Novel Hydrogenation Catalyst Prepared From an Amorphous $Cu_{70}Zr_{30}$ Precursor

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Thermal pretreatment of an amorphous $Cu_{70}Zr_{30}$ alloy in a hydrogen atmosphere results in a catalyst which contains small copper particles embedded in a zirconium oxide matrix and exhibits an activity which is about an order of magnitude higher for selective hydrogenation of buta-1,3-diene to butenes than polycrystalline copper.

It is only relatively recently that amorphous alloys prepared by rapid quenching techniques[1] were first used as catalyst materials.[2] Since then growing attention has been paid to the investigation of the intrinsic catalytic properties of such materials.[3] More recently, the potential of amorphous metal alloys as catalyst precursors has been pointed out.[4] It was found that the catalytic properties of amorphous alloys can be significantly improved by pretreatment procedures which improve the chemical and textural properties of the surface of the precursor materials. Here we report the transformation of an amorphous $Cu_{70}Zr_{30}$ precursor to a very active catalyst for the hydrogenation of buta-1,3-diene to butenes.

The amorphous and crystalline $Cu_{70}Zr_{30}$ ribbons used were prepared from the pre-mixed melt of the pure metals by means of the melt spinning technique.[1] Auger electron spectroscopy (A.E.S.) and ion scattering spectroscopy (I.S.S.) indicated that the surface and subsurface region of as-prepared ribbons contained mainly zirconium oxide and comparatively little metallic copper. The 5 mm wide and 20—30 µm thick ribbons were cut into clippings of about 1.5 cm length for use in the catalytic tests. The Brunauer–Emmett–Teller (B.E.T.) surface areas as measured by krypton adsorption at 77 K were $0.015 \pm 0.003\ m^2/g$ for both the amorphous and the crystalline materials. Thermal pretreatment of the amorphous and crystalline precursor alloys in hydrogen and subsequent hydrogenation of butadiene were carried out in a closed loop tubular reactor at 180 kPa total pressure. The apparatus has been described in detail elsewhere.[5] The product gas mixture was analysed by gas chromatography using a 9 m long column (5 mm i.d.) of benzyl cyanide and silver nitrate on Chromosorb P. Reactant gases, hydrogen (99.999%) and butadiene (99.5%), were taken from commercial cylinders without further purification.

The active catalysts were prepared by annealing the amorphous and the crystalline precursor alloys during 16 h at 473 K in flowing hydrogen. Changes in the bulk and surface properties during annealing were analysed by *X*-ray diffraction (X.R.D.), differential scanning calorimetry (D.S.C.), A.E.S., I.S.S., scanning electron microscopy (S.E.M.), and B.E.T. surface area measurements.

Figure 1 depicts bulk and surface changes of the amorphous precursor during annealing in hydrogen. A comparison of the *X*-ray patterns and the I.S.S. and A.E.S. results obtained for the amorphous precursor before and after annealing in hydrogen indicated the formation of large crystalline and small disordered copper particles which were embedded in an amorphous matrix of zirconium oxides. Partial transformation of the amorphous precursor into the crystalline state was confirmed by D.S.C. measurements, which showed that the specific heat released upon crystallization of the pretreated sample was 85—90% of that measured for the original amorphous precursor. Depth concentration profiles measured by A.E.S. and I.S.S. revealed that with the amorphous precursor, copper segregates onto the surface during the

Table 1. Activities for buta-1,3-diene hydrogenation of catalysts obtained by thermal pretreatment of amorphous and crystalline $Cu_{70}Zr_{30}$ precursors and polycrystalline copper foil. Conditions: 403 K; total surface area of catalyst in reactor, $0.066 \pm 0.003\ m^2/g$; total pressure, 180 kPa; partial pressure ratio butadiene/hydrogen = 1.

Precursor	Initial butadiene hydrogenation rate (µmol/m²s)	But-1-ene/ but-2-ene	*trans*-But-2-ene/*cis*-but-2-ene
$Cu_{70}Zr_{30}$ (amorph.)	29.9	0.8—1.6[a]	0.4—0.6[a]
$Cu_{70}Zr_{30}$ (cryst.)	3.2	4.0—7.0	0.6—0.8
Cu (foil)	3.3	4.0—6.0	0.6—0.8

[a] Depending on conversion.

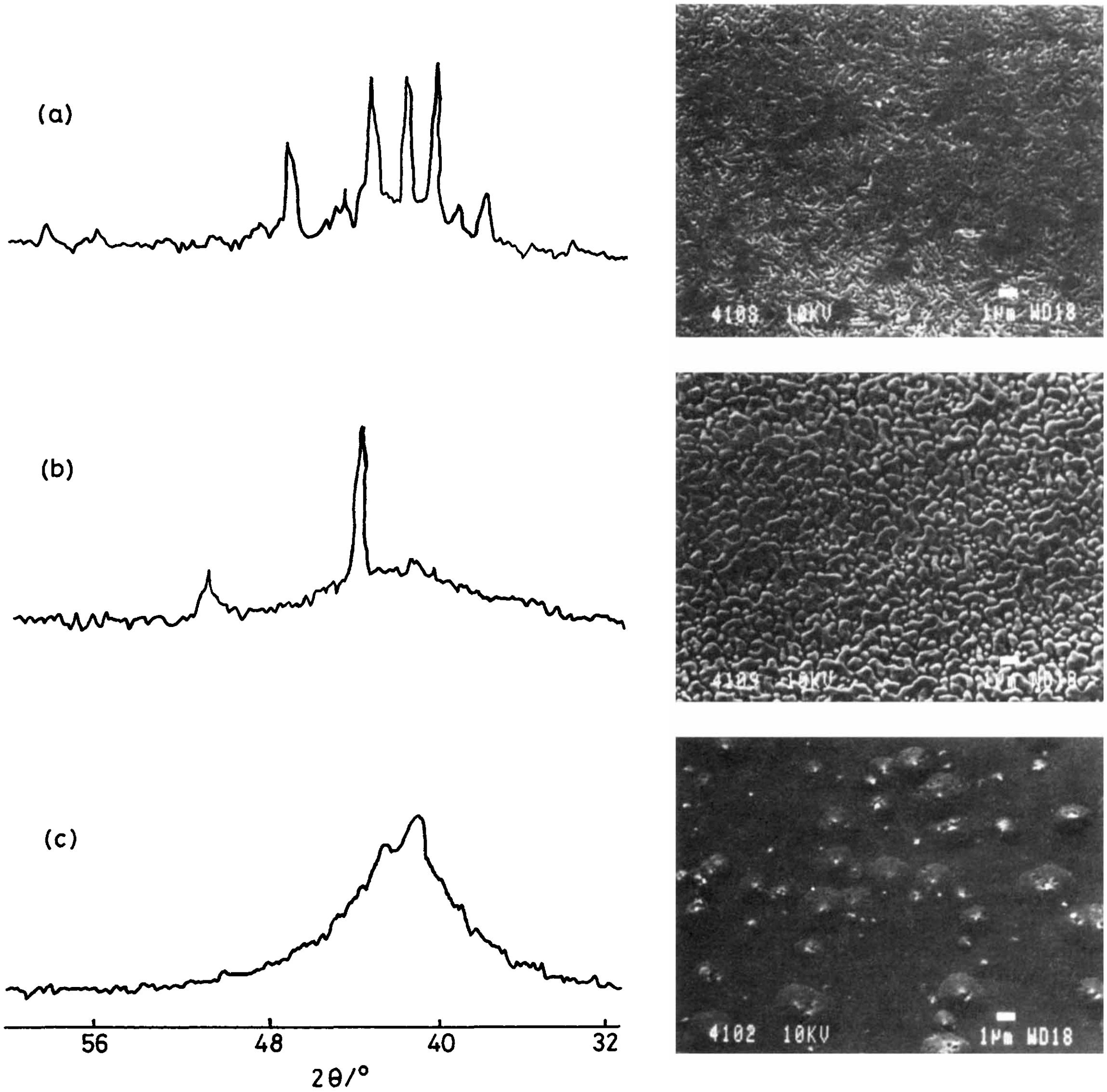

Figure 1. Changes of bulk structure (X.R.D., Cu-K_α) and surface morphology (S.E.M.) of Cu–Zr precursors upon thermal pretreatment in hydrogen. (a) Crystalline precursor; (b) active catalyst; (c) amorphous precursor. Note the formation of crystalline copper particles during pretreatment of the amorphous precursor. *X*-Ray patterns of the crystalline precursor show the presence of $Cu_{10}Zr_7$ and an unidentified phase. The crystalline precursor did not exhibit significant changes of the bulk structure upon pretreatment and therefore only results of the original sample are shown.

thermal pretreatment in hydrogen. As a result of this segregation, the B.E.T. surface area increased almost 40 times, from 0.015 (amorphous precursor) to 0.56 m^2/g. In contrast, the crystalline precursor did not exhibit significant changes in the bulk structure during the pretreatment. This is indicated by the fact that *X*-ray patterns of the crystalline sample did not change significantly during the pretreatment. Furthermore, no comparable segregation of copper onto the surface and no significant increase in the surface area could be observed with the crystalline precursor upon pretreatment in hydrogen.

Butadiene hydrogenation activities and product distributions of the catalysts obtained from the amorphous and crystalline Cu–Zr precursors are compared with the corresponding values measured for a polycrystalline copper foil in Table 1. The initial butadiene hydrogenation rate of the catalyst prepared from the amorphous precursor was about an order of magnitude higher than corresponding rates obtained with the crystalline Cu–Zr precursor and the polycrystalline copper foil. With all catalysts no n-butane was formed under the adopted conditions during the first stage of the reaction. The catalyst obtained from the crystalline precursor and the copper foil exhibited roughly similar activity and butene distribution. The butene distribution patterns for the two catalysts resemble those found by Phillipson *et al.*[6] (their 'type A'). This is not the case for the butene distribution measured for the catalyst prepared from the amorphous precursor, which shows a considerably lower value for the but-1-ene/but-2-ene ratio. Also the *trans*/*cis* ratio of the but-2-ene formed was slightly lower for this catalyst. Generally it did not depend significantly on temperature in the range 80—140 °C.

Our results demonstrate the potential of amorphous metal alloys as precursors for catalyst preparation. Thermally and chemically induced segregation processes can be applied to prepare highly active catalysts from such metastable precursors. Further work towards better understanding of these segregation processes should provide the means for 'tailoring' these novel catalysts.

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