Catalysis Letters 35 (1995) 345–351

The influence of microwave heating on the morphology and benzene hydrogenation activity of alumina- and silica-supported palladium catalysts

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Received 28 March 1995; accepted 8 August 1995

Alumina- and silica-supported palladium catalysts were prepared by conventional and microwave heating. The catalysts have been characterized by nitrogen adsorption, hydrogen chemisorption, X-ray powder diffraction and temperature-programmed reduction and tested for benzene hydrogenation activity. The results show that preparation of samples by microwave heating leads to enhanced crystallite size and increased hydrogenation activity.

Keywords: alumina-supported palladium catalyst; silica-supported palladium catalyst; microwave heating; X-ray powder diffraction; temperature-programmed reduction; benzene hydrogenation; nitrogen adsorption; hydrogen chemisorption

1. Introduction

Supported palladium catalysts have been extensively studied for the selective hydrogenation of a variety of organic compounds [1–4] and for the synthesis of methanol from carbon monoxide and hydrogen [5]. The hydrogenation of benzene has frequently been used as a model reaction to interpret the activity in terms of the fundamental properties of these catalysts [6–11]. A few attempts have also been made to correlate the method of preparation of the catalysts with their activity [12,13].

We report here on the use of microwave heating to modify crystal morphology and influence the performance of the catalysts for the hydrogenation of benzene. A comparison of the results is made with those obtained from catalysts prepared by conventional methods.

2. Experimental

10% Pd (by weight) catalysts were prepared by impregnating commercial alumina (gamma phase, Harshaw, Al-3996R, 18/25 BSS mesh size, SA: 178 m^2/g, PV: 0.65 ml/g), and silica (fluid silica, Ketjen, F-5, SA: 640 m^2/g, PV: 1.1 ml/g), with aqueous solutions of palladium nitrate. The catalysts were evaporated to near dryness on a water bath and dried in an oven at 120°C (12 h). A portion of each catalyst was subsequently calcined in air at 450°C (5 h) and the remaining portion was irradiated in a microwave oven (CEM Corporation, USA) at 100% power (5 min).

X-ray powder diffraction (XRD) patterns were obtained with a Siemens D-5000 X-ray diffractometer using Cu K_α radiation.

BET surface area was determined by nitrogen adsorption at −196°C using conventional all-glass high vacuum apparatus. The same apparatus was also used for the determination of hydrogen chemisorption capacities (at room temperature) of catalysts reduced in hydrogen at 250°C for 4 h. The double isotherm method proposed by Benson et al. [14] and revised (to eliminate the interference of palladium hydride formation in determining the chemisorbed hydrogen) by Bonivardi et al. [15] was adopted. The first isotherm gave the total adsorption capacity due to absorption (hydride formation) and chemisorption, whereas the second isotherm (generated after an intermittent evacuation for 30 min) gave absorption alone. The difference between the two values was taken as the chemisorption capacity of the catalyst.

Temperature-programmed reduction (TPR) of the catalysts was performed using a 10% hydrogen–90% nitrogen gas mixture at a heating rate of 16°C/min with a gas flow rate of 20 ml/min.

Catalytic evaluation was performed on catalysts which had been reduced in a flow of pure hydrogen (30 ml/min) at 250°C (4 h). Benzene (dried and thiophene-free) was fed into the reactor by means of a microfeed pump at a flow rate of 4 ml/h. Purified hydrogen, at a molar ratio 1 : 3, benzene to hydrogen, was also admitted into the preheater zone of the reactor. The catalyst was allowed to attain steady state for about 30 min at the desired reaction temperature before the product sample was collected and analysed by gas chromatography using a FID and carbowax 20 M column (1/8″ i.d. and 8′ long).

3. Results and discussion

Properties of the alumina- and silica-supported palladium catalysts are presented in table 1. The results show that in comparison with the conventional method of catalyst preparation, microwave heating decreases the total surface area in the case of the alumina-supported catalyst, presumably as a result of an increase in particle size. In contrast, a slight increase in total surface area occurs with the

Table 1
Properties of the catalysts

Catalyst[a]	Surface area (m^2/g)	H_2 uptake (μmol/g)	Dispersion (%)	Particle size[b] (Å)
Pd/Al_2O_3 (CH)	152	112	23.8	47
Pd/Al_2O_3 (MH)	117	23	5.0	229
Pd/SiO_2 (CH)	462	39	8.3	135
Pd/SiO_2 (MH)	499	33	7.0	160

[a] CH: conventional heating, MH: microwave heating.
[b] Particle size is calculated according to ref. [15].

silica-supported catalyst. This may be due to an increased microporosity caused by the microwave heating.

Fig. 1a gives the XRD pattern recorded from the alumina-supported catalyst. The broad nature of the peaks suggests that the alumina support is poorly crystalline. The appearance of lines characteristic of palladium(II) oxide in the XRD pattern is visible. Fig. 1b shows the XRD pattern for the same catalyst produced by microwave heating. The PdO seems to be less well characterized and this suggests that microwave heating does not overcome the strong interactions of the PdO with the alumina support. The XRD patterns of silica-supported palladium catalysts after conventional preparation and after the application of microwave heating are shown in figs. 1c and 1d respectively. The broad peak associated with silica indicates that the support is poorly crystalline. However, the lines characteristic of pal-

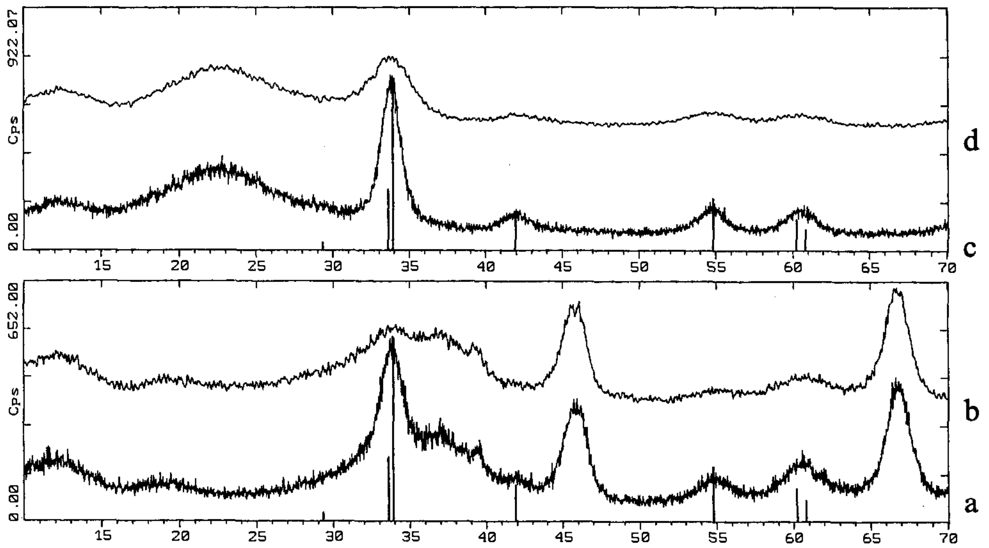

Fig. 1. XRD patterns of alumina- and silica-supported palladium catalysts (lines indicate PdO pattern): (a) conventionally heated Pd/Al_2O_3 catalyst, (b) microwave-heated Pd/Al_2O_3 catalyst, (c) conventionally heated Pd/SiO_2 catalyst, (d) microwave-heated Pd/SiO_2 catalyst.

ladium(II) oxide indicate better crystallinity as compared to that in the alumina-supported catalysts. The results suggest that the silica support interacts weakly with the palladium(II) oxide phase thus allowing sintering during heating.

Though an accurate estimate of the palladium particle size cannot be made from hydrogen chemisorption uptake because of variation in the H/Pd ratio with dispersion [15], the relative particle sizes reported in table 1 can be used for comparison. The considerable difference in mean particle size (from 47 to 229 Å) in the case of the alumina-supported catalysts compared to a moderate difference (from 135 to 160 Å) in the case of the silica-supported catalysts, reveals a significant weakening in the interaction of the alumina support with the palladium precursor during the microwave heating.

The TPR profiles recorded from the alumina-supported palladium catalysts after conventional heating and microwave heating are shown in figs. 2a and 2b respectively. The sample was initially flushed with hydrogen at room temperature. Under these conditions we calculate that β-palladium hydride can be formed:

$$\mathrm{PdO(s)} + 1.25\mathrm{H_2(g)} \rightleftharpoons \mathrm{PdH_{0.5}(s)} + \mathrm{H_2O(l)} \quad \Delta H^0_\mathrm{m} = -220.1\ \mathrm{kJ\ mol^{-1}}\,.$$

The negative peak obtained at 144°C in the case of the Pd/Al_2O_3 catalyst prepared by conventional heating can be associated with the decomposition of β-palladium

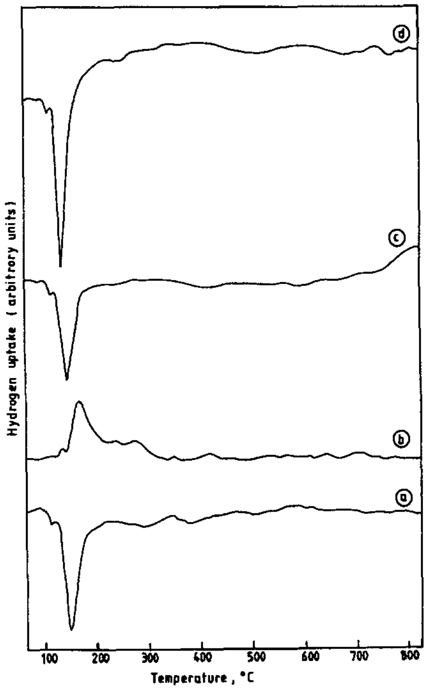

Fig. 2. TPR profiles of alumina- and silica-supported palladium catalysts: (a) conventionally heated Pd/Al_2O_3 catalyst, (b) microwave-heated Pd/Al_2O_3 catalyst, (c) conventionally heated Pd/SiO_2 catalyst, (d) microwave-heated Pd/SiO_2 catalyst.

hydride [16,17]. An important feature of the results is the absence of such a negative peak in the TPR profile of the Pd/Al_2O_3 catalyst prepared by microwave heating (fig. 2b). In contrast, the TPR profiles of the silica-supported catalysts obtained by conventional heating (fig. 2c) and by microwave heating (fig. 2d) both show hydrogen desorption peaks at around the same temperature. The comparatively larger area of the desorption peak in the case of the Pd/SiO_2 catalysts prepared by microwave heating gives indirect evidence for larger crystallite size since an increase in crystallite size leads to increased β-palladium hydride formation [6]. However, the Pd/Al_2O_3 catalyst prepared by microwave heating has a larger particle size (table 1) but shows no indication of β-palladium hydride formation (fig. 2b). The absence of the negative peak in the microwave-heated catalyst indicates that the palladium species formed is different in character from that formed on the conventionally heated catalyst.

Fig. 3 summarises the activity patterns obtained for conventionally heated and microwave heated alumina- and silica-supported palladium catalysts. An order of magnitude increase of turn-over number (TON), calculated from hydrogen uptake, in the case of the microwave-irradiated alumina-supported catalyst clearly illustrates the effect of microwave heating. The TPR results indicate that this catalyst

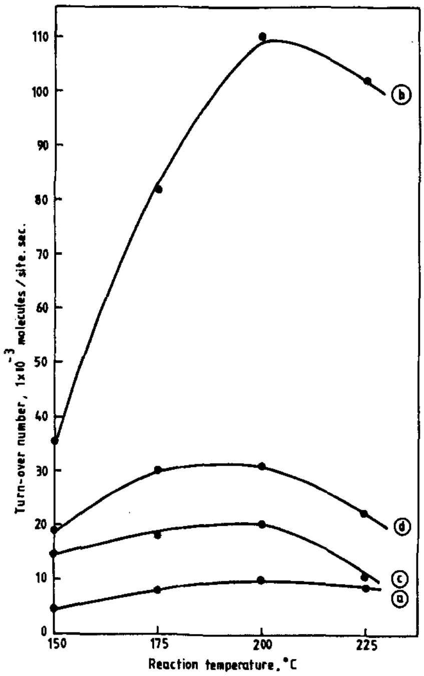

Fig. 3. Effect of microwave irradiation on the benzene hydrogenation activity of alumina- and silica-supported palladium catalysts: (a) conventionally heated Pd/Al_2O_3 catalyst, (b) microwave-heated Pd/Al_2O_3 catalyst, (c) conventionally heated Pd/SiO_2 catalyst, (d) microwave-heated Pd/SiO_2 catalyst.

does not form β-palladium hydride; it shows a low surface area consistent with large particle size (table 1) which given the X-ray diffraction results, are poorly crystalline. A similar, albeit lesser, increase in turn-over number is also observed in the microwave irradiated silica-supported catalyst. Our results show that when the Pd/Al_2O_3 catalyst is prepared using microwave heating we see: (a) a decrease in surface area and an increase in the (poorly crystalline) particle size, (b) no β-palladium hydride formation under the conditions of the TPR experiment and (c) an order of magnitude increase of the turn-over number. It is thought [4,16,17] that supported palladium catalysts in hydrogenation reactions form a hydride which acts as a reversible storage medium of active hydrogen. Our TPR results indicate that in the case of three of these catalysts this hydrogen is released at about 144°C. In the case of the Pd/Al_2O_3 catalyst prepared by microwave heating, the decreased chemisorption uptakes and enhanced TON suggest that the intrinsic activity per site is enhanced; this could indicate that strong bonding of hydrogen to palladium does not occur in this case and that weakly bound hydrogen is easily released at low temperatures. This suggests that the palladium oxide formed under the microwave heating regime is reduced to a form which is distinctly different from that generated under conventional calcination conditions.

Acknowledgement

We thank the British Council, UK and CSIR, India, for financial support. NL thanks UGC, India, for the award of a fellowship.

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