BEHAVIOUR OF Pd^0 PARTICLES IN A MODIFIED AND STABILIZED HY ZEOLITE.

G. Spector, M. BRIEND, R. Monque, D. Delafosse
Laboratoire de Réactivité de surface et structure,Université P. et M. Curie,
4 Place Jussieu, 75230 Paris Cedex 05

ABSTRACT

Palladium has been introduced onto a stabilized HY zeolite by ion exchange with the following complexes : $[Pd(NH_3)_4]Cl_2$, $[Pd(NH_3)_4](OH)_2$ and $PdCl_2$. After activation in flowing air at 773 K and subsequent hydrogen reduction, the catalysts were tested for benzene hydrogenation. The samples exhibit various catalytic behaviours, depending on their preparation and activation treatments. Models are proposed to tentatively explain the apparent structure sensitivity of benzene hydrogenation with these catalysts.

INTRODUCTION

Palladium containing stabilized HY zeolites form a class of bifunctional catalysts very important for the hydrocracking of heavy oils. Hydrothermal treatments suffered by these zeolites lead to a certain heterogeneity and to the formation of neutral or charged alumina species, located inside the zeolitic cavities (1). The location of Pd^{2+} ions introduced on such a carrier, and their subsequent hydrogen reducibility depend largely on the nature of the palladium precursor complex, the pH of the exchange solution and on the activating treatment conditions (2, 3). These catalysts are known to deactivate principally by a slow degradation of the hydrogenating function. In order to determinate the factors influencing the hydrogenating properties of industrial Pd/stabilized HY zeolites and their resistance to poisons, we tested these catalysts in the benzene hydrogenation reaction, before and after poisoning by sulphureous compounds. Benzene hydrogenation is generally assumed to be a structure insensitive reaction. The results of Aben et al. (4), in the case of Pd catalysts, are in agreement with this. They observed a constant specific activity for palladium particles of varying dispersions supported on silica and alumina. However, some authors noted variations in the hydrogenation reaction rate according to the particle size, the nature of the carrier or the reduction temperature of the metallic precursors. In order to explain the increased hydrogenation of benzene with dilution by alumina of a Pd/Al_2O_3 catalyst, Sancier (5) proposed that benzene was reacting with hydrogen spilled over the support. Figueras and co-workers (6) attributed the high activity of palladium dispersed on acidic supports such as protonic and rare-earth zeolites to its partial electrodeficiency due to electron transfer from the metallic clusters to the carrier. However, such an electronic transfer was not detected by ESCA and esr techniques on Pd loaded Y zeolites (7). Moss et al. (8) admitted that a size effect could occur for benzene hydrogenation on Pd/SiO_2, althoug no experimental evidence for it was given. Finally, the influence of metal dispersion was demonstrated on the specific hydrogenation activity of Pd/charcoal catalysts by Benedetti et al. (9, 11). It was attributed to the formation or not of a stable palladium hydride phase, according to the particle size. So, the results accumulated up till now, in some cases support and in other cases contradict, the structure insensitivity of benzene hydrogenation. In the present work, we present a new example where small particle sizes seem to favour an increase in the specific activity of this reaction.

EXPERIMENTAL

The initial, stabilized HY zeolite is a Union Carbide synthetic product delivered in the NH_4^+ form with the label LZY82. The overall Si/Al ratio is about 3, but that corresponding to the framework tetrahedra is $\geqslant$ 4. The unit cell parameter a is 2.455 nm and the weight percentage of sodium is 0.12

Catalyst preparation. Pd^{2+} ions were introduced by ion-exchange with dilute solution of the following salts : (1) $[Pd(NH_3)_4]\,Cl_2$: pH $\simeq$ 11 - sample A ; (2) $[Pd(NH_3)_4]\,(OH)_2$: pH $\simeq$ 13 - sample B ; (3) $PdCl_2$: pH $\simeq$ 3.5 - sample C. Reducible and non-reducible cations were also added in A and C to give the samples described in Table I.

Catalyst activation and poisoning. After exchange and drying at 393 K, the catalysts were slowly heated (13 K/min) in flowing air up to 773 K, kept for 6 hr and then evacuated at this temperature, in order to avoid preliminary reduction of Pd^{2+} ions by hydroxyls (12) or ammonia (13). The sample reduction was performed at 423 K either in flowing hydrogen (5 l/hr) or in static conditions (hydrogen pressure: 13.3 kPa). In order to simulate the constraints suffered by the catalysts under industrial hydrocracking conditions, the samples were submitted to sintering and poisoning treatments. These consisted either in heating under flowing hydrogen from 423 to 773 K, followed by 6 h at 773 K, or in heating at 673 K under 13.3 kPa H_2S, followed by 15 hr in flowing hydrogen at the same temperature.

Metal Dispersion. Particle sizes were measured by hydrogen chemisorption at 373 K (3) and by electron microscopy.

Catalytic activity. The rates of benzene hydrogenation of sintered and poisoned samples were measured in a conventional flow microreactor. The experimental conditions used were : temperature 353 to 378 K - hydrogen/benzene ratio : 12/1 - atmospheric pressure.

Table 1

Unit cell composition and metallic dispersion of H_2 sintered samples

Exchange complex	Pd % weight	Unit cell composition	Name	Mean particle size (nm)	Dispersion
$Pd(NH_3)_4\ Cl_2$	5.9	$Pd_{6.7}Na_1$ $(SiO_2)_{148}(AlO_2)_{44}$	PdA	2.8	0.38
$Pd(NH_3)_4\ Cl_2$ then $AgNO_3$	5.74	$Pd_{6.6}Ag_6Na_1$ $(SiO_2)_{148}(AlO_2)_{44}$	PdAgA	5.0 2.0 to 15	0.21 Heterogeneous
$Pd(NH_3)_4\ Cl_2$ then $Cu(NO_3)_2$	5.80	$Pd_{6.8}\ Cu_5Na_1$ $(SiO_2)_{148}(AlO_2)_{44}$	PdCuA	3.2	0.33
$Pd(NH_3)_4\ Cl_2$ then $Ce(NO_3)_3$	4.48	$Pd_5Ce_4Na_1$ $(SiO_2)_{148}(AlO_2)_{44}$	PdCeA	3.3	0.32
$Pd(NH_3)_4\ Cl_2$ then $La(NO_3)_3$	4.97	$Pd_{5.8}La_6Na_1$ $(SiO_2)_{148}(AlO_2)_{44}$	PdLaA	2.7	0.39
$La(NO_3)_3$ then $Pd(NH_3)_4\ Cl_2^*$	5.25	$La_7Pd_6Na_1$ $(SiO_2)_{146}(AlO_2)_{46}$	LaPdA	2.4	0.44
$Pd(NH_3)_4\ (OH)_2$	4.8	$Pd_{5.7}Na_{0.8}$ $(SiO_2)_{144}(AlO_2)_{48}$	PdB	2.8	0.38
$PdCl_2$	5.4	$Pd_{6.2}Na_1$ $(SiO_2)_{147}(AlO_2)_{45}$	PdC	4.6	0.23
$PdCl_2$ then $La(NO_3)_3$	4.57	$Pd_5La_3Na_1$ $(SiO_2)_{147}(AlO_2)_{45}$	PdLaC	6.4	0.17 Heterogeneous
$PdCl_2$ then $Ca(NO_3)_3$	5.1	$Pd_6Ca_2Na_1$ $(SiO_2)_{147}(AlO_2)_{45}$	PdCaC	5.6	0.19 Heterogeneous
$PdCl_2$ then $Ca(NO_3)_2$ **	5.1	$Pd_6Ca_2Na_1$ $(SiO_2)_{147}(AlO_2)_{45}$	PdCaC Dyn.	3.8 1.5 to 20	0.28 Heterogeneous

* Part of La^{3+} ions exists as $La_2O_3.CO_3$

** This sample was reduced in dynamic conditions

Table 2

Benzene hydrogenation rates before and after H_2S poisoning.

Sample	Reaction rate at 378K mmole/h/gmetal*	N	E Kcal/mole	Reaction rate at 378K after poisoning	N
PdA	134		15	5.4	1.6
PdB	134		15	6	1.7
PdLaA	112		15	3	0.8
LaPdA	270		15	7	1.7
PdCeA	128		15	2.4	0.7
PdCuA	38		15		0.4
PdAgA	4		15	-	-
PdC	13	6	6	4.4	2
PdLaC	25	16	7	5	2.7
PdCaC	27	1	6	8	4.4
PdCaC-Dyn	63	24	6	4	1.5

* Rate at the steady state for samples C and after one hour reaction for samples A and B.

RESULTS AND DISCUSSION.

Catalysts C. This series of catalysts are characterized by a fairly stable activity. The hydrogenation rates, measured at 378 K at the steady state, are listed in Table 2 . The activation energy for the reaction is 6-7 kcal.mole^{-1}, in agreement with previous works.

The presence of additives - La^{3+} or Ca^{2+} ions - results on the one hand in a change in the particle dispersion and on the other hand in a marked increase of the turnover frequency N. As it was previously shown (3), PdLaC and PdCaC catalysts appear heterodispersed, small clusters ($\geqslant$ 1 nm) being observed together with crystallites of up to 20 nm on the microphotographs. This heterogeneity is still more pronounced after a reduction in flowing hydrogen (PdCaC-Dyn sample). Pd particles smaller than 1 nm in size, although not detected by electron microscopy, could exist in the zeolite cavities have an electrodeficient character (14) and thus play a part in the enhancement of the catalytic activity. However, due to the good agreement between particle size determinations both by electron microscopy and hydrogen chemisorption methods, we do not think that clusters smaller than 1 nm are present in our samples. These small particles would exhibit a higher thioresistance than the larger ones. On the contrary, it appears (Table II) that the most highly dispersed C sample - PdCaC-Dyn - is also the most greatly poisoned by sulphur, although it has a population of little aggregates. It is more likely, considering the experimental conditions of this work (378 K and 94 kPa H_2) that both the low specific activity and the apparently greater thioresistance of the largest clusters are related to the formation of a β -hydride phase in the metallic palladium. This phase is known to be less active than the pure metal. Moreover, the dissolved atomic hydrogen is thought to bear a negative charge (15) so that Pd atoms may gain an electrodeficient character. The stability of the palladium β -hydride increases with the particle size (16, 17). In the smallest aggregates, due to the ease of formation and decomposition of this phase, a surface restructuration may also be postulated (10), resulting in an increase of the number of low density planes [111] compared to [100] planes, the former being considered to be the most effective for acetylene hydrogenation (18). In the case of benzene, it is difficult to put forward such a motive. However, the mechanism of hydrogen activation may be modified due to the β -hydride instability in the small crystallites. The decrease in the specific hydrogenating activity and the enhanced thioresistance of coarse Pd aggregates may thus be explained, in agreement with the observations of Benedetti et al. (10).

Catalysts A and B. The initial hydrogenation rate of samples A and B is very high compared to samples C, but it quickly decreases after a few hours and then slowly and continuously diminishes, without reaching a constant value. However, in order to compare the different catalysts A and B, we measured this rate after one hour of reaction and extrapolated to zero time. The rate values so obtained are given in table II. PdCuA and PdAgA samples of this series exhibit the lowest catalytic activity, presumably due to the formation of bimetallic particles and concomitant dilution of metallic palladium by copper and silver. The most active catalyst appears to be LaPdA which, as well as La^{3+} ions, contains a lanthanum oxycarbonate occluded in the structure. However, the metallic dispersion of this sample differs very little from the others. Moreover, it seems difficult to ascribe the enhanced activity of samples A and B with respect to samples C, to differences in palladium dispersions only, because of the abnormally high activation energy (15 $kcal.mole^{-1}$) which suggests a new reaction mechanism. We suspect an influence of the support and possibly that of spilled-over hydrogen. No benzene hydrogenation was detected by Angel and co-workers (19) by hydrogen activated on small rhodium clusters and possibly spilled over a mordenite carrier. However, in a previous work (2) we have shown that alumina species - and for the LaPdA sample also a lanthanum oxycarbonate - are found in the LZY-82 cavities. In the reduced samples, metallic particles in the zeolite supercages exist together with these extraframework entities. So, in spite of the low rate of H_2 spillover at 378K, the contribution of hydrogenation sites on the alumina phases inside the zeolite cavities may be postulated, due to their vicinity to the metal. Such an assumption was recently advanced by Vannice et al. (20) to explain the high benzene hydrogenation activity of Pd dispersed on SiO_2-Al_2O_3 and TiO_2 supports, with similar values of activation energies. As a matter of fact, we previously shown that, due to the catalyst preparation conditions (pH $\simeq$ 3.5) the alumina species in samples C are cationic and located in the sodalite cages, i.e. far from the palladium clusters. In that case, hydrogen migration distances are presumably too long to allow the appearance of new hydrogenation sites on the aluminic carrier.

Finally, because of their higher metal dispersion (the β-hydride phase is not stable), A and B catalysts are more poisoned by sulphur than C catalysts.

CONCLUSION

This work was undertaken with the aim of a better understanding of the catalytic behaviour of Pd/stabilized zeolites in the hydrogenation of benzene. Two main factors are assumed to govern the catalyst hydrogenation activity : the existence of extraframework entities in the zeolite cavities and the formation of a β -hydride phase in the metallic palladium which could, too, weaken the Pd-S interaction.

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