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CHARACTERIZATION OF Pd-Cu/γ-Al_2O_3 CATALYSTS BY XPS AND CATALYTIC MEASUREMENTS

KARAKTERIZACIJA Pd-Cu/γ-Al_2O_3 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-Al_2O_3 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-Al_2O_3 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-Al_2O_3 kot nosilec, so bili testirani na selektivno pretvorbo v vodi raztopljenega nitratnega iona 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 nitratnega v nitritni ion strukturno neselektivna reakcija s heterolitskim prenosom elektronov. Za minimalno produkcijo amonijevega iona kot stranskega produkta procesa katalitske redukcije vodnih raztopin nitratnega iona 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-Al_2O_3 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 nitratnega iona, 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 catalysts[1]. 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 analyses[3-5]. Skoda et al.[5] used also two test reactions 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-Al_2O_3 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-Al_2O_3 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-Al_2O_3 of high purity from Nikki-Universal; NST-3H type; S_{BET}: 154 m^2/g; average particle diameter: 25 μm; pore diameter: 10-25 nm) with aqueous solutions of copper and palladium nitrate. The monometallic Pd/γ-Al_2O_3 and Cu/γ-Al_2O_3 were labelled as CAT-C and CAT-D, while a physical mixture of the Pd/γ-Al_2O_3 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 H_2).

CAT-B: impregnation by palladium nitrate, drying, reduction (1 h, 773 K in H_2), impregnation by copper nitrate, drying, calcination (3 h, 773 K in air), reduction (1 h, 773 K in H_2).

CAT-C: impregnation by palladium nitrate, drying, calcination (3 h, 773 K in air), reduction (1 h, 773 K in H_2).

CAT-D: impregnation by copper nitrate, drying, calcination (3 h, 773 K in air), reduction (1 h, 773 K in H_2).

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_2O_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

[a]Measured in the process of catalytic liquid-phase nitrate reduction [b]Physical 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 $KHSO_4$ 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 Kα radiation (λ=1.5406 Å) in the 2θ range of 10 to 95°.

The XPS measurements were performed with a VG 310F Microlab system, using a monochromated Mg Kα 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 ±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-Al_2O_3 catalysts, and the physical mixture containing Pd/γ-Al_2O_3 (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 probability[6]. 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 examination[3], 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 paper[6].

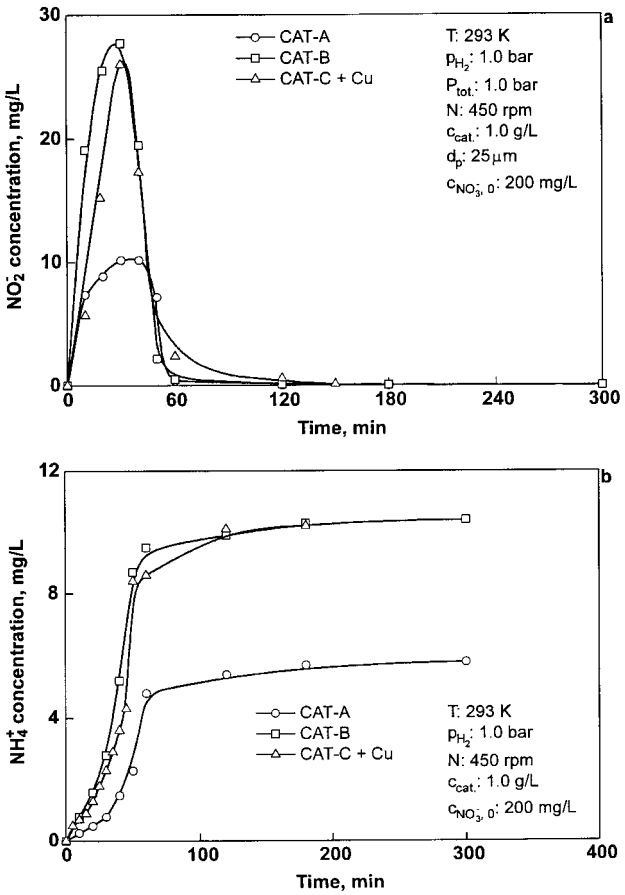

Figure 1: Nitrite (a) and ammonium (b) ions concentrations vs. time dependencies obtained in the slurry reactor over different bimetallic systems

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 examinations[8]. 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-Al_2O_3 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-Al_2O_3 lattice[9]. 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 removal[3]. 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-Al_2O_3, Cu/γ-Al_2O_3 and Pd-Cu/γ-Al_2O_3 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 results[10]. 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 Pd^0 on alumina and for metallic palladium[10]. 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, Cu^{2+} species shows a shake-up satellite at about 10 eV higher than the Cu $2p_{3/2}$ transition that is not shown by Cu^{1+} or Cu^0 species; this characteristic is used to differentiate between Cu^{2+} and Cu^{1+} or Cu^0. 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 H_2 at 773 K, the Cu $2p_{3/2}$ peak at 932.9 eV is accompanied by the characteristic Cu^{2+} 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 Cu^{1+}; however, it cannot be excluded that a small portion of Cu^0 species is also present. It is reported by Alejandre et al.[12] that γ-Al_2O_3 supported CuO catalysts calcined at temperatures lower that 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 Cu^{1+} ions to Cu^0 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 Cu^{2+} to Cu^{1+} and Cu^0 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 Cu^0 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 Cu^{1+} 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 Cu^{1+} and Cu^{2+} species into the metallic state.

Table 2: Pd $3d_{5/2}$ binding energy value (BE) of Pd/γ-Al_2O_3 and Pd-Cu/γ-Al_2O_3 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_2O_3	Calcined,1073K	337.1[a]	Pd^{2+}
6.8wt.%Pd/γ-Al_2O_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
[a]Data 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-Al_2O_3 and Pd-Cu/γ-Al_2O_3 catalysts

Sample	BECu$2p_{3/2}$ (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_2O	932.3[b]	916.6	1848.9	Cu^{1+}
CuO	933.8[b] (≈943.8)	917.6	1851.4	Cu^{2+}

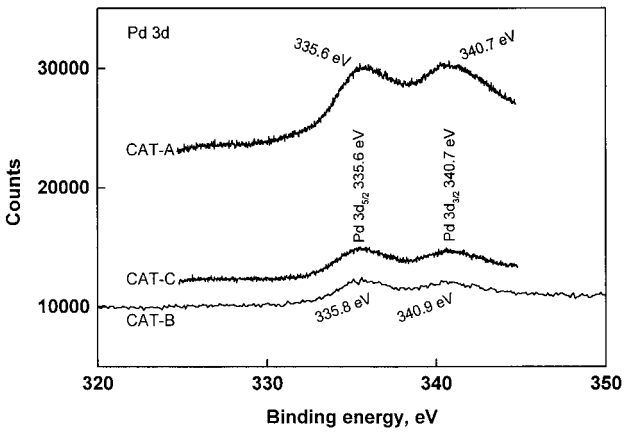

Figure 2: XPS Pd 3d spectra of reduced catalysts
Slika 2: Pd 3d XPS spektri reduciranih vzorcev katalizatorjev

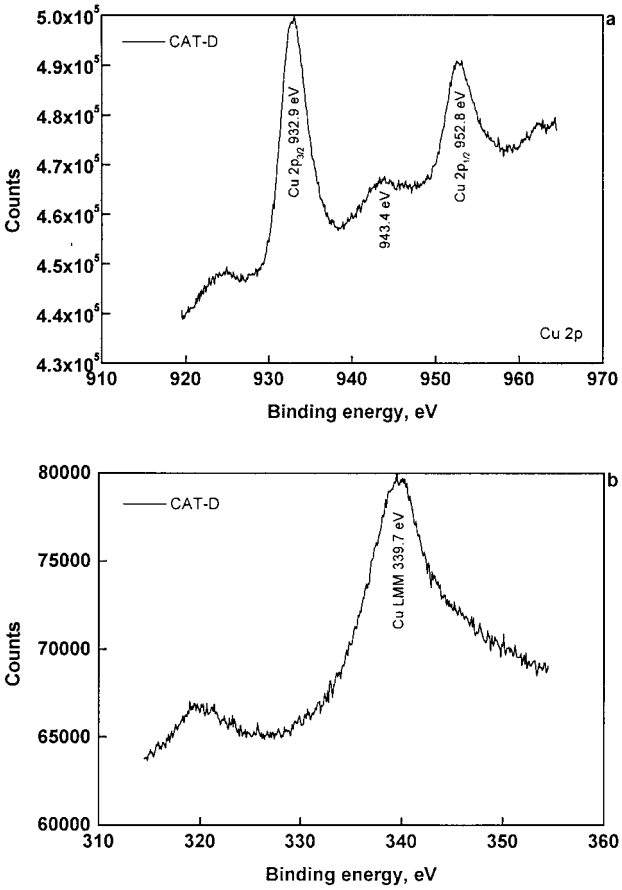

Figure 3: Cu 2p photoelectron spectra (a) and Cu-LMM Auger spectra (b) of CAT-D sample

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

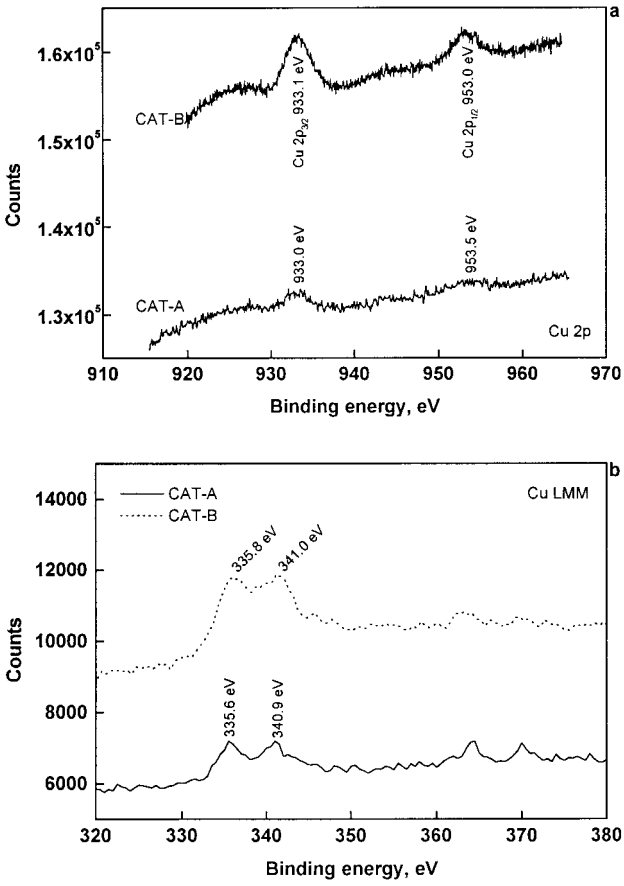

Figure 4: Cu 2p photoelectron spectra (a) and Cu-LMM Auger spectra (b) of CAT-A and CAT-B samples

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

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

[a]Modified Auger parameter = BE (Cu 2$p_{3/2}$) + KE (Auger Cu-LMM)

[b]Data 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-Al_2O_3 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-Al_2O_3 catalyst; addition of noble metal enables its reduction into zero-valent state.

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5 REFERENCES

[1] S. Hörold, K. D. Vorlop, T. Tacke and M. Sell, *Catal. Today*, 17 (1993) 21

[2] K. D. Vorlop and T. Tacke, *Chem. Ing. Tech.*, 61 (1989) 836

[3] A. Pintar, J. Batista, I. Arčon and A. Kodre, *Stud. Surf. Sci. Catal.*, 118 (1998) 127

[4] M. Fernandez-García, J. A. Anderson and G. L. Haller, *J. Phys. Chem.*, 100 (1996) 16247

[5] F. Skoda, M. P. Astier, G. M. Pajonk and M. Primet, *Catal. Lett.*, 29 (1994) 159

[6] A. Pintar and T. Kajiuchi, *Acta Chim. Slovenica*, 42 (1995) 431

[7] A. Pintar, J. Batista, J. Levec, and T. Kajiuchi, *Appl. Catal. B: Environ.*, 11 (1996) 81

[8] J. Batista, A. Pintar and M. Čeh, *Catal. Lett.*, 43 (1997) 79

[9] B. R. Strohmeier, D. E. Leyden, R. S. Field and D. M. Hercules, *J. Catal.*, 94 (1985) 514

[10] J. S. Shyu, K. Otto, W. L. H. Watkins, G. W. Graham, R. F. Belitz and H. S. Gandhi, *J. Catal.*, 114 (1988) 23

[11] A. Corma, A. Palomares and F. Márquez, *J. Catal.*, 170 (1997) 132

[12] A. Alejandre, F. Medina, A. Fortuny, P. Salagre and J. E. Sueiras, *Appl. Catal. B: Environ.*, 16 (1998) 53