A Highly Active Catalyst for the Oxidation of Carbon Monoxide, Prepared from Amorphous Palladium–Zirconium Alloy

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In situ activation of an amorphous Pd_1Zr_2 alloy leads to a zirconia-supported palladium catalyst which exhibits more than one order of magnitude higher activity for carbon monoxide oxidation than a similar catalyst prepared by impregnation of zirconia with a palladium salt.

Amorphous metal alloys have raised considerable interest as new materials in catalysis research.[1] More recently, their potential as catalyst precursors has been demonstrated. Supported metal catalysts have been prepared by pretreatment or *in situ* activation from amorphous metal alloys.[2—5] Thereby one or more components of the amorphous alloy were transformed to the corresponding oxides which then acted as a support and stabilized the dispersed metal particles. As-prepared catalysts have so far been applied predominantly for reactions carried out under reducing conditions, such as the hydrogenation of CO[2] and alkenes,[4] and ammonia synthesis.[5] Here we report the successful application of an amorphous Pd_1Zr_2 alloy for preparation of a highly active catalyst for carbon monoxide oxidation.

The amorphous Pd_1Zr_2 used as catalyst precursor was prepared from the pre-mixed melt of the pure metals by rapid quenching using the technique of melt spinning. For use in the catalytic tests, the 5 mm wide and 20—30 μm thick ribbons fabricated by the melt spinning were ground to flakes of 0.1—1 mm size under liquid nitrogen. The Brunauer–Emmett–Teller (B.E.T.) surface area of this material, as measured by krypton adsorption at 77 K, amounted to 0.031 $m^2\ g^{-1}$. *X*-ray diffraction indicated that the ground material was still completely amorphous (Figure 1).

A conventionally prepared zirconia supported palladium catalyst was used as a reference. The catalyst, containing 1 wt. % of palladium, was prepared by impregnation of ZrO_2 made up of 20—25 nm particles of crystalline baddeleyite. The impregnation was carried out with an aqueous solution of $(NH_4)_2PdCl_4$ using the incipient wetness technique. Subsequent to drying for 12 h at 120 °C, the precursor was calcined and reduced under a flowing hydrogen–nitrogen mixture ($H_2 : N_2 = 10 : 1$) for 15 h at 200 °C, 1 h at 300 °C, and finally 1 h at 400 °C.

The amorphous Pd_1Zr_2 alloy, as well as the catalysts prepared from it and the reference catalyst, were investigated with regard to their physical and chemical properties using gas adsorption (N_2, CO, and krypton), *X*-ray diffraction (XRD),

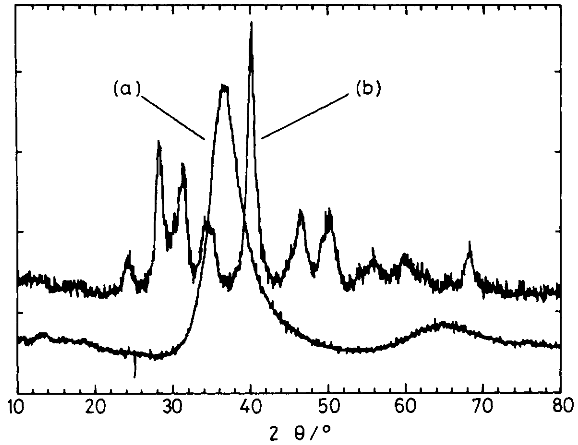

Figure 1. X-Ray diffraction patterns (Cu-K_α) of (a) the amorphous Pd_1Zr_2 precursor and (b) the active catalyst (Pd supported on zirconia) prepared from it.

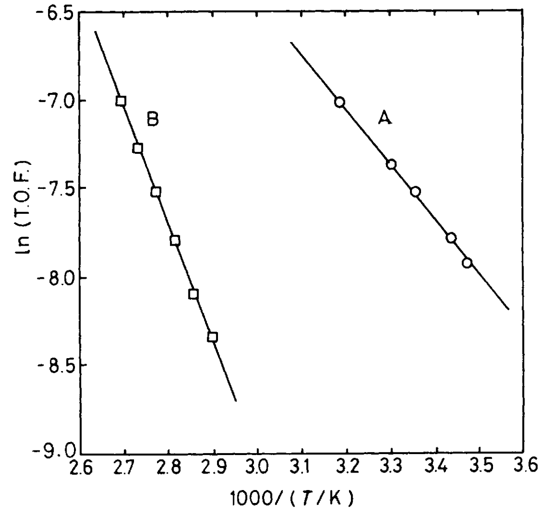

Figure 2. Arrhenius plots of CO oxidation rates (turnover frequencies, T.O.F.) of zirconia supported palladium catalysts. (A) Catalyst prepared by *in situ* activation of amorphous Pd_1Zr_2. (B) Catalyst prepared by impregnation of zirconia with palladium salt.

differential thermal analysis (DTA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Catalytic CO oxidation tests were performed in a continuous tubular glass reactor in the temperature range 300—500 K under atmospheric pressure. The kinetic runs were carried out using a reactant feed of 150 ml (s.t.p.) min^{-1} which contained a mixture of 1700 p.p.m. of CO, and 1700 p.p.m. of O_2 in nitrogen. Two continuous i.r. analysers were used to measure the concentration of CO and CO_2 at the reactor inlet and outlet, respectively. The precursor alloy was activated under reaction conditions at 550 K. The activities of the two differently prepared $Pd–ZrO_2$ catalysts are compared on the basis of the measured turnover frequencies (T.O.F.) which are defined as molecules of CO converted per surface atom of palladium and per second. The number of palladium atoms accessible for the reactants was determined for both catalysts by CO chemisorption at 300 K. Reported rates are steady-state values.

Figure 1 depicts the bulk structural changes that the amorphous Pd_1Zr_2 precursor undergoes during *in situ* activation at 550 K. Under these conditions, the amorphous precursor crystallizes and zirconium is oxidized to ZrO_2 adopting predominantly the structure of baddeleyite. These processes resulted in a marked increase of the B.E.T. surface area from 0.031 (precursor) to 45.9 $m^2\ g^{-1}$ (active catalyst). The metal surface area (palladium) of the active catalyst, as measured by CO adsorption, was 6.9 $m^2\ g^{-1}$, corresponding to a metal dispersion of 6%. The corresponding properties measured for the conventionally prepared reference catalyst were: B.E.T. surface area, 45.5 $m^2\ g^{-1}$; metal surface area, 0.52 $m^2\ g^{-1}$; and metal dispersion, 11.6%.

The kinetic results of the CO oxidation performed on the catalysts are presented as Arrhenius plots in Figure 2. We note the markedly higher turnover frequencies measured for the catalyst prepared from the amorphous metal alloy precursor. The higher activity of this catalyst results from a significantly lower activation energy (26.2 ± 0.6 as compared to 54.9 ± 0.9 kJ mol^{-1} of the conventionally prepared catalyst). It is important to note that the pure support material (ZrO_2) did not exhibit significant activity for CO oxidation under the experimental conditions used. Transmission electron microscopy and X-ray diffraction revealed that the catalyst prepared from the amorphous alloy was made up of small disordered and larger crystalline palladium particles of *ca.* 8 nm mean size. These palladium particles were embedded in the zirconia matrix containing small disordered particles as well as larger crystalline particles (6—10 nm) adopting the structure of baddeleyite.

The catalyst prepared by impregnation consisted of crystalline palladium particles of *ca.* 8 nm mean size supported on crystalline zirconia particles (baddeleyite) of *ca.* 23 nm size. Thus the two catalyst preparations differed markedly in their morphology.

The oxidation of carbon monoxide over palladium was shown to be structure-insensitive in several investigations.[6] Our investigation indicates that the intrinsic activity of zirconia supported palladium prepared from an amorphous Pd_1Zr_2 alloy is markedly higher than the one of zirconia supported palladium prepared by impregnation. Further work will be necessary to determine the reason for the higher activity of the zirconia supported palladium particles prepared from the amorphous metal alloy precursor, and this is being investigated.

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