

The Role of Palladium in Dehydrogenation of Cyclohexane over Pt-Pd/Al₂O₃ Bimetallic Catalysts

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Supported catalysts of platinum, palladium and platinum-palladium/Al₂O₃ with metallic contents from 1.0 to 0.2% were prepared by ion exchange or co-impregnation and physical mixture. The metallic dispersion was determined by hydrogen-oxygen titration and electron microscopy studies; a good agreement was obtained. The catalytic activity was studied in a conventional flow reactor at low conversions (<1%) to avoid mass and heat transfer limitations. The reaction rate was measured under atmospheric pressure at 160-200°C with hydrogen flow and with nitrogen as diluent. The activation energy found is 17 kcal/mol. The results obtained show that the catalytic activity of bimetallic catalysts is five times smaller than that of platinum/Al₂O₃ catalysts. These lower activities of bimetallic catalysts, are explained by a mechanism involving hydride coordination by platinum and the competition of palladium to occupy the oxidizing centers on the alumina surface.

INTRODUCTION

In the past 25 years supported metal systems, such as platinum/alumina, have been one of the major areas of investigation of heterogeneous catalysis. These systems find wide application in the reforming of petroleum fractions and in the production of high quality gasolines (1). Numerous reviews have been devoted to these systems (2-4). Nevertheless, the recent patent of Klusksdahl (5) concerned with the preparation of an important reforming catalyst, opened an important subject in catalysis, that of bimetallic supported catalysts. The initial patent contained few details of the influence of the second element and fell into the traditional mold of platinum/alumina catalysts.

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Metal alloy catalysts have been employed for some time to investigate the relationship between catalytic activity and the electronic properties of the metals, such as a work function and percentage of "d" character (6-10).

To study the effect of the second element on the activity of a platinum/alumina catalyst, a more appropriate catalyst would be one prepared under similar conditions as has been recently reported by Sinfelt (11) in Os/Cu and Ru/Cu bimetallic supported catalysts. In that study, it is shown that the catalytic activities of ruthenium and osmium are significantly modified by the copper addition. It is suggested that the formation of bimetallic clusters, involving an electronic factor in addition to a purely structural factor, is important in understanding the variation in catalytic activity. Recently, for platinum-palladium bimetallic supported catalysts (12), it was reported that the rate

of benzene hydrogenation on platinum/alumina is modified by the addition of palladium, even though, X-ray diffraction measurements did not show any alloy formation in the bimetallic surface.

To elucidate the mechanism of the interaction between palladium and platinum-supported catalysts, the dehydrogenation of cyclohexane to benzene was chosen as a test reaction. From the numerous works published (6-12), it is possible to conclude that two catalytic systems can be used to study the bimetallic behavior, and for simplicity, we suggest to call "alloy catalysts" those in which the metals employed are in the miscible region and "bimetallic catalysts" in which the alloy formation cannot occur, but important electronic effects are found in catalytic activity. In the present work, the term "bimetallic catalysts" is employed.

EXPERIMENTAL METHODS

Catalyst Preparation

The starting material was alumina Pechiney SCS-350, 230-270 mesh with a BET area of 350 m²/g. Separate aqueous solutions, containing chloroplatinic acid and palladium chloride (Merck, analytical quality grade), were employed to impregnate the support by the ion exchange method (13). Two series of bimetallic catalysts were prepared: by co-impregnating both metals and by simple physical mixture of the pure metal supported catalysts in order to obtain the desired metallic proportions. After drying for 12 hr at 120°C in air, catalysts were stored until reduction. Metal concentrations of the final catalysts are given in Table 1.

Dispersion Measurements

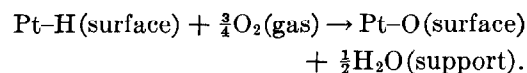
Dispersion values for the various catalysts were determined by the gravimetric method in a Cahn RGUHV electrobalance. Catalysts were reduced *in situ* at 400°C under hydrogen flow (1.8 liter/hr) for 6 hr

TABLE I
Dispersion and Crystallite Size for Pt, and Pt/Pd Bimetallic Catalysts

Metal content		Dispersion <i>D</i> (%)	Crystallite size (Å) \bar{d}	
% Pt	% Pd		Chemisorption	Electron microscopy
0.2		48	21	
0.4		50	20	
0.6		52	19	19
1.0		51	20	
	0.2	33	31	
	0.8	37	27	32
	1.0	37	27	
Bimetallic catalysts		Mean dispersion		
		Co-impregnation technique		
0.2	0.8	42	24	
0.4	0.6	42	23	27
0.8	0.2	43	25	
Physical mixture				
0.2	0.3	42	23	
0.3	0.2	42	24	30
0.4	0.1	43	25	

and then evacuated at 10⁻⁵ Torr for 12 hr at the reduction temperature. Hydrogen and oxygen (Matheson UHP) were adsorbed at room temperature under pressures of 10 and 100 Torr, respectively, in order to apply the H₂-O₂ titration method for platinum, palladium and bimetallic platinum-palladium catalysts (14, 15, 12).

The dispersion values for monometallic catalysts and the mean dispersion values of the bimetallic catalysts were calculated from the oxygen adsorption employing the following reaction proposed by Barbaux *et al.* (16):



The absolute dispersion values cannot be obtained by this method on the bimetallic catalysts, since the method is not selective. Nevertheless, the adsorptive

TABLE 2
Cyclohexane Dehydrogenation Activity at 190°C of Pt, Pd and Pt/Pd Bimetallic Catalysts

Metal content		E_a (kcal/mol°C)	Total conversion (%)	Specific rate (mol/g cat sec) $\times 10^6$	Intrinsic rate (mol/g Pt sec) $\times 10^6$	Molecules con- verted/surface Pt atom sec $N \times 10^3$
% Pt	% Pd					
0.2		14.3	1.05	369	185	740
0.4		15.7	1.60	570	142	560
0.6		18.0	3.70	1174	195	730
1.0		17.1	4.70	1500	150	570
					— ^a	— ^b
	0.2	14.0	0.08	14.9	7.5	24
	0.8	15.7	0.09	15.3	2.0	6
	1.0	16.9	0.15	25.9	2.5	8
Bimetallic catalysts						
Co-impregnation technique						
0.2	0.8	14.9	0.44	79.9	38.8	184
0.4	0.6	15.3	0.83	118.6	30.0	116
0.8	0.2	15.3	0.84	216.0	27.0	134
Physical mixture						
0.2	0.3	18.0	0.43	77.1	38.5	178
0.3	0.2	16.5	0.80	118.0	40.0	192
0.4	0.1	17.0	0.85	125.0	31.0	150

^a Mol/g Pd sec.

^b Molecules/S Pd sec.

properties of platinum and palladium were not modified in our bimetallic systems. Mean dispersion values for bimetallic platinum-palladium catalysts were reported in detail in a previous publication (12).

Data on the characteristics of the metallic phase are given in the Table 1, where D is the number of surface metal atoms divided by the total number of metal atoms contained in the catalysts; \bar{d} is the mean diameter of particles, calculated assuming spherical shape for the particles. The values were corroborated by electron microscopy by a replica technique and the particle sizes obtained were found by means of the volume/surface ratio $\bar{d} = n_s d_s^3 / n_t d_t^2$.

Catalytic Activity

Merck (Uvasol quality grade) cyclohexane was used for the reaction. Initial

rates of dehydrogenation were obtained in a conventional flow reactor at low conversion (<1%) to avoid heat and mass transfer limitations; the conversion values larger than 1% were calculated in order to maintain constant the quantity of used catalyst. The experimental condition were: 50 Torr for cyclohexane and 90 and 440 Torr for hydrogen and nitrogen, respectively, in order to have a total pressure of 580 Torr corresponding to that of Mexico City. The catalytic apparatus was coupled to a gas chromatograph; the products of the reaction were benzene and hydrogen. No other products, such as cyclohexene and cyclohexadiene, could be detected by the chromatographic analysis.

Samples of catalyst (25–50 mg) used for dispersion measurements were reactivated for 2 hr at 400°C under hydrogen flow. Activity measurements for all runs were performed between 150–220°C. Under these

conditions no activity decline was observed after 10 hr.

For each of the supported catalysts, specific activities for cyclohexane dehydrogenation are reported in Table 2. The values correspond to the number of molecules converted per surface metallic atom per second and are, therefore, a turnover number N ; the calculations for all catalysts were made from the following relation:

$$N = \frac{rw}{MN_0D},$$

where, r is the rate (molecules/sec g cat); M is the weight of metal (g/g cat); D is

the dispersion values; u is the atomic weight of the metal; and N_0 Avogadro's number.

For bimetallic catalysts, the calculations of N were made on basis of surface platinum atom concentrations assuming as reported in previous work (12) that the adsorptive properties and the dispersion values of the monometallic catalysts do not change in the bimetallic systems. Palladium adsorption values were not considered because palladium has a negligible catalytic activity under the experimental conditions used. It should be noted that we did not consider any spillover effects.

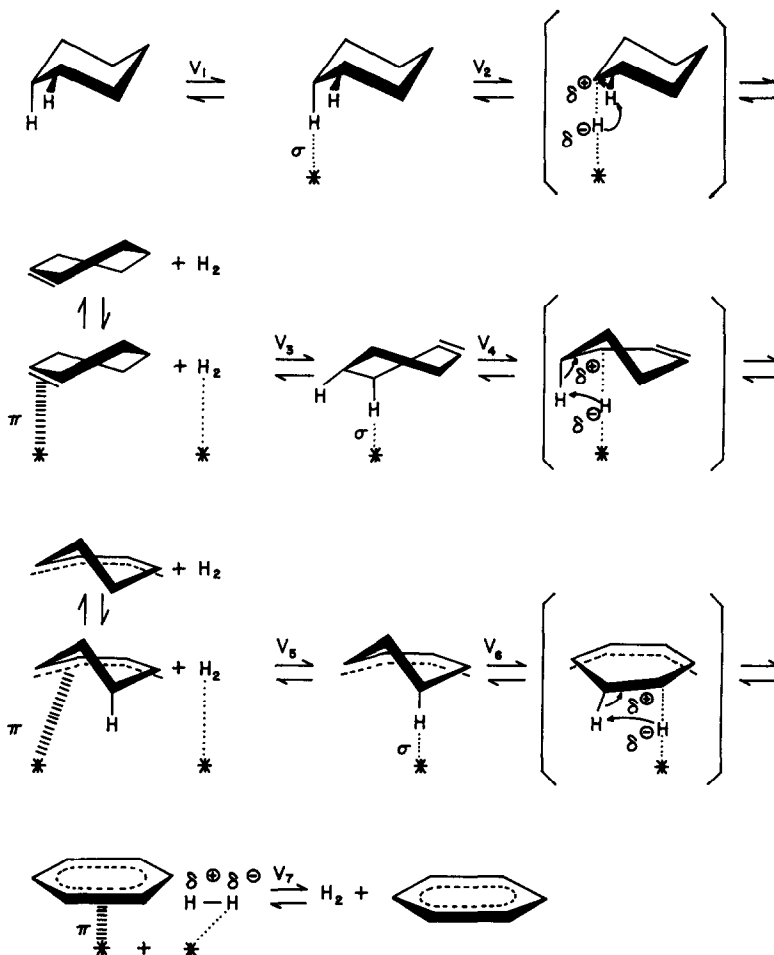


FIG. 1. Mechanism for cyclohexane dehydrogenation over Pt, Pd and Pt-Pd bimetallic supported catalysts.

For palladium catalysts, the turnover number is given in terms of molecules converted by the surface palladium atoms and it is given as a reference value. The absence of any significant variation in the values of N as the amount of platinum or palladium increases, can be taken as good evidence that the influence of transport phenomena is not important under the experimental conditions utilized (17).

RESULTS AND DISCUSSION

The most important results are presented in Tables 1 and 2 and are summarized below:

1. The total rate of conversion of cyclohexane decreases as palladium is added to platinum on co-impregnated catalysts.

2. The activity of palladium catalysts at the temperature considered is negligible so that all activity of bimetallic platinum-palladium catalysts can be attributed to the platinum.

3. The activation energy of the reaction of cyclohexane with platinum catalysts is not influenced by the presence of palladium in bimetallic platinum-palladium catalysts.

4. The dehydrogenation activity of bimetallic catalysts is not influenced by changing the atomic ratio Pt/Pd within the range of 2.1-0.13.

At this moment, we must point out that the catalytic systems studied do not show any alloy formation. This has been demonstrated in previous work by X-ray diffraction (12).

The interpretation of our experimental results on the basis of the mechanism presently accepted (18) is very difficult since it is required to have at the surface two active sites that must be "deactivated" by the presence of palladium.

In the studies on chemisorption of hydrogen over bimetallic catalysts Pt-Pd/ Al_2O_3 (12), we observed that the total

chemisorption of hydrogen over these catalysts is the sum of the individual metals chemisorption. If the mechanism involves abstraction of hydrogen atoms, we must expect that the total rate of the reaction must at least increase by the addition of palladium and not decrease as was observed, and it would be depend on the atomic ratio Pt/Pd: we do not detect any change when the atomic ratio changes from 2.1 to 0.13.

The role of palladium in the rate of the reaction of dehydrogenation of cyclohexane could be explained on the basis of the mechanism presented in Fig. 1.

The chemisorption of cyclohexane and cyclohexene over an active site, will depend on the intrinsic capacity of the metal to coordinate not one hydrogen atom, but to coordinate one "hydride." The degree of coordination with the metal will give the driving force for elimination of a H_2 molecule.

As the degree of coordination increases, the velocity must increase. The degree of coordination of "hydride" with the metal will play an important role in all steps of the reaction. The observed results, that the total velocity of the reaction of platinum catalysts is approximately 100 times faster than on palladium catalysts, are in agreement with the larger capacity of platinum to coordinate hydrides than palladium (19). According to the softness character concept of metal ions presented by Pearson (20), the small activity of palladium and the great activity of platinum can be respectively related to the small and large metal "hydride" coordinations. Evidence for the postulated mechanism of the dehydrogenation of cyclohexane is the presence of electropositive forms of the hydrogen bound in hydrides of palladium (21) and platinum (22).

On the series of co-impregnated and physical mixture bimetallic catalysts, activities about five times smaller than platinum catalysts were observed. The

decrease of total rate must be attributed to the presence of palladium in these catalysts. The role of palladium in these bimetallic systems could be explained by a competition of palladium (23, 24) with platinum to occupy the oxidizing centers of alumina surface during the reduction. The decrease of the number of platinum atoms deposited over the oxidizing centers will decrease the number of active platinum sites for the coordination of "hydride" and therefore the total rate of reaction will decrease.

On the bimetallic systems prepared by physical mixture there exists the same situation as in co-impregnated catalysts, because physical mixtures were made before reduction and the palladium could migrate to occupy the oxidizing centers of the total alumina surface.

In the previous work for the inverse reaction of hydrogenation of benzene (12) the same effect of palladium in co-impregnated bimetallic catalysts was observed (one-third of the total activity); in the same work for physical mixture catalysts we did not observe the decrease of activity probably because the effect was much lower than in the dehydrogenation reaction and hence more difficult to detect.

In conclusion, the role of palladium in bimetallic Pt-Pd/Al₂O₃ catalysts could be interpreted on the basis of a mechanism involving hydride coordination by platinum and with the competition of palladium to occupy the oxidizing centers on the alumina surface, decreasing the number of active platinum sites for the coordination of "hydride," and therefore the total rate of cyclohexane dehydrogenation.

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