
CAT-A	933.0	912.7, 918.0	1845.7, 1851.0	Cu ⁰ , Cu ¹⁺
CAT-B	933.1	912.6, 917.8	1845.7, 1850.9	Cu ⁰ , Cu ¹⁺
CAT-D	932.9 (943.4)	913.9	1846.8	Cu ¹⁺ , Cu ²⁺
Cu (metal)	932.4 ^b	918.6	1851.0	Cu ⁰
Cu ₂ O	932.3 ^b	916.6	1848.9	Cu ¹⁺
CuO	933.8 ^b (≈ 943.8)	917.6	1851.4	Cu ²⁺

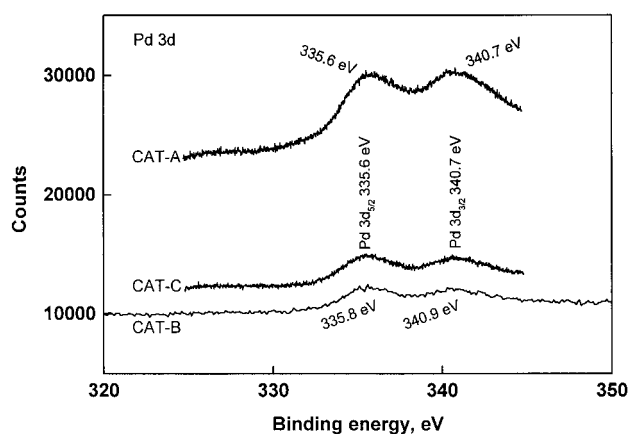


Figure 2: XPS Pd 3d spectra of reduced catalysts

Slika 2: Pd 3d XPS spektri reduciranih vzorcev katalizatorjev

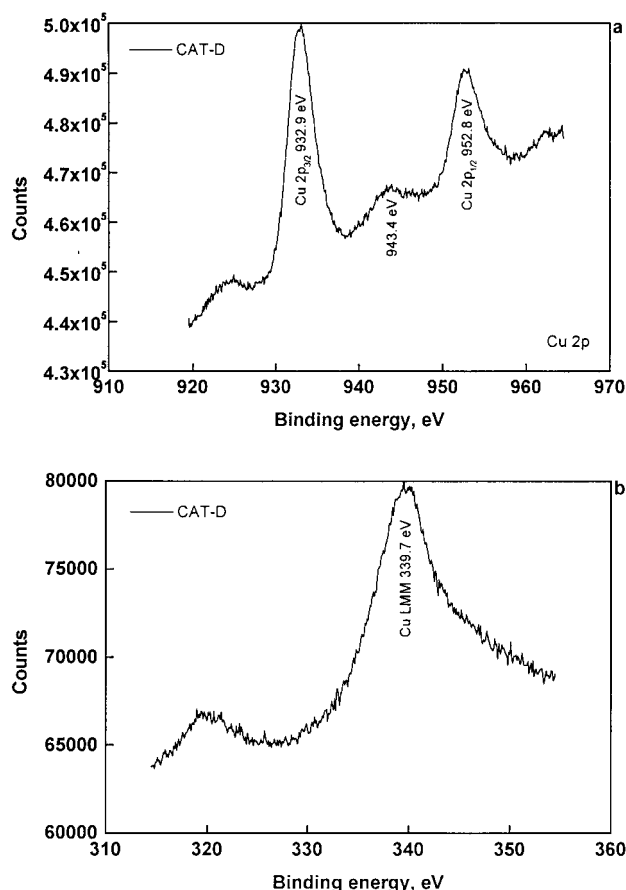


Figure 3: Cu 2p photoelectron spectra (a) and Cu-LMM Auger spectra (b) of CAT-D sample

Slika 3: Cu 2p XPS spekter (a) in Cu-LMM AES spekter (b) vzorca CAT-D

Note: BE referenced to C 1s (284.6 eV). The error in BE determination is ± 0.2 eV

^aModified Auger parameter = BE (Cu 2p_{3/2}) + KE (Auger Cu-LMM)

^bData taken from Ref. 11

4 CONCLUSIONS

The behaviour of variously synthesized Pd-Cu bimetallic solids in the process of catalytic liquid-phase hydrogenation of aqueous nitrate solution differs in the amount of accumulated nitrites and the final concentrations of ammonium ions produced. The reaction selectivity is appreciably dependent on the catalyst preparation procedures; the specific spatial distribution of metallic copper and palladium phases on γ -Al₂O₃ results in a minimal formation of ammonium ions. XPS analysis of Pd monometallic and Pd-Cu bimetallic catalysts shows that palladium is present in the metallic form. Due to the SMSI effect, copper prevails in mono-valent state in a reduced Cu/ γ -Al₂O₃ catalyst; addition of noble metal enables its reduction into zero-valent state.

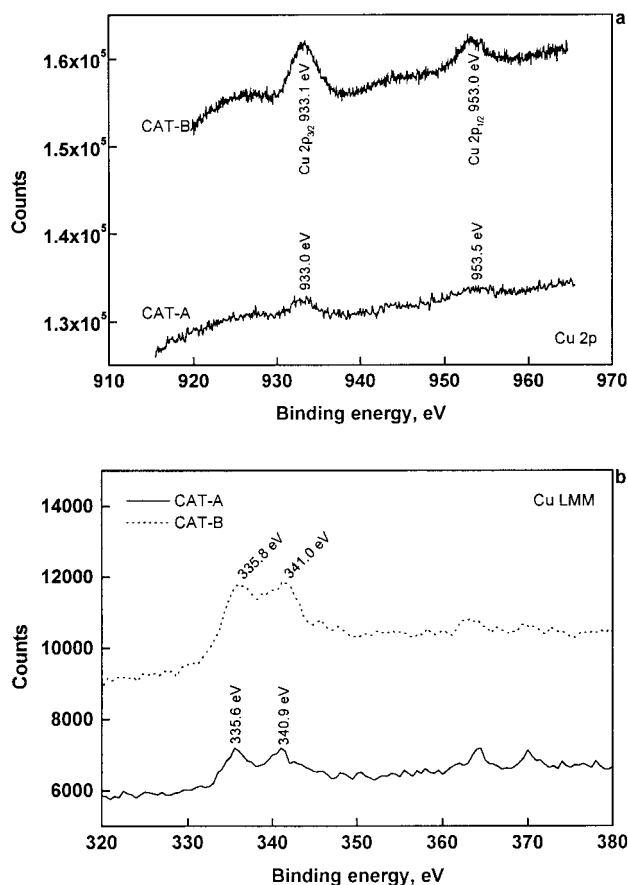


Figure 4: Cu 2p photoelectron spectra (a) and Cu-LMM Auger spectra (b) of CAT-A and CAT-B samples

Slika 4: Cu 2p XPS spektra (a) in Cu-LMM spektra (b) vzorcev CAT-A in CAT-B

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