Catalysis Letters 5 (1990) 67–72

PARTIAL HYDROGENATION OF PHENYLACETYLENE ON COPPER-PROMOTED IRON CATALYST

Yuriko NITTA, Shin MATSUGI and Toshinobu IMANAKA

Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received 6 November 1989; accepted 16 March 1990

Phenylacetylene, partial hydrogenation, iron catalyst

Coprecipitation of a proper amount of copper(II) sulfate with iron(III) sulfate on ultrafine silica gel by using an excess Na_2CO_3 resulted in a Fe-Cu/SiO_2 catalyst with remarkably enhanced activity and selectivity for partial hydrogenation of phenylacetylene. The efficient elimination of water formed during the reduction of precursors much improved the activity.

1. Introduction

Iron catalysts are known to have high selectivity, but extremely low activity, for the partial hydrogenation of alkynes to alkenes [1–5]. Recently we have reported that, in the preparation of Fe/SiO_2 catalysts, the use of ferric sulfate, ultrafine silica gel (UFP-SiO_2), and an excess Na_2CO_3 results in an active and selective catalyst for the hydrogenation of phenylacetylene to styrene, and that the selectivity for styrene increases with increasing dispersion of Fe metal in the catalysts [6]. In order to increase the dispersion of iron, and hence the selectivity as well as the activity of the catalyst, coprecipitation of different metals seems promising. In the present study, we examined the effects of various metals added to the precursor of the most active Fe/SiO_2 catalyst on the hydrogenation of phenylacetylene under mild conditions. It has been found that the addition of proper amount of copper leads to remarkable increases in the activity and selectivity of the resulting catalysts. The effects of reduction conditions of the precursor have also been studied.

2. Experimental

Catalyst precursors were prepared by a precipitation method as follows: A solution (25 ml) of an excess Na_2CO_3 (1.5–1.6 molar equivalent) in hot water was added to an aqueous suspension (150 ml) of ultrafine silica gel (UFP-SiO_2;

Nippon Aerosil, Aerosil-300, 320 m^2g^{-1}), iron(III) sulfate and the sulfate of another metal (total amount = ca. 18 mmol) at 75 °C with vigorous stirring and aged for 15 min, followed by washing three times with hot water and drying at 110 °C for 20 h. The detailed procedures are identical to those described for the preparation of silica-supported basic nickel carbonate [7]. The reduction of a dried precursor (1 g) to give a Fe-M/SiO$_2$ catalyst (metal loading = ca. 50%) was carried out by heating in flowing hydrogen (8 lh^{-1}) to 500 °C at a temperature ramp of 10 °C min^{-1} and holding at this temperature for 1 h unless otherwise noted. The Raney-Fe catalyst was prepared for comparison from the 50 wt% Fe-Al alloy by leaching with 20% solution of NaOH at 70 °C for 0.5 h.

The hydrogenation of phenylacetylene (0.6 mmol) was carried out in ethanol (27 ml) at 60 °C under 1.0 MPa of hydrogen by using a glass autoclave (TEM-U-50, Taiatsu Glass Industry Co.) equipped with a vigorous stirring system. Powder X-ray diffraction (XRD) patterns of the catalyst separated from the reaction mixture were measured using a Shimadzu VD-1 diffractometer with CuKα radiation. The mean crystalline size (D_c) of iron in a catalyst was calculated from the half-maximum breadth of the (110) peak of α-Fe metal after correction for instrumental broadening [8]. The initial hydrogenation rates (R_0) and styrene selectivities at 50% conversion (S_{50}) were obtained from the GLC data of the reaction products at different times.

3. Results and discussion

Effects of coprecipitation of various metal sulfates were examined for partial hydrogenation of phenylacetylene. The properties of the resultant catalysts are shown in table 1. Addition of nickel enhanced the activity but slightly lowered the selectivity probably because nickel catalysts have higher activity and lower selectivity than iron catalysts [5]. Although the smaller D_c of the Ni-promoted catalyst could also explain the higher activity, it cannot account for the lower selectivity of the catalyst; the selectivity for styrene increases with increasing dispersion of Fe metal in the catalysts [6]. The addition of cobalt had negligible effects, while La, Mn, Mg, and Zn much lowered both activity and selectivity in harmony with the decrease in the dispersion of iron. On the other hand, a dramatic increase in the activity and selectivity was brought about by the coprecipitation of copper(II) sulfate and iron(III) sulfate. As shown in fig. 1, both activity and selectivity increased with increasing content of copper in the Fe-Cu/SiO$_2$ catalysts up to 30% in total metal and reached maximum values; the selectivity of 99.5% at 50% conversion and the activity more than twenty times higher than that of the catalyst free from copper. The activity is even three times higher than that of a Raney-Fe catalyst, the selectivity of which is only 70% under the same reaction conditions. The catalysts containing more then 60% of copper

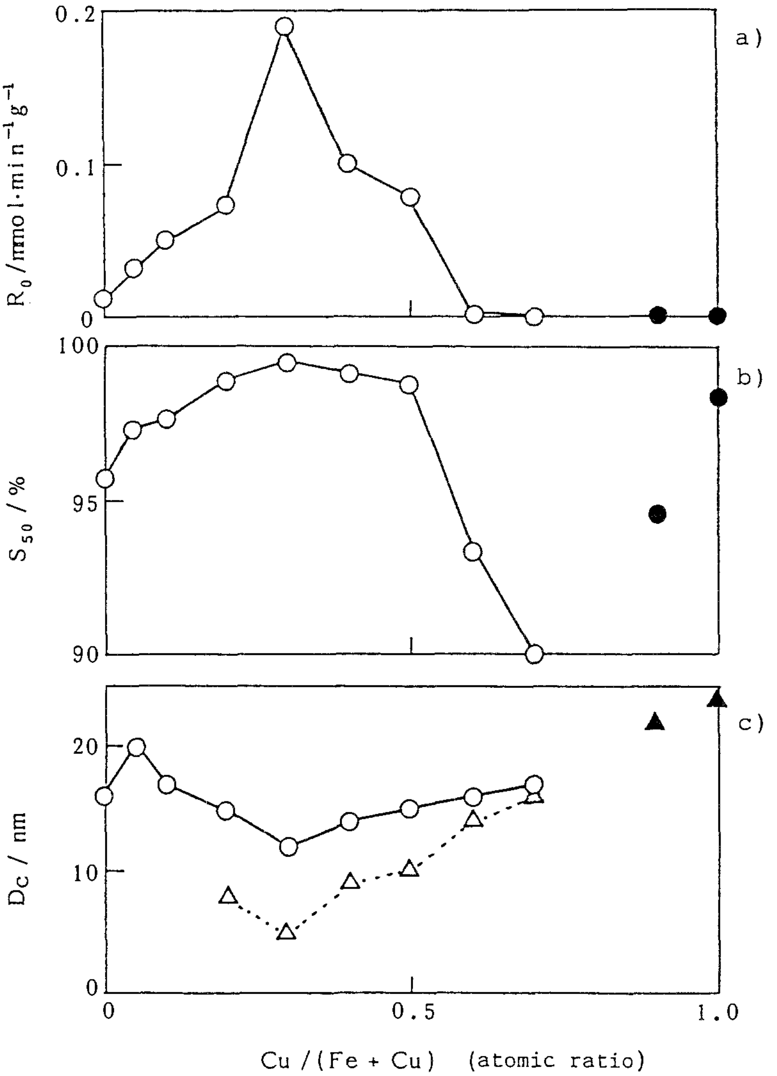

Fig. 1. Effects of the composition of Fe-Cu/SiO$_2$ catalysts on their (a) activities, (b) selectivities, and (c) the mean crystallite sizes of Fe(○) and Cu(△). ●, ▲: Reduced at 300 °C instead of 500 °C.

were almost inactive and showed relatively low selectivities. This might arise from the difference between bulk and surface compositions.

The mean crystallite sizes of iron and copper in the Fe-Cu/SiO$_2$ catalyst with the highest activity and selectivity were both the smallest in all the catalysts with different copper contents. However, it seems difficult to explain the remarkable increase in the activity of the Fe-Cu(7 : 3)/SiO$_2$ catalyst only on the basis of the decrease in the mean crystallite size of iron or of the increase in the extent of reduction caused by the presence of copper [9,10]. Irrespective of the presence of

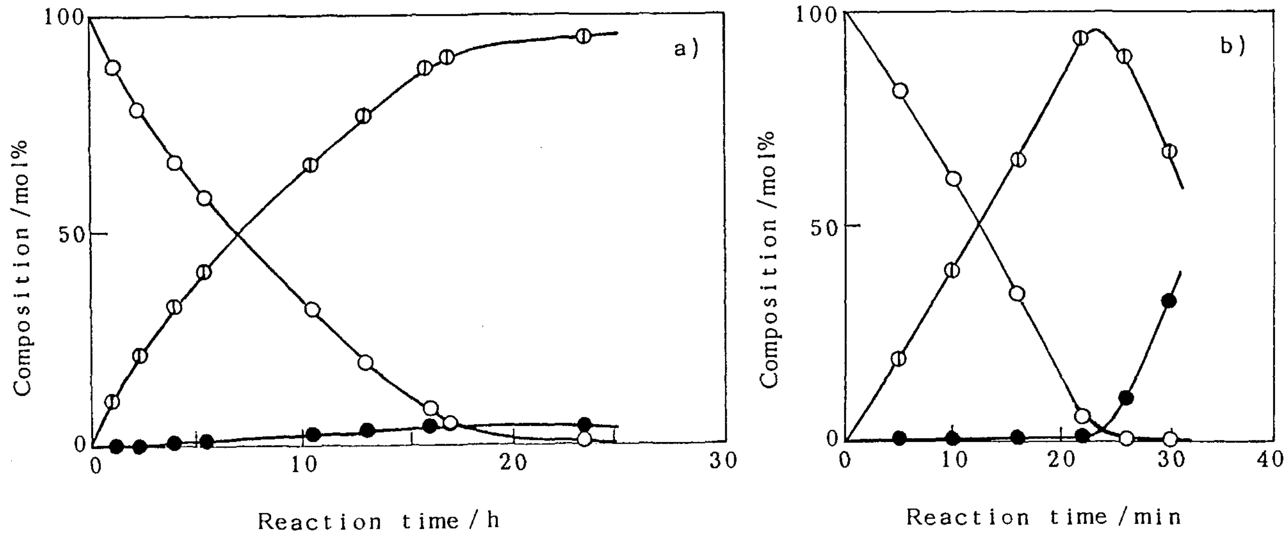

Fig. 2. Hydrogenation of phenylacetylene on (a) Fe/SiO_2 and (b) Fe-Cu/SiO_2(Cu = 30%) catalysts. ○: Phenylacetylene, ⦶: styrene, ●: ethylbenzene.

copper, the degrees of reduction estimated from the weight losses in thermogravimetric measurements were not less than 95% under our experimental conditions. The mean crystallite size or iron, obtained from the X-ray line broadening, does not exactly reflect the dispersion of iron. The presence of very small crystallites of iron, which are not detected by the XRD method, will strongly affect the activity of the catalyst. Therefore, the effect of copper on the crystallite size distribution of iron as well as a synergistic effect between iron and copper should be considered.

The Fe-Cu(7 : 3)/SiO_2 catalyst prepared from metal nitrates exhibited much lower activity, slightly lower selectivity, and larger D_c of iron (2.4×10^{-2} mmol · $\text{min}^{-1} \cdot \text{g}^{-1}$, 97.2%, and 20 nm, respectively). Thus, the presence of sulfate anion as well as a proper amount of copper seems essential for the preparation of a highly active and selective catalyst. Although XPS studies showed that the sulfate anion remaining in the precursor was reduced to sulfide in some cases, its possible poisoning effect is not compatible with the improved activity of the catalyst prepared from metal sulfates. Studies on the surface composition and on the roll of copper and sulfur are now in progress.

The reduction conditions of catalyst precursors have been reported to affect the dispersion of Fe metal, leading to the different properties of the resulting catalysts [11–14]. Table 2 shows the effects of the heating and the hydrogen-flow rates in the reduction of the Fe-Cu(7 : 3)/SiO_2 precursor. The activity was much improved by the slow heating and/or the high rate of hydrogen flow, while the selectivity was held constant at the highest value. The higher dispersion of Fe metal in the improved catalyst is attributable to the efficient elimination of the water formed during the reduction of the precursor. The temperatures of hydrogen reduction in the range of 450 ° C to 550 ° C had little effects on both activity and selectivity of the resultant catalyst.

Figure 2 shows the time-course of the hydrogenations on Fe/SiO_2 and Fe-Cu(7 : 3)/SiO_2 catalysts. The high selectivities to styrene on both catalysts were maintained until conversions went up to over 90%; 95.4% selectivity at 98.7% conversion for the Fe/SiO_2 catalyst and 99.3% selectivity at 96.5% conversion for the Fe-Cu(7 : 3)/SiO_2 catalyst. However, on the latter catalyst, styrene was hydrogenated rapidly to ethylbenzene when phenylacetylene was thoroughly consumed. Further studies on reaction conditions, additives, or pretreatments of the catalyst will help to suppress the hydrogenation of styrene on the Fe-Cu(7 : 3)/SiO_2 catalyst.

References

[1] R. Paul and G. Hillys, Bull. Soc. Chim. Fr. [5] 6 (1939) 218.
[2] A.F. Thompson and S.B. Wyatt, J. Am. Chem. Soc. 62 (1940) 2555.
[3] W. Reppe, Ann. 596 (1955) 38.

[4] S. Taira, Bull. Chem. Soc. Jpn. 35 (1962) 840.
[5] R.S. Mann and K.C. Khulbe, Can. J. Chem. 45 (1967) 2755.
[6] Y. Nitta, S. Matsugi and T. Imanaka, Chem. Express 4 (1989) 547.
[7] Y. Nitta, F. Sekine, T. Imanaka and S. Teranishi, J. Catal. 74 (1982) 382.
[8] B.E. Warren, J. Appl. Phys. 12 (1941) B75.
[9] R.N. Pease, H.S. Taylor, J. Am. Chem. Soc. 43 (1921) 2179.
[10] Y. Murata and S. Kasaoka, Kogyo Kagaku Zasshi 62 (1959) 1195.
[11] Y. Murata and S. Kasaoka, Kogyo Kagaku Zasshi 61 (1958) 1440.
[12] E. Ruckenstein and X.D. Hu, J. Catal. 100 (1986) 1.
[13] J.W. Geus, Appl. Catal. 25 (1986) 313.
[14] A.F.H. Wielers, A.J.H.M. Kock, C.E.C.A. Hop, J.W. Geus and A.M. van der Kraan, J. Catal 117 (1989) 1.