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Platinum Catalysts Supported on Activated Carbons

II. Isomerization and Hydrogenolysis of *n*-Butane

F. RODRÍGUEZ-REINOSO,*[,1] I. RODRÍGUEZ-RAMOS,* C. MORENO-CASTILLA,†
A. GUERRERO-RUIZ,† AND J. D. LÓPEZ-GONZÁLEZ‡

**Departamento de Química Inorgánica, Universidad de Alicante, Alicante, Spain; †Departamento de Química Inorgánica, Universidad de Granada, Granada, Spain; and ‡Departamento de Química Inorgánica, Universidad Nacional de Educación a Distancia, Madrid, Spain*

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A series of carbon-supported Pt catalysts prepared using different precursors and methods and covering a wide range of metal dispersion (0.08–0.51) have been studied in the reaction of *n*-butane with hydrogen. These are basically hydrogenolysis catalysts in which the splitting of the terminal C–C bond predominates. The hydrogenolysis of *n*-butane is a reaction sensitive to the structure of the catalysts, whereas this is not the case for isomerization. The selectivity for hydrogenolysis increases with decreasing mean Pt particle size. The apparent activation energies for the two reactions (larger for isomerization) are independent of particle size. © 1987 Academic Press, Inc.

INTRODUCTION

The reactions of hydrocarbon reforming catalyzed by metals are very important in oil refining for obtaining high-octane gasolines and the study of catalysts whose activity and selectivity might be related to their metallic structure is consequently of interest.

There have been many reports in the last few years about the reactions of hydrogenolysis and isomerization of hydrocarbons catalyzed by noble metals, especially Pt (*1–8*). Most of these studies were aimed at determining the mechanism by which the rearrangement or splitting of the hydrocarbon chain takes place and also at relating the catalytic activity to the metal particle size. A general conclusion found by many authors is that in many cases the reactions are structure sensitive.

The characteristics of a series of Pt catalysts supported on activated carbons prepared using different precursors and methods and covering a wide range of Pt dispersion (0.08–0.51) have been described in a previous paper (*9*). The behavior of some of these catalysts toward the reaction of *n*-butane with hydrogen in which both hydrogenolysis and isomerization are simultaneously taking place is described in this paper.

EXPERIMENTAL

The preparation and characterization of the catalysts have been reported in a previous paper (*9*); it suffices here to mention that all catalysts have about 1% Pt loading and have been prepared from H_2PtCl_6 $6H_2O$ or $Pt(NH_3)_4Cl_2$, the supports being activated carbons with a wide range of porosity (all of them prepared from almond shells and olive stones); carbons from these sources seem to be very appropriate for catalyst supports since they are granular, their porosity can be tailored, and they have very low ash content (*9–12*). The Pt particle size of the catalysts ranged from 13.5 to 2.1 nm (*9*).

The butane–H_2 reaction has been studied in a glass, plug-flow microreactor; about 1 g of catalyst was introduced into the reactor, the reactant gases flowing through it in the

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[1] Author to whom correspondence should be addressed.

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TABLE 1

Dispersion and Particle Size for Supported Pt Catalysts

Catalyst	D (H_2)	$\bar{d}$ (H_2) (nm)
C1–0.95% Pt	0.18	6.0
C1–0.86% Pt	0.27	4.0
C2–0.86% Pt	0.51	2.1
C3–0.83% Pt	0.42	2.6
C3(H_2O)–0.91% Pt	0.41	2.6
C3–1.32% Pt(N)	0.08	13.5
C4–0.90% Pt	0.30	3.6
H1–0.91% Pt	0.42	2.6
H2–0.93% Pt	0.50	2.2
H2–0.93% Pt[a]	0.40	2.7
H3–0.88% Pt	0.35	3.1
H4–0.80% Pt	0.33	3.3
H5–0.86% Pt	0.26	4.2

[a] Reduced at 773 K for 1 h.

ascending direction. The reaction was generally carried out at temperatures ranging from 573 to 623 K; the temperature of the reactor was kept within ±0.5 K by means of a fluidized sand bath (Techne, SB5-4). The pretreatment of the catalysts has already been described (*9*) and the reduction conditions were taken as 12 h at 673 K using a H_2 flow of about 50 cm^3 min^{-1}. After reduction the sample was cooled in flowing hydrogen to the reaction temperature before introducing the $H_2/n\text{-}C_4H_{10}$ (10/1 ratio) mixture. The flows of H_2 and $n\text{-}C_4H_{10}$ were controlled by mass flow controllers (Hasting-Raydist).

In order to reach steady-state conditions in the reactor, the reactant gases were flowed through the catalyst for 30 min before analyzing the reaction products; after the analysis only H_2 was flowed through the catalysts for 20 min in order to regenerate and clean the platinum surface (*13*); after this process the $H_2/n\text{-}C_4H_{10}$ mixture was again introduced into the reactor in order to study the reaction at different temperatures. The gases were analyzed by gas chromatography (Perkin-Elmer, 3920-B) using Chromosorb 102 columns. The flame detector was previously calibrated with standard gas mixtures (Supelco). The reactor was operated at atmospheric pressure and conversion was kept low, below 15%.

The activity for both hydrogenolysis and isomerization was calculated from the expression

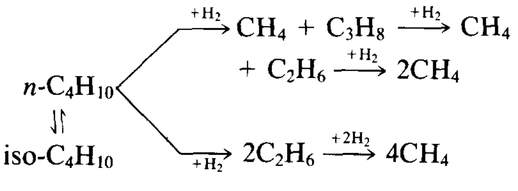
$$r_x = 44.61 \cdot \frac{P_x \cdot F_{n\text{-}C_4H_{10}}}{W},$$

where r_x is the activity for isomerization (r_I) or hydrogenolysis (r_H) (in μmol s^{-1} g^{-1}), P_x is the proportion of n-butane converted to iso-butane (P_I) or the proportion undertaking hydrogenolysis (P_H), $F_{n\text{-}C_4H_{10}}$ is the flow rate (in cm^3 min^{-1}) of n-butane through the reactor, and W is the weight (in g) of the catalyst.

RESULTS AND DISCUSSION

Metal dispersion (D) and mean particle size ($\bar{d}$) of the catalysts, as determined by H_2 chemisorption at 298 K, are given in Table 1; the validity of these results was discussed in a previous paper (*9*). All catalysts described except two were prepared using an incipient wetness technique and $H_2PtCl_6 \cdot 6H_2O$ dissolved in a benzene–ethanol mixture; catalyst C3(H_2O)–0.91% Pt was prepared using water as solvent and catalyst C3–1.32% Pt(N) was prepared from $Pt(NH_3)_4Cl_2$ dissolved in water. All catalysts were reduced in H_2 at 673 K for 12 h before characterization.

The $H_2/n\text{-}C_4H_{10}$ reaction catalyzed by Pt yields iso-butane and degradation products (propane, ethane, methane) simultaneously according to the following scheme:



Since n-butane has only four carbon atoms the formation of cyclic isomerization products is not probable, the only isomerization product being iso-butane. This reaction is produced in the presence of H_2

which is believed to regulate the concentration of surface intermediates of different degrees of dissociation (*14, 16*).

The hydrogenolysis of *n*-butane might take place through the rupture of a terminal C–C bond yielding CH_4 and C_3H_8 or by the rupture of the central C–C bond producing ethane; in the first case, the propane produced might in turn undergo hydrogenolysis to yield ethane and methane, the former being later degraded to methane. However, it has been shown (*14*) that in the temperature range covered here Pt/Al_2O_3 catalysts exhibit a lower reactivity for the hydrogenolysis of propane and ethane than for butane. Table 2 shows that the percentages of methane and propane produced are practically coincident in all cases. It is then possible to assume that the methane obtained in the reaction is produced by terminal C–C bond splitting and that there is no multiple hydrogenolysis of *n*-butane as happens in the case of Ni catalysts (*17, 18*), which has been attributed to demethylation. It has also been assumed that the secondary reaction of iso-butane hydrogenolysis has not essentially modified the product distribution. At this point it should be noted that when the supports (reduced under the same experimental conditions as the catalysts) were tested in the $H_2/n\text{-}C_4H_{10}$ reaction no activity was detected.

The catalytic activities of the different catalysts were used to calculate the turnover frequency (N_I for isomerization and N_H for hydrogenolysis) which is the most adequate parameter to characterize and compare metal catalysts with different metal dispersion. The N_I and N_H values listed in Table 2 have been calculated from r_I and r_H obtained at 603 K, the number of surface metal centers being obtained from the H_2 chemisorption measurements at 298 K (*9*).

The effect of Pt particle size on the turnover frequency is of special interest. The

TABLE 2

Turnover Frequency and Selectivity for the *n*-Butane/H_2 Reaction at 603 K

Catalyst	Turnover frequency (s^{-1})		Selectivity		Product distribution (%)[a]			
	$N_I \times 10^3$	$N_H \times 10^3$	S_I[b]	S_E[c]	C_1	C_2	C_3	*i*-C_4
C1–0.95% Pt	1.9	3.5	0.35	0.27	29	22	31	18
C1–0.86% Pt	2.4	8.4	0.22	0.27	31	23	33	13
C2–0.86% Pt	1.4	6.9	0.17	0.25	33	23	35	9
C3–0.83% Pt	1.8	6.6	0.21	0.26	32	23	34	12
C3(H_2O)–0.91% Pt	1.7	9.1	0.15	0.20	35	19	37	8
C3–1.32% Pt(N)	0.9	0.8	0.54	0.29	23	18	23	36
C4–0.90% Pt	1.5	4.7	0.24	0.24	32	20	34	14
H1–0.91% Pt	2.0	11.3	0.15	0.27	33	25	34	8
H2–0.93% Pt	1.1	10.2	0.10	0.26	34	25	36	5
H2–0.93% Pt[d]	1.5	10.2	0.13	0.31	31	29	33	7
H3–0.88% Pt	1.7	6.6	0.20	0.24	33	21	35	11
H4–0.80% Pt	1.9	5.9	0.26	0.23	32	20	34	14
H5–0.86% Pt	2.2	6.1	0.27	0.22	32	19	34	16

[a] Calculated as mole percentage of products.

[b] Selectivity for isomerization; $S_I = N_I/(N_I + N_H)$.

[c] Selectivity for ethane production; $S_E = (C_2/2)/(C_1/4 + C_2/2 + 3C_3/4)$.

[d] Reduced at 773 K for 1 h.

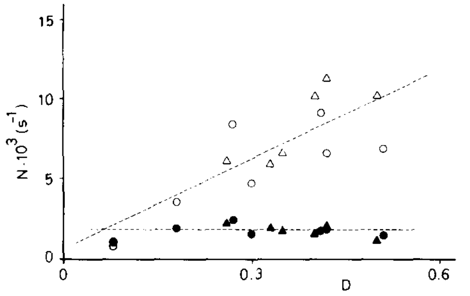


FIG. 1. Turnover frequency for catalysts of series H (△) and series C (○) as a function of metal dispersion. Open symbols, hydrogenolysis of *n*-butane; solid symbols, isomerization.

results of Table 2 show that N_I values are within a narrow range, whereas those of N_H are much more spread. The effect of metal dispersion is better shown in Fig. 1 where it is seen that N_I in fact remains almost constant in the 0.08–0.51 dispersion range; this means that the catalytic activity for isomerization seems to be insensitive (*19*) to the size and geometry of the metal crystallites, being only a function of the number of Pt atoms accessible to the reactants.

The evolution of N_H with metal dispersion is different from that of N_I and Fig. 1 shows what seems to be an increase in N_H for increasing metal dispersion; this could indicate that hydrogenolysis of *n*-butane may be catalyzed by specific active centers with adequate geometry and disposition, independent of the specific surface area of the metal. This implies that this reaction is "demanding," i.e., sensitive to the geometry of the metal catalysts. This is in agreement with the results obtained for Pt/Al_2O_3 catalysts (*20, 23*).

Since N_I is almost independent of metal dispersion but N_H is not, the selectivity for isomerization will also change for the different catalysts. This is shown in Fig. 2, where the data obtained at 603 K have been plotted. As the metal particle size decreases (increasing dispersion) the isomerization of *n*-butane is less favored than hydrogenolysis (there is a fivefold decrease in S_I in the 0.08–0.51 dispersion range). In other words, since N_I remains almost constant, a decrease in the mean metal particle size will favor the hydrogenolysis reaction. On the other hand, although the splitting of the *n*-butane chain may take place at either the terminal or the central C–C bond, the S_E values (selectivity for the production of ethane) of Table 2 ranging from 0.20 to 0.31 indicate that approximately only 20–30% of the *n*-butane molecules undergo hydrogenolysis by rupture of the central C–C bond, and, consequently, the splitting of the most of *n*-butane molecules is taking place in the terminal C–C bond when these catalysts are used.

It has been previously postulated (*24*) that the case of the rupture of a terminal as opposed to a central C–C bond may be affected by the support; thus, it was shown that whereas Pt/C catalysts basically produce the rupture of terminal C–C bonds in *n*-hexane this is not the case for Pt/Al_2O_3 catalysts. It then seems that for both *n*-hexane and *n*-butane the carbon support may be in part responsible for the preference in splitting terminal C–C bonds.

These results could be explained according to a mechanism (*25–28*) in which hydrogenolysis takes place through an adsorbed π-allyl complex requiring only one surface Pt atom:

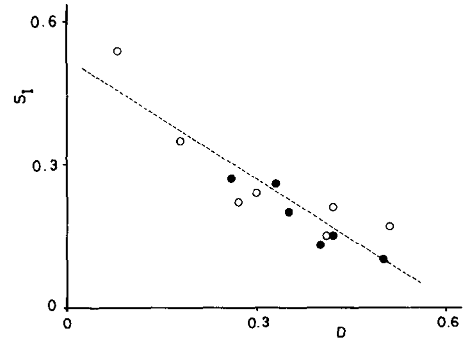
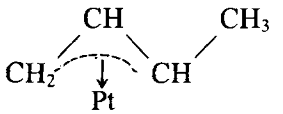


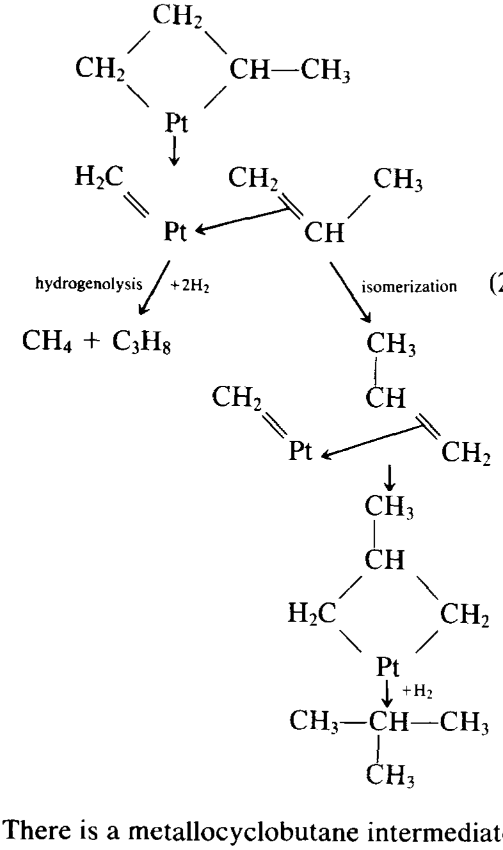
FIG. 2. Selectivity toward isomerization of *n*-butane as a function of metal dispersion. Open symbols, series C; solid symbols, series H.



(1)

The formation of this intermediate has been postulated for the hydrogenolysis of saturated hydrocarbons on Pt (*14, 29, 30*) for which the presence of olefin species on the surface of the catalysts during the reaction has been shown by IR. Following Foger and Anderson (*28*) and Somorjai (*31*), the active metal centers are the Pt atoms of low coordination number located on the apices, edges, and surface defects of metal crystallites.

The reaction mechanism may also be described by the so-called "iso-type" model which is valid for *n*-butane on other metals (*32*).



(2)

There is a metallocyclobutane intermediate and hydrogenolysis takes place by hydrogenation of the methylene group and the π-olefin bond producing basically methane and propane. This mechanism would explain the isomerization of *n*-butane which would require the rotation of the π-bond of the intermediate, the formation of the C_3 cycle, and desorption by means of H_2 addition.

Both mechanisms could take place on the same catalysts; mechanism (1) may explain the hydrogenolysis products (internal fission or terminal splitting) and mechanism (2) may explain isomerization and the larger abundance of methane and propane in the hydrogenolysis. In both cases, the intermediate is produced by either a π-allyl (mechanism (1)) or a π-olefin (mechanism (2)) complex which according to the Dewar–Chatt–Duncanson model (*33*) is formed by a dative π-bond from the hydrocarbon to empty *d*-orbitals of the metal and a retrodonating π-bond from the filled *d*-orbitals of the metal to the empty antibonding π^* of the hydrocarbon; both bonds are reinforced by a synergic mechanism.

The above results indicate that the hydrogenolysis of *n*-butane is favored by a decrease in mean Pt particle size. This tendency could possibly be due (although there is no experimental evidence) to a stronger adsorption of reaction intermediate (π-allyl or π-olefin complexes of mechanisms (1) and (2), respectively) on smaller Pt particles which have different electronic properties than those of the larger particles (*20, 34*).

Arrhenius plots were used to calculate the apparent activation energy for isomerization (E_I) and hydrogenolysis (E_H). A typical example of such plots for catalyst H4–0.80% Pt is shown in Fig. 3; the numbers for the experimental points indicate the order in which they were determined and there is good agreement for data obtained in increasing and decreasing temperature cycles. This is a good indication of the fact that in the experimental procedure followed the Pt surface is clean in each activity measurement and that there is no deactivation of the catalyst. The activation energies and the corresponding frequency factors (ln A_I

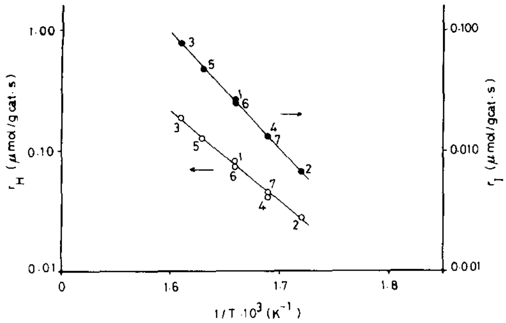


FIG. 3. Arrhenius plots for catalyst H4–0.80% Pt reduced for 12 h at 673 K. Open symbols, r_H; solid symbols r_I.

and ln A_H) can be found in Table 3. The activation energy is larger for the isomerization reaction, indicating again that hydrogenolysis is the preferred reaction with the catalysts described here. Both E_I and E_H are in a relatively narrow range for all the catalysts and this indicates that in the metal dispersion range covered there is no change in the reaction mechanism which is taking place.

CONCLUSIONS

The carbon-supported Pt catalysts described here are basically hydrogenolysis catalysts in which the splitting of the terminal C–C bond predominates. The hydrogenolysis of *n*-butane is a reaction sensitive to the structure of the catalysts, but this is not the case for isomerization. The selectivity for hydrogenolysis increases with decreasing mean Pt particle size. The apparent activation energies for the two reactions (larger for isomerization) are independent of particle size and consequently there are no changes in the reaction mechanism in the dispersion range studied (0.08–0.51).

TABLE 3

Activation Energy and Frequency Factors for the *n*-Butane/H_2 Reaction

Catalyst	Temperature range (K)	Activation energy (kJ mol⁻¹)		ln A_I	ln A_H
		E_I	E_H		
C1–0.95% Pt	573–623	191	172	35	30
C1–0.86% Pt	573–623	201	155	36	29
C2–0.86% Pt	573–623	215	168	39	32
C3–0.83% Pt	573–623	208	179	38	34
C4–0.90% Pt	583–623	210	168	38	31
C3(H_2O)–0.91% Pt	583–623	174	141	31	26
C3–1.32% Pt(N)	603–643	183	173	31	29
H1–0.91% Pt	573–613	196	141	36	27
H2–0.93% Pt	573–613	207	159	38	30
H2–0.93% Pt[a]	573–613	193	154	35	29
H3–0.88% Pt	573–623	201	156	36	29
H4–0.80% Pt	583–623	188	151	34	38
H5–0.86% Pt	583–623	176	164	31	30

[a] Reduced at 773 K for 1 h.

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