Characterization of supported Pd–Cu bimetallic catalysts by SEM, EDXS, AES and catalytic selectivity measurements

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Received 26 June 1996; accepted 2 October 1996

Pd–Cu/γ-Al_2O_3 bimetallic catalysts were prepared according to different impregnation sequences of γ-Al_2O_3 and characterized by XRD, SEM, EDXS and AES. The catalysts were tested for the selective hydrogenation of aqueous nitrate solutions to nitrogen. The reaction selectivity was found to be dependent on the catalyst preparation procedures, which affect the spatial distribution of metallic copper and palladium phases. A catalyst prepared by impregnating γ-Al_2O_3 with copper followed by palladium gives higher selectivity to nitrogen than a catalyst prepared by impregnating the support with palladium followed by copper. The AES examination shows that in the catalyst exhibiting a higher nitrogen production yield, a reaction zone for the liquid-phase nitrate reduction is located in the interior of particles and covered by a layer of Pd atoms.

Keywords: Pd–Cu bimetallics, SEM, EDXS, AES, catalytic liquid-phase nitrate hydrogenation

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. Supported Pd–Cu bimetallic catalysts promote nitrate reduction in spite of inadequate selectivity towards nitrogen production [1,2]. The preparation procedure was found to exhibit remarkable effects on the surface properties of these solids [3]. 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 [4,5]. It was observed that the nitrate-to-nitrite reduction step is a structure-insensitive reaction, catalysed only by metal ensembles composed 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. Behaviour of various Pd–Cu solids was found to be different only in the amounts of accumulated nitrite ions; its higher production results in lower reaction selectivity. However, a correlation between Pd–Cu/γ-Al_2O_3 preparation procedures and reaction selectivities has not been studied so far.

The objective of this work was to determine the structure–selectivity relationships of Pd–Cu/γ-Al_2O_3 catalysts in the process of liquid-phase nitrate reduction. The prepared samples were characterized by XRD, SEM, EDXS, AES, and selectivity measurements.

2. Experimental

2.1. Catalyst preparation

Pd–Cu bimetallic catalysts were prepared by impregnation of the powdered alumina support (γ-Al_2O_3 of high purity from Nikki-Universal; NST-3H type; 180 m^2/g; average particle diameter: 25 μm; pore diameter: 10–25 mm) with aqueous solutions of copper and palladium nitrate. After every alumina impregnation step, the resulting solids were dried at 423 K. The bimetallic catalysts were designated as CAT-A and CAT-B; the calculated loadings of Pd and Cu were equal to 5 and 1.5 wt%, respectively. The monometallic Pd (5 wt%)/γ-Al_2O_3 was labelled as CAT-C, while a physical mixture of the Pd/γ-Al_2O_3 and powdered copper particles as CAT-C + Cu. 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,

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calcination (3 h, 773 K in air), reduction (1 h, 773 K in H_2).

It should be noted that Pd–Cu catalysts have been recently prepared also by some other impregnation sequences of aluminas [3,4]. However, with regard to the observed catalytic properties for liquid-phase nitrate reduction, their behaviour was found to be identical to one of the above described bimetallic systems.

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 XRD patterns were recorded on a Philips PW 1710 diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) in the 2θ range of 10 to 95°.

SEM and EDXS examinations were carried out in a Jeol JXA 840A electron probe microanalyser equipped with a Tracor Z-Max 30 EDX detector. For microanalysis, polished flat surfaces of catalysts were prepared by conventional metallographic techniques. The working conditions for the EDX linescan analysis were set for 20 kV voltage and 0.5 nA beam (diameter$\approx 0.2\,\mu$m) current. The positioning of the beam was controlled by computer software and spectra were acquired for 100 s at each point (10 to 15 points in each line). The maximum analysed depth under these conditions is about 1 μm. A semi-quantitative analysis was performed using the Tracor Series II X-ray microanalysis system. For the quantification of the EDX spectra, the PRZ matrix correction procedure was used.

AES sputter depth profiles of the catalyst grains were measured in a Perkin-Elmer PHI-545 A instrument. To prevent the charging effect during AES depth profiling, the samples were embedded in a silver paste and fixed on the nickel foil [6]. A static primary electron beam of 8 keV energy, 0.5 μA beam current and about 20 μm diameter was used. The samples were ion-sputtered with two symmetrically inclined beams of 3 keV Ar^+ ions, rastered over a surface area of about 5 mm × 5 mm at an incidence angle of 47°. The sputter rate of about 10 nm/min was calibrated on a Cr/Ni multilayer structure with a known thickness [7]. The CAT-A and CAT-B samples were sputtered to a depth of about 1000 nm. The Auger peak-to-peak heights of Al (1396 eV), Pd (330 eV), Cu (920 eV) and O (510 eV) were registered against the sputtering time. The concentration of elements was calculated on the basis of relative elemental sensitivity factors $S_{\mathrm{Al}} = 0.16$, $S_{\mathrm{Pd}} = 0.60$, $S_{\mathrm{Cu}} = 0.20$ and $S_{\mathrm{O}} = 0.35$. The possible matrix and preferential sputtering effects were not corrected and the procedure is considered as a semi-quantitative analysis [8]. However, the samples were investigated at the same analysing parameters and the results are comparable between themselves.

The 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 fig. 4. The apparatus, the procedure for these measurements, and the analysis (concentrations of nitrate, nitrite and ammonium ions) of the representative aqueous samples are described elsewhere [4].

3. Results and discussion

The XRD patterns of the prepared catalysts show all the main characteristic peaks of the γ-Al_2O_3 support. No characteristic reflections for Pd- or Cu-containing phases were recorded. The particle sizes of the Pd and Cu metallic phases in the catalysts were either too small to be detected or in the amorphous phase. According to the bulk chemical analysis, the catalysts have the following content of deposited metals: Pd = 4.7 and Cu = 1.4 wt% for CAT-A; Pd = 4.9 and Cu = 1.5 wt% for CAT-B. Metal deposition on the γ-Al_2O_3 support during the preparation of CAT-A, CAT-B and CAT-C causes the lowering of the specific surface area (BET method) to 131, 121 and 146 m^2/g, respectively.

The SEM micrographs of CAT-A and CAT-B samples are shown in figs. 1a and 1b. The appearance and morphology of the CAT-A and CAT-B particles is similar. Both catalysts are composed of single crystallites ($\leqslant 20\,\mu$m) and agglomerates which appear to be larger in the CAT-A catalyst. Higher magnification of these agglomerates shows that they are composed of very small particles (fig. 1c). The existence of agglomerates indicates that minor sintering of single crystallites occurs during the preparation of both catalysts. EDXS linescan analysis was used to determine the concentration of Pd and Cu across individual catalyst crystallites. Single crystals were chosen, ranging from 20 to 30 μm in diameter. Typical elemental profiles for Pd and Cu in CAT-A and CAT-B are illustrated in fig. 2. It can be seen that the concentration of Cu in both samples is relatively constant from the surface of crystallites to the measured depth of approximately 20 μm. In contrast, Pd shows a different distribution: the concentration profiles exhibit the maxima. The results presented in fig. 2 are very similar, so one cannot explain the otherwise distinctive effect of investigated catalysts on the reaction selectivity in the liquid-phase nitrate hydrogenation discussed below. It is speculatively concluded that pronounced differences in Pd and Cu distribution should appear in the very first surface sub-layers. Since the EDX technique probes a depth of about 1 μm, an examination with higher resolution should be carried out.

To obtain a relation between microscopic (i.e., structure) and macroscopic (i.e., reaction selectivity) obser-

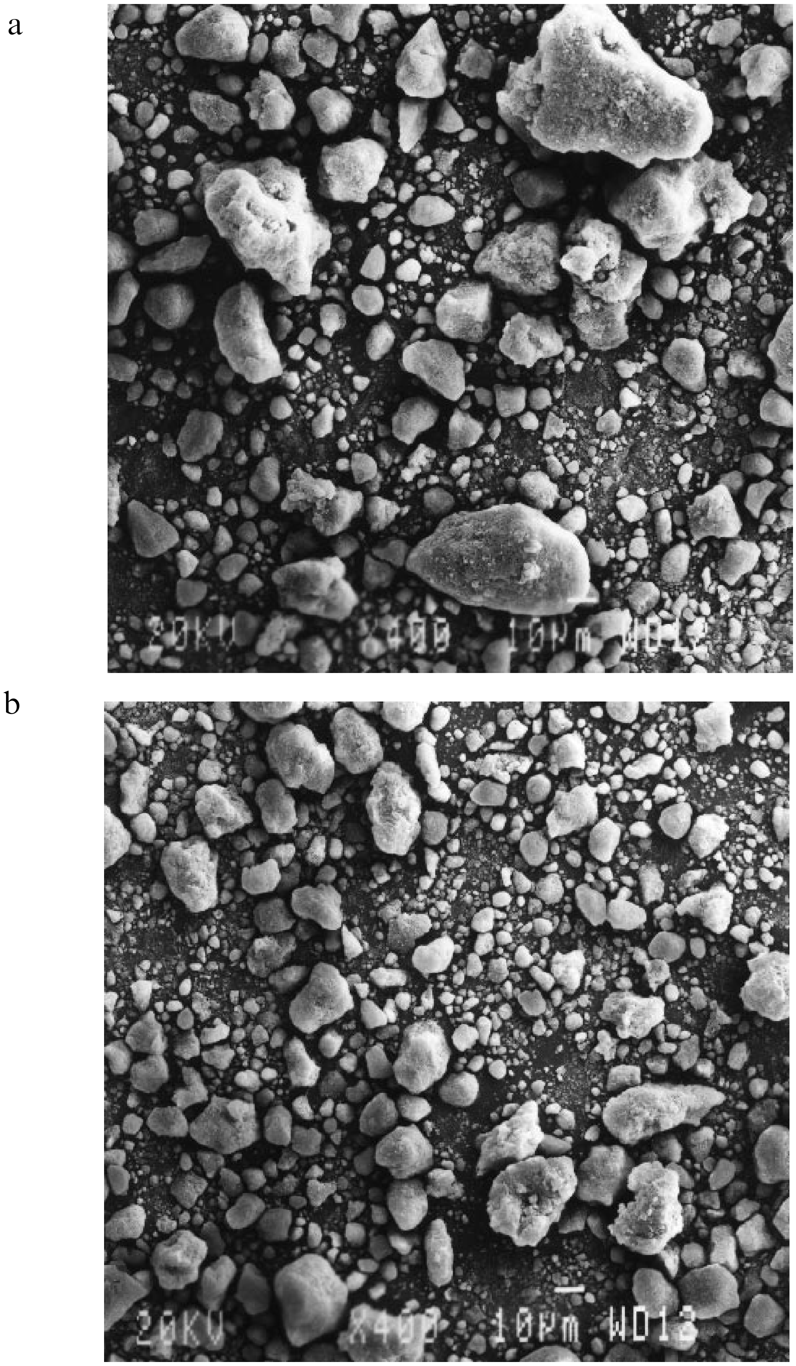

Fig. 1. Scanning electron micrographs of prepared catalyst powders: (a) CAT-A; (b) CAT-B; (c) higher magnification of an agglomerate in CAT-B. (Continued on next page.)

vations, AES was employed to determine depth profiles of the elemental composition of the catalysts CAT-A and CAT-B. The depth distribution of constituents is shown in fig. 3. The surface and the thin layers beneath the surface are composed of aluminium, palladium, copper and oxygen. The AES analysis of the CAT-A sample (fig. 3a) revealed copper atoms (0.5 at%) only in layers located about 300 nm under the surface. The copper concentration then raises to 1.5 at% (approximately up to 600 nm), and does not change significantly with further increasing depth. It is interesting to note that the palladium concentration simultaneously increases from the surface to the layers up to about 100 nm below the CAT-A surface. Then the Pd content decreases with increasing depth. To summarize, the depth distribution of Pd and Cu metallic phases in the CAT-A indicates more Pd in the thin layers under the surface, while in the same depth region Cu was not detected. The averaged AES depth profiles of elements in the CAT-B sample are shown in fig. 3b. The lowest palladium concentration and, at the

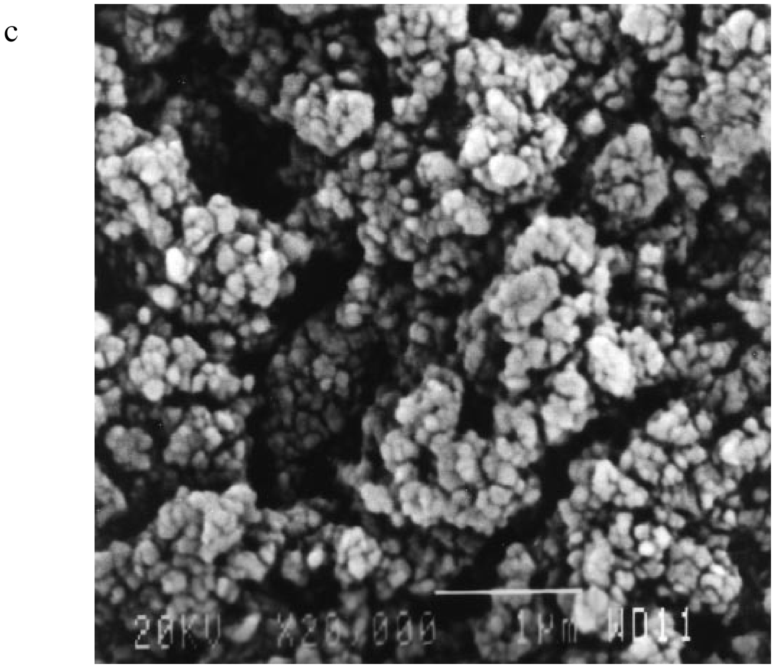

Fig. 1. (Continued.)

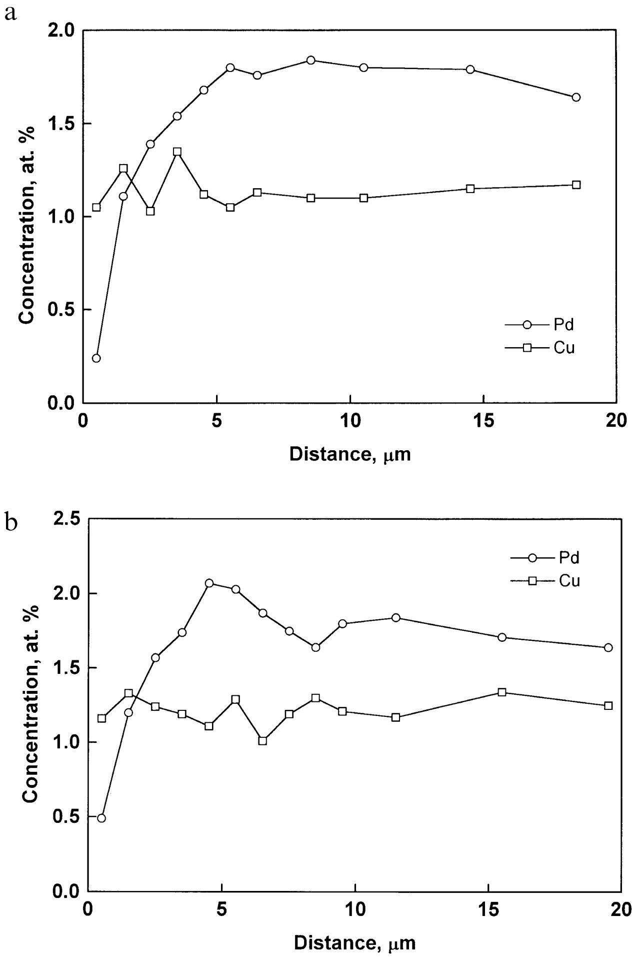

Fig. 2. Results of EDX line analysis of the (a) CAT-A and (b) CAT-B samples.

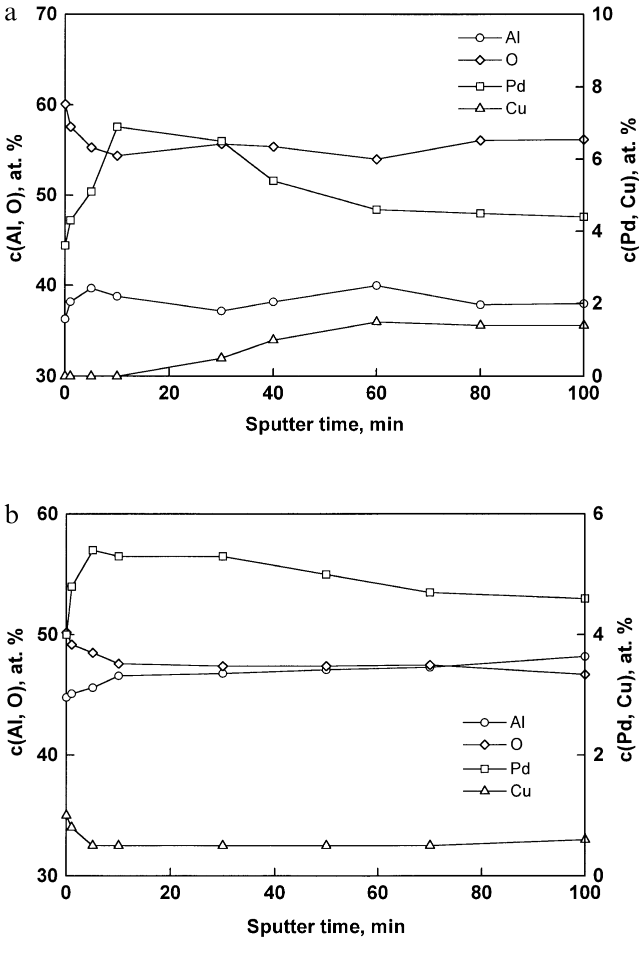

Fig. 3. AES sputter depth profiles of the aluminium, copper, oxygen and palladium in the investigated layers of the (a) CAT-A and (b) CAT-B samples.

same time, the highest copper concentration were determined on the surface of the catalyst. In depths of about 10 to 50 nm beneath the surface, the copper content decreases slowly, and then remains almost unchanged in deeper layers. On the other hand, the palladium concentration first slightly increases and then slowly decreases in the same depth region. Its surface concentration (4.0 at%) is lower than at any analysed depths. In contrast to the results for the CAT-A sample, the surface and the thin sub-layer (approximately up to 10 nm) of the CAT-B are enriched with Cu. To conclude, the obtained AES depth profiles of the elemental composition of both catalysts clearly reflect the influence of preparation conditions on the spatial distribution of metallic phases.

Temporal course of the liquid-phase nitrate reduction over various catalysts is shown in fig. 4. The results demonstrate that differently prepared Pd–Cu/γ-Al_2O_3 catalysts, and the physical mixture containing Pd/γ-Al_2O_3 and metallic copper particles exhibit a very similar activity. In the latter case, the Pd–Cu active sites were formed by collision of particles. The nitrite ions concentration vs. time dependencies obtained during the catalytic nitrate reduction are illustrated in fig. 5. It can be seen that the lowest nitrite amounts are determined for the CAT-A sample. Appropriate concentrations as a function of time for ammonium ions formed during the nitrate reduction are presented in fig. 6. The minimum concentrations of ammonium ions produced were observed again for the CAT-A sample. The comparison of ammonium ion concentration vs. time dependencies shows that the selectivity of CAT-B equals the one evaluated for the physical mixture consisting of CAT-C and metallic copper particles. This finding and in fig. 4 shown results allude that dispersion of Pd and Cu atoms has no influence on the observed activity and selectivity. Figs. 5 and 6 further 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, enhances the nitrogen production yield. The influence of the catalyst synthesis on the distribution of active sites and consequently on the reaction selectivity can be explained by taking into account the results of AES examinations and catalytic tests. As reported above, copper appears only in layers about 300 nm under the surface of CAT-A, which means that a reaction zone for nitrate reduction (consisting of Pd and Cu phases) is located in the interior of a particle and covered by a layer composed of Pd atoms. Due to the higher adsorption affinity of nitrate ions towards Pd–Cu clusters [4], NO_2^- once formed is forced to migrate into the aqueous solution. During its counter-diffusion from catalyst pores, the nitrite is selectively transformed to nitrogen in the Pd layer, which results in a lower accumulation of nitrite in the bulk solution. After the nitrate has been consumed, the accumulated nitrite is

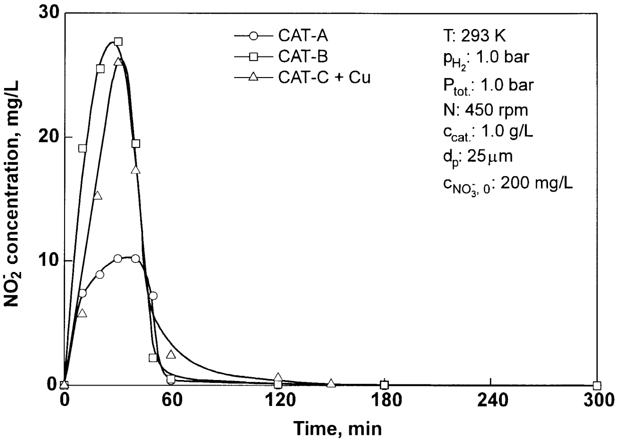

Fig. 5. Nitrite ion concentrations as a function of time for the liquid-phase nitrate reduction over the CAT-A, CAT-B and (CAT-C+ Cu) samples.

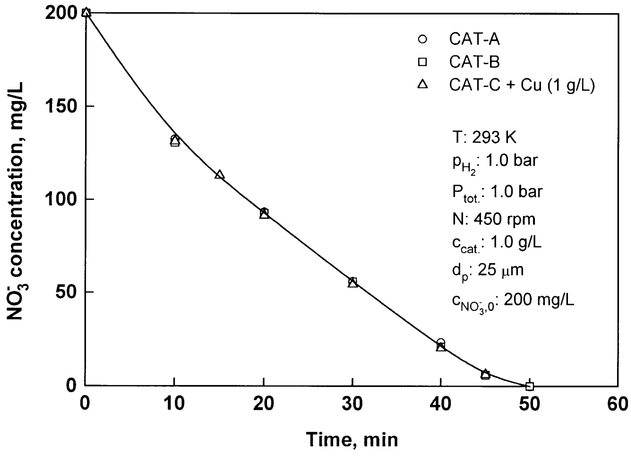

Fig. 4. Temporal course of the liquid-phase nitrate reduction over the CAT-A, CAT-B and (CAT-C + Cu) catalysts.

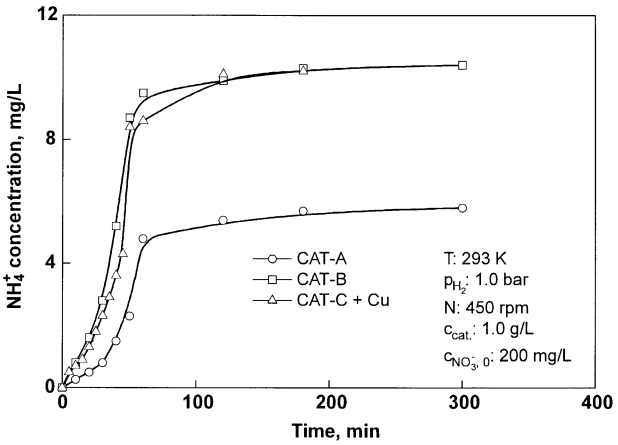

Fig. 6. Ammonium ion concentration vs. time dependencies obtained during the catalytic hydrogenation of aqueous nitrate solution over the CAT-A, CAT-B and (CAT-C + Cu) samples.

converted at the Pd–Cu sites nonselectively to ammonia [4]. However, it is obvious that during the in situ generation of Pd–Cu active sites (CAT-C + Cu), no Pd layer playing the same role as mentioned above is created, which leads to lower nitrogen formation (fig. 6). Since the behaviour of the CAT-B and (CAT-C + Cu) systems is almost identical also with respect to the maximum amounts of nitrites accumulated in the aqueous phase (fig. 5), it can be concluded that in the presence of CAT-B sample nitrate is reduced mainly on the surface of particles.

4. Conclusions

Auger electron spectroscopy was applied to measure palladium, copper, aluminium and oxygen concentration profiles on the CAT-A and CAT-B samples. The supported Pd–Cu bimetallic catalyst (CAT-A) with copper atoms mainly distributed in deeper layers below the surface was prepared by procedures in which alumina was impregnated first by copper salt. When the palladium salt was deposited first on the alumina support, higher concentration of metallic copper was attained on the surface of the bimetallic catalyst (CAT-B). The specific distribution of metallic copper and palladium in the CAT-A sample results in minimal formation of ammonium ions during the catalytic liquid-phase hydrogenation of aqueous nitrate solutions.

Acknowledgement

The authors wish to thank the Nikki-Universal Co., Ltd. (Tokyo, Japan), for their co-operation in catalyst preparation, as well as Dr. A. Zalar and Mr. B. Praček (Institute of Surface Engineering and Optoelectronics, Ljubljana) for AES measurements and valuable discussions.

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