SHIP-IN-A-BOTTLE FORMATION OF Pd$_{13}$(CO)$_x$ CLUSTERS IN ZEOLITE NaY

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Received 22 December 1988; accepted 9 January 1989

FTIR spectra of CO adsorbed on gently reduced Pd/NaY show very sharp bands and are markedly different from the familiar broad band CO/Pd/support spectra. New bands are formed when part of the CO is removed. It is proposed that Pd$_{13}$(CO)$_x$ clusters are formed with singly and multiply bonded CO, including a butterfly configuration. Very similar spectra are obtained, if Pd ions are initially located in the sodalite cages or in the supercages.

1. Introduction

Recently, the detailed mechanism of Pd particle formation in NaY, prepared by the sequence ion exchange/calcination/reduction, has largely been unravelled [1,2]. In particular, specific calcination conditions have been defined which leave the vast majority of the Pd ions either in the supercages as diammine complexes, Pd(NH$_3$)$_2^{2+}$, or in the sodalite cages as bare Pd$^{2+}$ ions. In the former case, reduction creates small Pd oligomers which migrate rapidly through the supercage channel system and coalesce to form larger particles. In the latter case, reduction takes place inside the sodalite cages; and at elevated temperatures the Pd atoms migrate into supercages and agglomerate. An open question is, however, whether the reduced metal particles carry memory of their reduction mechanism (as appears to be the case for Pt in NaY [3]) or whether Pd particles of similar size and shape are formed via both routes, e.g. clusters which are smaller than the supercage, but larger than the cage window. Once such particles have been formed and all Pd atoms and smaller oligomers have been consumed, further growth would require high activation energy mechanisms, e.g. Ostwald ripening or local collapse of the zeolite matrix.

In the present research Pd particles have been characterized by adsorbing carbon monoxide and recording FTIR spectra. It is to be expected that spectra of well defined Pd$_y$(CO)$_x$ clusters, if formed by this ship-in-a-bottle technique, are

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distinctly different from the spectra of CO adsorbed e.g. on SiO$_2$ supported Pd, reported in the literature [4]. It has been previously found in this lab that Pd/NaY catalysts differ from Pd/SiO$_2$ by a markedly superior turnover frequency for neopentane conversion [5].

2. Experimental

2.1. CATALYST PREPARATION

2.1.8 wt% (or 7.30 wt%) Pd on NaY was prepared by ion-exchange of Linde NaY(LZY-52, Lot #968083061080-S-9, Na$_{57}$(AlO$_2$)$_{57}$(SiO$_2$)$_{135}$-375H$_2$O). The exchange was carried out by adding a (0.01 M) aqueous solution of [Pd(NH$_3$)$_4$](NO$_3$)$_2$ (Strem Chemicals, Lot #19167) to a dilute (200 ml/g) zeolite slurry in doubly deionized water and leaving this at 25°C for 20 hours. Fletcher and Townsend [6] reported that exchange was complete at 25°C; this was verified by atomic absorption. Our Pd load corresponds to roughly 4 (or 13.4) Pd atoms per unit cell.

2.2. CALCINATION

Calcination was done in pure O$_2$, at 1 bar and a flow rate of 300 ml/min/300 mg. The temperature ramp was programmed at 0.5°C/min from 25°C to the specified calcination temperature ($T_c$), then held at this temperature for 2 hours. After cooling to 25°C, 20 mg of the catalyst powder was pressed into a 10 mm diameter wafer. The wafer was then transferred to the IR cell and recalcined at $T_c$ for 10 minutes. O$_2$ was then replaced by Ar, flushing for 10 min. at $T_c$. After cooling to 25°C, the absence of H$_2$O or OH groups was verified by absence of bands near 1640 cm$^{-1}$ and 3650 cm$^{-1}$ [7,8].

2.3. REDUCTION

The wafer was heated from 25°C to the specified reduction temperature ($T_R$) at a rate of 8°C/min, then held at $T_R$ for a specific time ($t_R$) under flowing hydrogen. The gas was then changed to Ar at $T_R$ for 20 min to remove most of the adsorbed hydrogen. After this reduction the FTIR spectra showed a strong band at about 3650 cm$^{-1}$, confirming that Pd atoms and H$^+$ ions are formed, with the latter occupying cation sites and forming hydroxyl groups.

In this paper we shall use the sample notation Pd$_x$NaY($T_c/T_R/t_R$), where $x$: number of Pd atoms per unit cell of NaY; $T_c$: Calcination temperature in °C; $T_R$: Reduction temperature in °C, and $t_R$: Reduction time in minutes.