

Amorphous alloy catalysis IX. Isomerization and hydrogenation of allyl alcohol over an amorphous copper–zirconium alloy

Tamás Martinek^a, Árpád Molnár^{a,*}, Tamás Katona^a, Mihály Bartók^{a,b},
Antal Lovas^c

^a Department of Organic Chemistry, Dóm tér 8, H-6720, Szeged, Hungary

^b Organic Catalysis Research Group of the Hungarian Academy of Sciences, József Attila University[†], Dóm tér 8, H-6720, Szeged, Hungary

^c Central Research Institute for Physics, Solid State Physics Department, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest 114, Hungary

Received 10 November 1995; accepted 4 June 1996

Abstract

The transformation of allyl alcohol was studied over an amorphous Cu₄₁Zr₅₉ alloy and, for comparison, on copper powder in the presence of hydrogen at 448–573 K. The amorphous Cu–Zr alloy precursor can be activated to exhibit high activity in the isomerization and hydrogenation of allyl alcohol to produce propanal and 1-propanol as major products. The activity of the as-received alloy increases and the selectivity changes with time on stream due to the rapidly increasing copper surface area. 1-Propanol formation is correlated with the number of Cu(0) surface sites.

Keywords: Isomerization; Hydrogenation; Allyl alcohol; Amorphous alloy; Copper–zirconium; Copper; Propanal; 1-propanol; Selectivity

1. Introduction

Zirconium-containing bimetallic amorphous alloys, especially Cu–Zr, have been extensively studied as catalyst precursors in the transformation of various compounds [1,2]. In most studies simple molecules such as CO [2–4], CO₂, [4–7], methane [8], alkenes and acetylenes [1,2] were chosen. Exceptions are dienes [9,10] and unsaturated carbonyl compounds [11]. In our early

work in this field, 2-propanol was used to study the structure and catalytic properties of copper-containing alloys [12–18]. Recently the main interest in amorphous alloy catalysis has been the structural changes induced by activation procedures and the chemical transformation itself. It can be expected, however, that the use of more complex molecules can provide additional information which are useful to more fully explore catalytically active surfaces.

Allyl alcohol and its substituted homologues can undergo isomerization, hydrogenation, dehydrogenation and deoxygenation. This complex pattern of transformations allows to gather valuable information about catalytic systems. Consequently, allylic alcohols are widely stud-

* Corresponding author. Tel.: +36-62-454277; fax: +36-62-312921; e-mail: amolnar@chem.u-szeged.hu.

[†] This is a part of the Center for Catalysis, Surface and Materials Science

ied in both homogeneous and heterogeneous catalytic processes (see, for example, [19,20] and [21–29], respectively). Additionally, copper seems to be an especially suitable catalyst since it can catalyze all possible transformations [21,22,25,26,28].

A study of allyl alcohol, therefore, was undertaken with the aim of testing the activity of an amorphous Cu–Zr amorphous alloy as catalyst. Copper powder was also studied to acquire information of the nature of the active sites by comparing the characteristics of the two catalyst preparations.

2. Experimental

1 by 5 mm pieces of a $\text{Cu}_{41}\text{Zr}_{59}$ ribbon produced by the melt quenching method under argon at a cooling wheel velocity of 6000 cm s^{-1} were used. Copper powder ($45 \mu\text{m}$, 99%, Janssen) was reduced before use at 573 K for 10 min. Zirconia powder (99.99%) was an Aldrich product. Allyl alcohol (Merck, 98%) was used without further purification. The hydrogen used was oxygen free prepared with a Matheson 8326 generator, operating with a palladium membrane.

The catalytic tests were carried out in a flow-type microreactor. The vapour of allyl alcohol was introduced through a saturator with

hydrogen as carrier gas (a total flow of 20 or 30 ml min^{-1}). The reaction products were subjected to GC analysis (Shimadzu 8A equipment, thermal conductivity detector, CWAX 20M column, 343 K, flow rate of hydrogen carrier gas = 25 ml min^{-1}). A detailed description of the experimental setup including an automatic sampling device is given in Ref. [30].

The Cu(0) surface area of the catalysts was measured by N_2O titration based on the reaction of nitrous oxide with Cu(0) species. The GC pulse method [31,32] was used (363 K, small sample size, large excess of N_2O). All surface measurements were carried out in situ without exposing the samples to air (see, however, Table 1). BET surfaces (multipoint method) were determined using nitrogen adsorption at 77 K (Micromeritics Gemini 2375 equipment).

Catalysts were further characterized by differential scanning calorimetry (Perkin Elmer DSC-2 equipment) and by X-ray diffraction analyses (DRON-3 equipment, Cu $\text{K}\alpha$ radiation).

3. Results and discussion

Over the amorphous Cu–Zr alloy allyl alcohol yields two major products, propanal and 1-propanol (Fig. 1). Minor amounts of propene and, occasionally, acrolein were also detected.

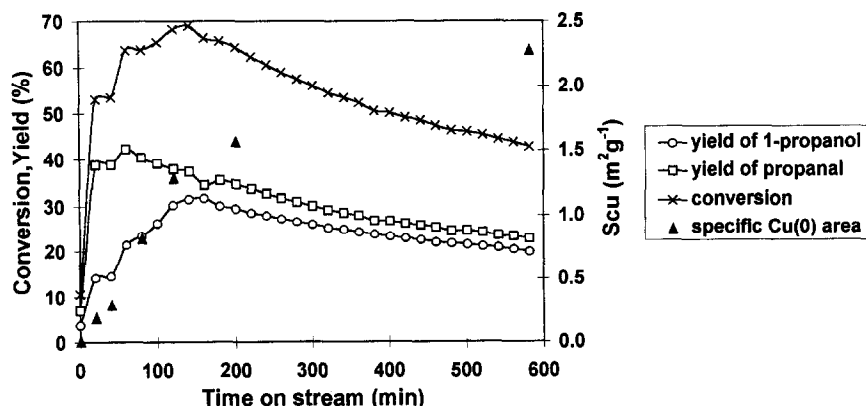


Fig. 1. Changes in the selectivity and copper surface area of Cu–Zr in the transformation of allyl alcohol (catalytic measurement was carried out on 3.4 mg of catalyst; Cu(0) surface areas were measured with a 150-mg sample; reaction temperature: 573 K; flow rate: 20 ml min^{-1}).

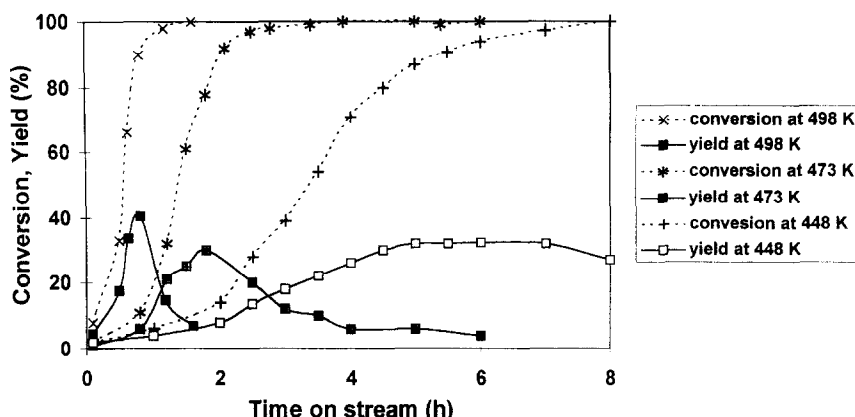


Fig. 2. Changes in catalytic activity and propanal yield in the transformation of allyl alcohol on an amorphous Cu–Zr alloy sample at different temperatures (200 mg catalyst; conversion = yield of propanal + yield of propanol; flow rate: 30 ml min⁻¹).

The as-received Cu–Zr alloy exhibited the usual behaviour observed earlier in the dehydrogenation of 2-propanol [12–14]. This includes the continuous in situ activation manifested in increasing conversion on time on stream and the concomitant marked increase of copper surface area (Fig. 1). In addition, during the transformation of allyl alcohol the selectivity of the two products also changed. The rate of in situ catalyst activation and selectivities strongly depend on temperature and catalyst quantity (Fig. 2 and Fig. 3). At 498 K, for example, on a large amount of catalyst (200 mg) selective formation of 1-propanol takes place after about two hours on stream (Fig. 2). On the other hand, selective

formation of propanal can be achieved on a smaller amount of catalyst (50 mg) at 473 K in the initial period of a 25-h catalytic test (Fig. 3).

Activity data determined over Cu–Zr and, for comparison, on Cu powder are given in Fig. 4. After an initial transient period observed on Cu–Zr, both catalysts exhibit similar activities and a slight deactivation.

By searching for possibilities to reactivate the spent catalysts oxidation–reduction treatments were found to be effective. In a systematic study significant increases in activity of Cu–Zr after successive treatments (oxidation at reaction temperature for 1 h followed by a 5-min reduction at 573 K) were observed (Fig. 5). The

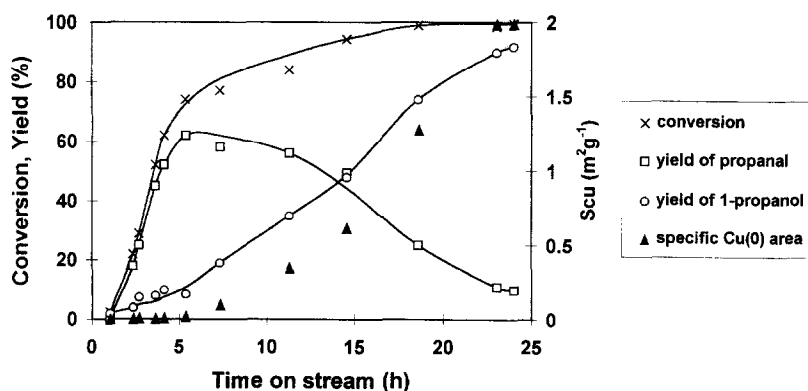


Fig. 3. Changes in catalytic activity, product yields and copper surface area in the transformation of allyl alcohol on an amorphous Cu–Zr alloy sample (50 mg catalyst, reaction temperature: 473 K; flow rate: 30 ml min⁻¹).

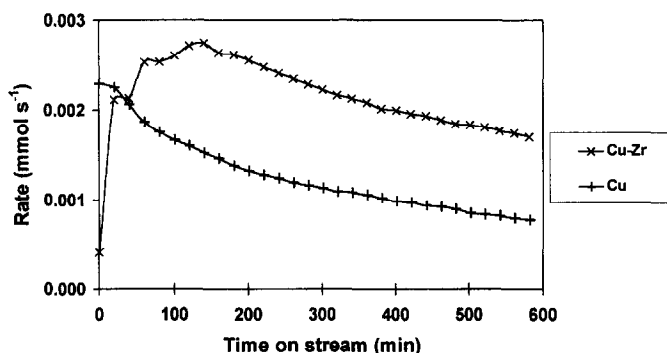


Fig. 4. Changes in catalytic activities in the transformation of allyl alcohol (catalyst quantities are 3.4 mg for Cu–Zr and 20 mg for Cu both corresponding to about 50 cm² Cu(0) surface; reaction temperature: 573 K; flow rate: 20 ml min⁻¹).

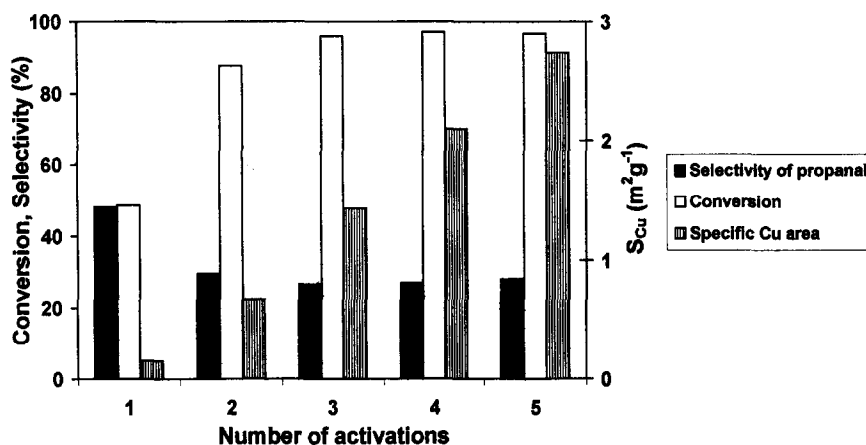


Fig. 5. Changes in the activity and selectivity of Cu–Zr in the transformation of allyl alcohol at 473 K as a result of oxidative and reductive treatments (5 mg catalyst, air oxidation at 573 K for 1 h followed by reduction at 573 K for 5 min. Activities were determined at 5 min-on-stream; flow rate: 20 ml min⁻¹).

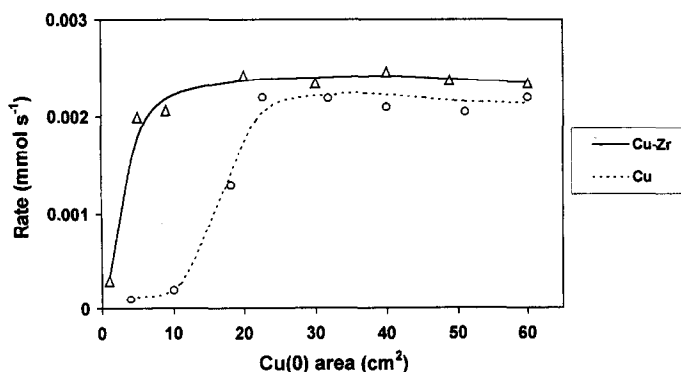


Fig. 6. Reaction rates as a function of copper surface area (Cu: fresh catalyst samples with weights corresponding to the Cu(0) values indicated were used to determine each experimental point; Cu–Zr: data were calculated from experimental data in Fig. 1. Reaction temperature: 573 K; flow rate: 20 ml min⁻¹).

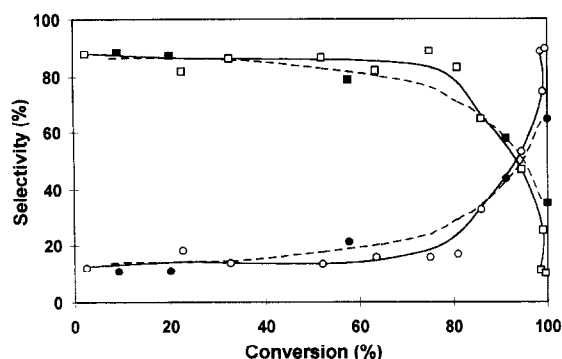


Fig. 7. Selectivities as a function of conversion (reaction temperature: 573 K). Cu (shaded symbols and broken lines): initial selectivities determined over 1.3, 2.2, 20.0, 98.0 and 220.0 mg Cu powder; Cu–Zr (open symbols and solid lines): data from Fig. 3. Squares: propanal, circles: 1-propanol.

changes in activity and selectivity (increasing catalytic activity and decreasing propanal selectivity) and in surface area (increasing concentration of surface Cu(0)) are very similar to those occurring during in situ activation. In other words the formation of the catalytically active surface could also be achieved by oxidation–reduction sequences.

When catalytic activities are plotted against copper surface areas a marked increase is observed in the low surface area region on Cu powder (Fig. 6). (The shape of the curve may be due to some poisoning effect caused by products formed in the condensation of propanal and the oligomerization of acrolein.) This is due to the high feeding rate relative to the number of available surface active sites. This change is

even more pronounced on Cu–Zr. The difference in the behaviour of the two catalysts may be attributed to the presence of different types of active sites in the early stages of the transformation on Cu–Zr. Saturation type curves are observed at higher surface areas with slight changes in activities at very high surfaces. Diffusion control with almost complete conversion is characteristic in this region. The two catalysts exhibit similar activities which is indicative of the involvement of similar active sites.

Selectivities determined on the two catalysts are plotted against conversion in Fig. 7. When selectivities at identical conversion are compared the two catalyst samples show very similar behaviour.

It is known from earlier studies that amorphous Cu–Zr alloys undergo substantial structural changes when applied in catalytic transformations. It was shown that hydrogen plays a crucial role in such in situ activations [1,2,10,14,15,33,34]. By penetrating into the bulk hydrogen brings about copper segregation to the surface, changes in surface morphology, and eventually bulk crystallization.

Similar observations were made in the present study. Fig. 8 displays the changes in the Cu(0) surface area as a function of time-on-stream at various temperatures. On the basis of these data it is not surprising to observe the changes in activity and selectivity in the transformation of allyl alcohol over the Cu–Zr samples. The marked increase in overall activity in

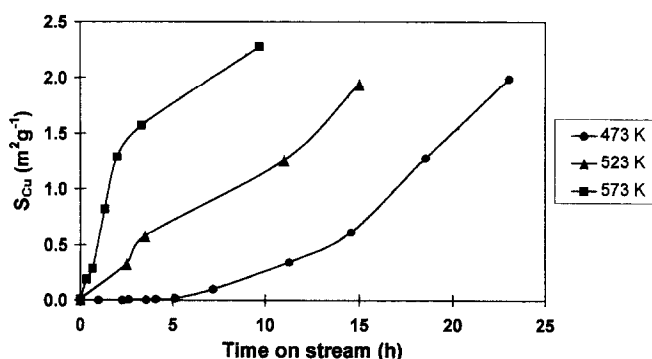


Fig. 8. Changes in Cu(0) surface areas as a function of time-on-stream at various temperatures.

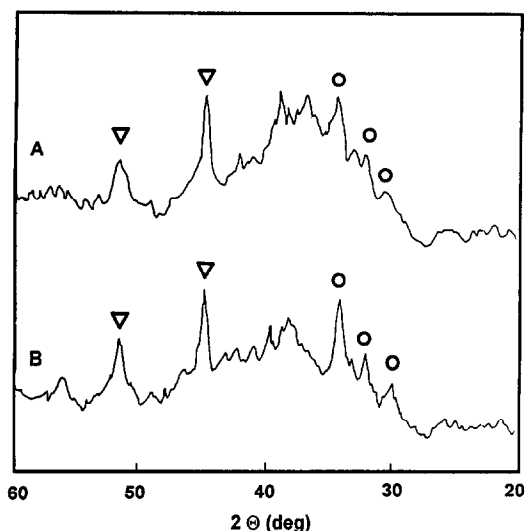


Fig. 9. XRD diffractograms of Cu–Zr samples; (A) after 2.5 h reaction, (B) after 24 h reaction; reaction temperature: 573 K; flow rate: 20 ml min⁻¹; sample size: 1 g. ▽: Cu, ○: ZrO₂.

the early stages of the reaction (first few hours at 573 K) is attributed to the rapidly developing new copper surface.

The results of structural characterization provide additional information on the transformation of the amorphous precursor into an active catalyst. X-Ray diffractograms (Fig. 9) show the partial crystallization and oxidation of the samples (appearance of peaks attributed to metallic

copper and ZrO₂). It is also seen, however, that amorphous phase (a broad band centred at about 40°) is still present after 24-h reaction, although in a diminishing amount. The corresponding DSC curves (Fig. 10), interestingly, do not show the presence of the amorphous structure (the exothermic peaks seen in the scan of as-received alloy). Instead, the used samples exhibit a broad endothermic peak which can be due to solid state transformations.

These data clearly show that the alloy is still in the transient state after 24 h-on-stream, i.e., the generation of the active surface still continues afterwards. In fact, further increases in Cu(0) surface areas were detected even after prolonged reactions (Table 1). BET surface areas of the samples show a trend similar to that observed for the changes in Cu(0) surface area, although BET surfaces are always higher. It is also seen that oxidative–reductive treatments can induce similar structural changes as in situ activation under reaction conditions. The spectacularly high BET surface of the oxidized sample resulting from the accelerated formation of zirconia is especially noteworthy (Table 1). Note, however, that neither the Cu(0) value nor the corresponding catalytic activity (Fig. 5) is exceptional, indicating that oxidation itself is

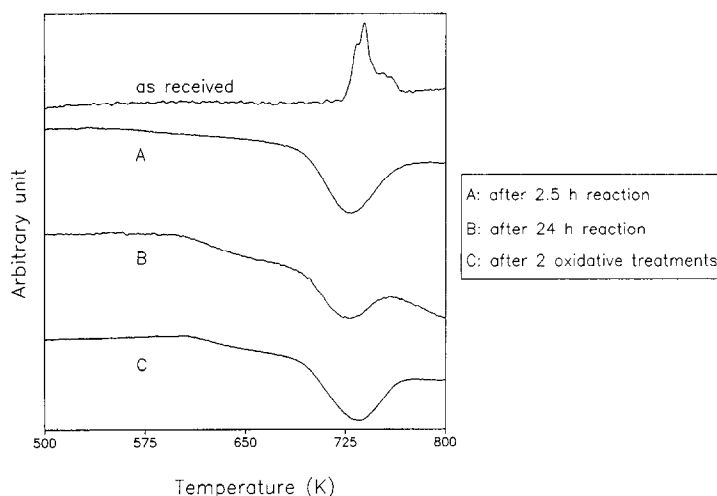


Fig. 10. DSC scans of Cu–Zr samples; (A) and (B) same as in Fig. 9, (C) after 2 oxidations and reductions; for reaction conditions see Fig. 5. Sample size: 5 mg, heating rate: 20 K min⁻¹.

Table 1

Results of surface area measurements of Cu–Zr alloy after various pretreatments (573 K, 20 ml min⁻¹ flow rate)

Reaction time	BET surface area (m ² g ⁻¹)	Cu(0) surface area (m ² g ⁻¹) ^a
2.5 h	0.48 ^b	0.27 ^b
24 h	1.62 ^b	0.47 ^b / 2.77 ^c
48 h	nd	3.04 ^c
96 h	nd	3.55 ^c
2 sequences of oxidation + reduction ^d	10.27 ^b	1.15 ^c

^a After exposed to air samples were reduced with flowing hydrogen (20 ml min⁻¹) at 573 K for 0.5 h before measurement.^b A sample of 1 g was used.^c A sample of 50 mg was used.^d For reaction conditions see Fig. 5.

nd: not determined.

not effective to increase the surface concentration of copper. The amorphous precursor eventually is transformed into an active catalyst containing reduced copper as the active site embedded into a zirconia matrix. It is very important to point out, however, that zirconia itself did not exhibit any catalytic activity under the experimental conditions used (573 K, 20 ml min⁻¹ flow rate).

The possible reaction routes to transform allyl alcohol to propanal and 1-propanol (Scheme 1) indicate a complicated reaction scheme. It is known that copper is able to catalyze the formation of propanal (a net isomerization process) via a hydrogen transfer from allyl alcohol to acrolein formed initially in a small amount [21]. Direct hydrogenation of acrolein is also possible. This was observed to be the case over clean and oxygen-covered Cu(110) [25] and on Cu₂O(100) [27]. Allyl alcohol was also shown to react with the former surfaces to yield 1-propanol [25]. A direct hydrogenation was sug-

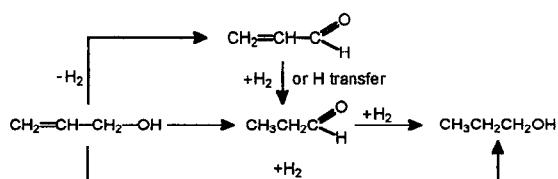
gested facilitated by the hydroxyl group by tethering the carbon–carbon double bond to the surface.

In our system the continuously increasing activity in 1-propanol formation is correlated with surface Cu(0) atoms formed during the in situ activation of the Cu–Zr alloy. The maximum curve for propanal formation, on the other hand, may indicate that oxidized copper species are also involved in isomerization. Since the generation of Cu(0) sites were shown to require long reaction time, in the initial stages of the transformation propanal may be formed on such sites.

The two catalysts exhibit very similar changes in selectivity at high conversion (Fig. 7) which can be indicative of a change in the relative contribution of the different reaction routes to 1-propanol formation. Direct hydrogenation of the starting allyl alcohol and that of propanal intermediate may accelerate substantially with increasing conversion, which, in turn, is brought about by the high number of surface active sites. All these changes are due to the rapidly increasing number of Cu(0) sites available for hydrogen addition (Cu–Zr) or the large quantity of catalyst used to achieve high conversion (Cu powder).

Acknowledgements

Financial supports to this work by the Hungarian National Science Foundation (Grants OTKA T4311 and T014315) and by the Foundation for Hungarian Higher Education and Research (Grant 477/94) are gratefully acknowledged.



Scheme 1. Possible reaction routes in the transformation of allyl alcohol to 1-propanol.

References

- [1] Á. Molnár, G.V. Smith and M. Bartók, *Adv. Catal.* 36 (1989) 329.
- [2] A. Baiker, in eds. H. Beck and H.-J. Güntherodt, *Metallic Glasses III* (Springer-Verlag, Berlin, 1993) p. 121; *Faraday Discuss. Chem. Soc.* 87 (1989) 239.
- [3] A. Baiker, M. Maciejewski and S. Tagliaferri, *Ber. Bunsenges. Phys. Chem.* 97 (1993) 286.
- [4] M. Maciejewski and A. Baiker, *J. Phys. Chem.* 98 (1994) 285.
- [5] C. Schild, A. Wokaun and A. Baiker, *Fresenius' J. Anal. Chem.* 341 (1991) 395.
- [6] R.A. Koeppel, A. Baiker, Ch. Schild and A. Wokaun, *J. Chem. Soc., Faraday Trans.* 87 (1991) 2821.
- [7] Ch. Schild, A. Wokaun and A. Baiker, *Surf. Sci.* 269–270 (1992) 520.
- [8] P.E. Marti, M. Maciejewski and A. Baiker, *J. Catal.* 139 (1993) 494.
- [9] H. Yamashita, M. Yoshikawa, T. Kaminade, T. Funabiki and S. Yoshida, *J. Chem. Soc., Faraday Trans.* 1 82 (1986) 707.
- [10] A. Baiker, H. Baris, M. Erbudak and F. Vanini, In: eds. M.J. Phillips and M. Ternan, *Proc. 9th Int. Congr. Catal.*, Calgary, 1988, Vol. 4 (The Chemical Society of Canada, Ottawa, 1988) p. 1928.
- [11] M. Shibata, N. Kawata, T. Masumoto and H. Kimura, *J. Chem. Soc., Chem. Commun.* (1988) 154.
- [12] T. Katona, Z. Hegedűs, Cs. Kopasz, Á. Molnár and M. Bartók, *Catal. Lett.* 5 (1990) 361.
- [13] Á. Molnár, T. Katona, M. Bartók and K. Varga, *J. Mol. Catal.* 64 (1991) 41.
- [14] Á. Molnár, T. Katona, M. Bartók, I.V. Perczel, Z. Hegedűs and Cs. Kopasz, *Mater. Sci. Eng. A* 134 (1991) 1083.
- [15] Á. Molnár, T. Katona, M. Bartók, I.V. Perczel, Cs. Kopasz and Z. Hegedűs, *Surf. Interf. Anal.* 19 (1992) 519.
- [16] Á. Molnár, T. Katona, Cs. Kopasz and Z. Hegedűs, In: eds. L. Guczi, F. Solymosi and P. Tétényi, *New Frontiers in Catalysis, Proc. 10th Int. Congr. Catal.*, Budapest, 1992 (Akadémiai Kiadó, Budapest, 1993) p. 1759.
- [17] T. Katona, Á. Molnár and M. Bartók, *Mater. Sci. Eng.* A181–182 (1994) 1095.
- [18] T. Katona and Á. Molnár, *J. Catal.* 153 (1995) 333.
- [19] K. Felföldi and M. Bartók, *J. Organomet. Chem.* 297 (1985) C37.
- [20] S.H. Bergens and B. Bosnich, *J. Am. Chem. Soc.* 113 (1991) 958.
- [21] G. Eadon and M.Y. Shiekh, *J. Am. Chem. Soc.* 96 (1974) 2288.
- [22] M. Bartók and I. Török, *Acta Chim. Acad. Sci. Hung.* 88 (1976) 35.
- [23] J.V.N. Vara Prasad, A.G. Samuelson and C.N. Pillai, *J. Catal.* 75 (1982) 1.
- [24] J.V.N. Vara Prasad and C.N. Pillai, *J. Catal.* 88 (1984) 418.
- [25] R.L. Brainard, C.G. Peterson and R.J. Madix, *J. Am. Chem. Soc.* 111 (1989) 4553.
- [26] R. Hubaut and J.P. Bonnelle, *React. Kinet. Catal. Lett.* 47 (1992) 73.
- [27] K.H. Schulz and D.F. Cox, *J. Phys. Chem.* 97 (1993) 647.
- [28] B. Kozma, Á. Molnár and M. Bartók, *React. Kinet. Catal. Lett.* 51 (1993) 61.
- [29] R. Shekhar and M.A. Barteau, *Surf. Sci.* 319 (1994) 298.
- [30] L. Domokos, T. Katona, Á. Molnár and A. Lovas, *Appl. Catal. A*, in press.
- [31] J.W. Evans, M.S. Wainwright, A.J. Bridgewater and D.J. Young, *Appl. Catal.* 7 (1983) 75.
- [32] B. Denise, R.P.A. Sneeden, B. Beguin and O. Cherifi, *Appl. Catal.* 30 (1987) 353.
- [33] F. Vanini, St. Büchler, X. Yu, M. Erbudak, L. Schlapbach and A. Baiker, *Surf. Sci.* 189–190 (1987) 1117.
- [34] F. Vanini, M. Erbudak, G. Kostorz and A. Baiker, In: *Mater. Res. Soc. Symp. Proc. (Microstruct. Prep. Catal.)* 111 (1988) 375.