Surface Interaction in the Pt/γ-Al₂O₃ System. III. The Reaction of Neopentane with H₂

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The reaction of neopentane with hydrogen over a Pt/γ-Al₂O₃ catalyst is examined as a function of Pt-loading in the range of 0.48 to 12.3 μmol/m² (BET). It is found that the turnover frequency and the activation energy are not significantly different when the Pt changes from a dispersed phase to a particulate phase but the product distribution is affected. While the dispersed phase catalyzes only a stepwise hydrogenolysis to yield isobutane, propane, ethane, and methane, the particulate phase promotes mainly an isomerization to form isopentane which is then hydrogenolyzed to *n*-butane, isobutane, propane, ethane, and methane. A large increase of isomerization selectivity has been achieved by sintering the catalyst in H₂ at 500°C or by increasing Pt concentration in the particulate phase.

INTRODUCTION

The reaction of neopentane with H₂ over a supported Pt catalyst has been a subject of several investigations (*1–4*). Earlier, Boudart et al. (*1, 2*) found that the reaction of neopentane with H₂ over a supported Pt catalyst proceeded by two parallel paths: isomerization to isopentane and hydrogenolysis to isobutane and methane. The ratio of the rate of isomerization to that of hydrogenolysis, defined as the selectivity, varied by a factor of 100 for the catalysts studied and increased with catalyst pretreatment temperature from 425 to 900°C. Recently, Foger and Anderson (*3, 4*) studied the same reaction over a supported Pt catalyst having d_{Pt} (avg diameter of Pt particles) in the range of 1 to 20 nm. They found also that the selectivity decreased with the decrease of d_{Pt} while the activation energy increased. They concluded that there are two reaction paths for neopentane: one is the isomerization on low index faces of the crystallites and the other is the hydrogenolysis on Pt surface atoms of low coordination.

Recently, in this laboratory (*5, 6*), a series of Pt/γ-Al₂O₃ catalysts with various Pt concentrations was characterized. By using temperature-programmed reduction, transmission electron microscopy, and selective chemisorption, it was established that the Pt deposited on γ-Al₂O₃ is present in two phases, a two-dimensional dispersed phase and a three-dimensional particulate phase. At Pt concentrations below 2.2 μm Pt/m² (BET) and after calcination in O₂ at 500°C, all the Pt is in the dispersed phase. At high Pt concentrations and after calcination in O₂ at 500°C, the Pt in the dispersed phase reaches a saturation concentration and is in equilibrium with the excess Pt in the particulate phase. Reduction by H₂ at 300°C does not alter significantly these distributions but reduction at 500°C aggregates the Pt in the dispersed phase. Difference of properties between Pt in the two phases was shown by studies of chemisorption of CO (*7*) and of the reduction of NO by H₂ (*8*). Thus, it was shown from an ir study that CO molecules chemisorbed on Pt in the particulate phase were thermally more stable than those in the dispersed phase. In the NO reduction by H₂, it was indicated that the Pt in the particulate phase was more reactive than the Pt in the dispersed phase.

In the present work, the structure-sensitive reaction of neopentane with H₂ over Pt is reexamined to differentiate the catalytic

behavior of Pt in the two distinct and well-characterized phases.

EXPERIMENTAL

The preparation of the γ-Al$_2$O$_3$ support and the deposition of Pt from aqueous H$_2$PtCl$_6$ solution onto the support have been described elsewhere (5, 6). The catalysts were initially calcinated in air at 500°C for 3 hr, then reduced in H$_2$ at 300°C for 1 hr before use. The apparatus and the procedure for rate measurements and the products analysis used in this study were the same as those used in the previous one (9).

A Pyrex batch-recycle reactor equipped with a reciprocating glass pump and a Dynasciences pressure transducer, described previously (12), was used for the rate measurements. The circulation rate was approximately 420 cm^3 min^{-1}, and the system volume was 590 ml. The reacting gases were premixed at a ratio H$_2$: hydrocarbon = 10 and stored in a 5-liter flask. Before the rate measurement, the gas mixture of 110 Torr was introduced into the recycle reactor containing the Rh/γ-Al$_2$O$_3$ catalyst and was further diluted with helium to increase the total pressure to about 750 Torr. During the reaction, the gases passed through an injection valve connected to a gas chromatograph equipped with an ionization detector. The injected gas sample, approximately 0.2 ml, was split into two streams. One half was analyzed for individual hydrocarbons by separation over a ¼-in. diameter, 20-ft long column filled with 10% DC-200 (Alltech Associates) supported on 60/80 mesh Gas Chrom Q (Applied Science Laboratories) and the other half passed directly to the ionization detector. A hydrocarbon gas mixture of a known composition was used to calibrate the system.

RESULTS AND DISCUSSION

I. Reaction Rate and Turnover Frequency

The overall reaction rates and turnover frequencies, determined from the initial rate of neopentane consumption at 252°C over five Pt/γ-Al$_2$O$_3$ catalysts of different Pt-loading, are summarized in Table 1. The overall reaction rate, $-d$(neo-C$_5$)/dt, increases with Pt-loading, reaching a maximum at the saturation concentration of Pt in the dispersed phase (~2.2 μmol Pt/m^2 (BET) (5)). With further increase of Pt-loading, the overall rate declines. These results show that the overall reaction rate over Pt in the particulate phase is slightly lower than that over Pt in the dispersed phase. This difference of overall rate is apparently too small to give a clear distinction in terms of turnover frequency and activation energy (Table 1).

II. Product Distribution and Reaction Paths

The product distribution and the path of the reaction of neopentane with H$_2$ over Pt/γ-Al$_2$O$_3$ catalyst of various Pt-loading

TABLE 1

Kinetic Data

Catalyst	Pt-Loading		Active sites[a] (μmol/m^2 (BET))	Rate (Torr/min · m^2 (BET))	Turnover frequency (sec × 10^4)	E_a (kcal/mol)
	wt% Pt	μmol/m^2 (BET)				
2	1.64	0.48	0.48	1.8 × 10^{-4}	2.20	24.2
3	3.30	1.17	1.17	4.6	2.27	—
4	7.39	2.82	2.2	10.9	2.85	—
5	13.8	4.60	2.2	8.2	2.15	—
6	23.1	12.30	2.2	7.0	1.85	25.4

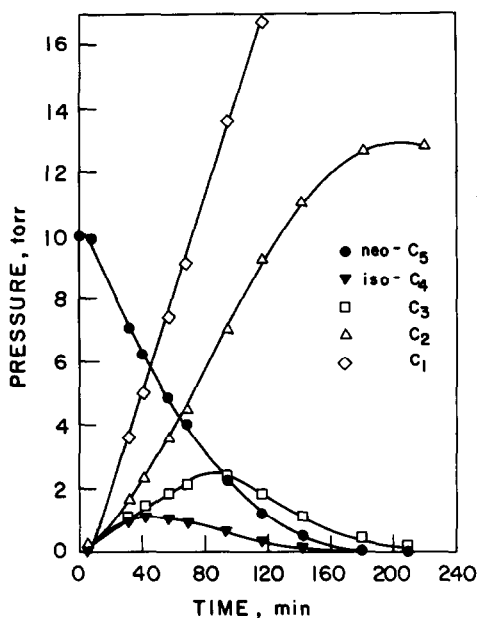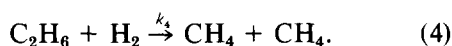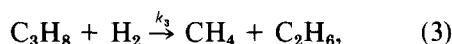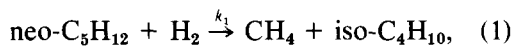[a] The active sites were determined previously by H$_2$ and CO chemisorption (see Ref. (5)).

FiG. 1. Reaction of neopentane with H_2 over a 1.2-μmol Pt/m² (BET) catalyst at 252°C.

have been examined by measuring the partial pressure changes of neopentane and all reaction products up to ~90% completion. The results indicate that both the product distribution and the reaction path vary with the Pt-loading of the catalysts. Distinct differences are found between catalysts of low Pt-loading (below ~2 μmol Pt/m² (BET)) and those of high Pt-loading ($\geq$ 2.8 μmol Pt/m² (BET)) as noted below.

A. Catalysts of low Pt-loadings. Over Pt/γ-Al$_2$O$_3$ catalysts of Pt-loading below 2 μmol Pt/m² (BET) only hydrogenolysis products are observed: methane, ethane, propane and isobutane. A typical example is given in Fig. 1. The partial pressure of neopentane decreases and that of methane increases throughout the reaction but the partial pressures of isobutane, propane, and ethane each increase initially and pass through a maximum with time. No carbon deposits are formed and all reacted neopentane is transformed into lower hydrocarbons. Although the relative amounts of the products change in time, the following relationship holds at all times:

$$5(p^0_{C_5H_{12}} - p_{C_5H_{12}})$$
$$= 4p_{C_4H_{10}} + 3p_{C_3H_8} + 2p_{C_2H_6} + p_{CH_4},$$

where $p^0_{C_5H_{12}}$ is the initial partial pressure of neopentane and the p's are the partial pressures of the reactants and products at any time in the reaction. These results indicate a stepwise reaction according to the following scheme:

$$\text{neo-}C_5H_{12} + H_2 \xrightarrow{k_1} CH_4 + \text{iso-}C_4H_{10}, \quad (1)$$

$$\text{iso-}C_4H_{10} + H_2 \xrightarrow{k_2} CH_4 + C_3H_8, \quad (2)$$

$$C_3H_8 + H_2 \xrightarrow{k_3} CH_4 + C_2H_6, \quad (3)$$

$$C_2H_6 + H_2 \xrightarrow{k_4} CH_4 + CH_4. \quad (4)$$

A similar sequence was observed previously over Rh/γ-Al$_2$O$_3$ catalysts of both low and high Rh-loading (1.22–5.62 μmol Rh/m² (BET)) for which a rate expression has been given (9) as

$$- \frac{dP_{\text{alkane}}}{dt} = kP_{\text{alkane}}P_{H_2}^{-1.5} . \quad (5)$$

This rate expression was verified not only for the hydrogenolysis of neopentane and *n*-pentane over Rh (9), Pt (10), Ru (10), and Ir (10) catalyst, but also for the hydrogenolysis of ethane over Pt and Rh catalysts (11). By using the rate expression, Eq. (5), the k_1 values of Eq. (1) can be obtained from the initial rate of neopentane consumption (Table 1, for example) and the other k values in Eqs. (2), (3), and (4) can then be derived from the three rate maxima (see Fig. 1, for example). At the respective maxima the rates of formation of the three hydrogenolysis intermediates becomes zero, i.e.,

$$\left[\frac{dP_{C_4H_{10}}}{dt}\right]_{\text{max}-1} = \left[\frac{dP_{C_3H_8}}{dt}\right]_{\text{max}-2}$$
$$= \left[\frac{dP_{C_2H_6}}{dt}\right]_{\text{max}-3} = 0 \quad (6)$$

and the ratios of the rate constants can be derived as follows (9)

$$\frac{k_1}{k_2} = \left[\frac{P_{C_4H_{10}}}{P_{C_5H_{12}}}\right]_{max-1} \quad \frac{k_2}{k_3} = \left[\frac{P_{C_3H_8}}{P_{C_4H_{10}}}\right]_{max-2}$$

$$\frac{k_3}{k_4} = \left[\frac{P_{C_2H_6}}{P_{C_3H_8}}\right]_{max-3} \quad . \quad (7)$$

By measuring the initial rate of the disappearance of neopentane and the partial pressures of C_5H_{12}, C_4H_{10}, C_3H_8, and C_2H_6 at the three maxima in plots such as shown in Fig. 1, all the four rate constants can be obtained from Eq. (7). The four rate constants, k_1 to k_4, measured in this fashion for the hydrogenolysis of neopentane over a 0.48-μmol Pt/m² (BET) catalyst at two different reaction temperatures are summarized in Table 2.

B. *Catalysts of high Pt-loadings.* The reaction of neopentane with H_2 over a 2.8-μmol Pt/m² (BET) catalyst may serve as an example of high Pt-loading. The change of partial pressures of reactant as well as the products as a function of time for the reaction of neopentane with H_2 over a 2.8-μmol Pt/m² (BET) catalyst (reduced at 300°C in H_2) is plotted in Fig. 2A. The distinct difference in this case compared to the same reaction but over a catalyst of a lower Pt-loading is the appearance of a small amount of isomerization products, isopentane and *n*-butane (Fig. 2A). For the other reaction products, the distribution appears similar. That is, the partial pressure of neopentane decreases and that of methane increases with time throughout the reaction but those of isobutane, propane, and ethane increase initially and pass through a maximum.

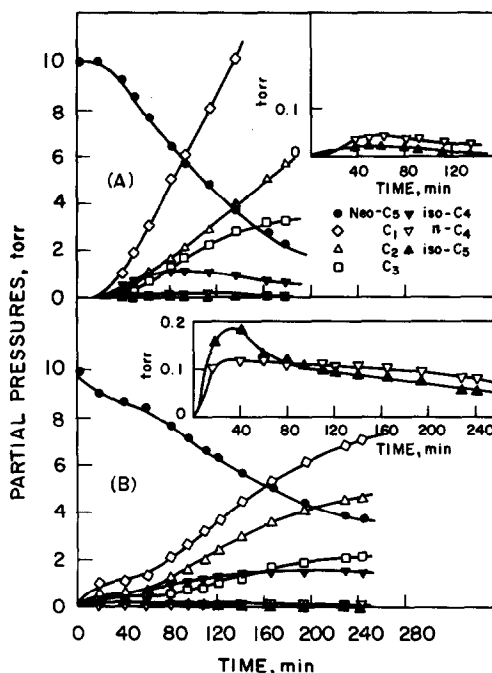Heating the catalyst in flowing H_2 at 500°C for 2 hr lowers the overall activity

FIG. 2. Reaction of neopentane with H_2 over a 2.8-μmol Pt/m² (BET) catalyst at 252°C. (A) catalyst reduced by H_2 at 300°C for 2 hr. (B) catalyst reduced by H_2 at 500°C for 2 hr. (C), (D) are enlarged portions of (A) and (B), respectively.

and changes significantly the product distribution (Fig. 2B). Both the partial pressures of isopentane and *n*-butane attain the peak values which are four times higher than those in Fig. 2A. The increase of partial pressures of other products, methane, ethane, propane, and isobutane, is markedly attenuated and no maxima are reached after 240 min of reaction.

The isomerization activity of the catalyst can be enhanced further by an increase of Pt-loading. Figure 3 shows the results of a catalyst of very high Pt-loading (61 wt% Pt or 36.8 μmol Pt/m² (BET)). This catalyst, which is not included in Table 1, gives a much higher yield of isopentane, compared to the catalyst of lower Pt-loading, and a small amount of *n*-pentane. Also, the pressure maxima for ethane, propane, and isobutane formation disappear. Thus, the higher the Pt-loading of the catalyst the more significant are the isomerization of
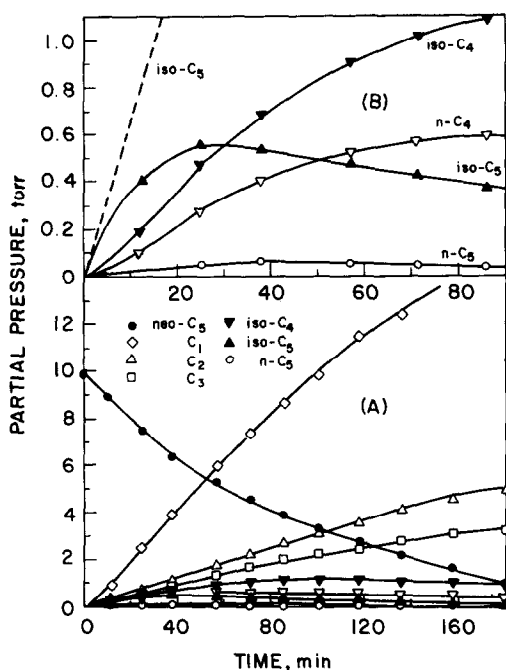
TABLE 2

Rate Constants for Hydrogenolysis of Neopentane over a 0.48-μmol Pt/m² (BET) Catalyst

T (°C)	Rate constants $Torr^{1.5}$/min · m² (BET))			
	k_1	k_2	k_3	k_4
232	.00046	.00437	.00073	.000135
252	.0018	.0140	.0036	.00056

FIG. 3. Reaction of neopentane with H_2 over a 36.8-μmol Pt/m² (BET) catalyst at 252°C. Upper section (B) is an enlarged portion of the lower section (A). The broken line in (B) is the calculated amount of isopentane formation in a presumed absence of its subsequent hydrogenolysis.

pentane. These initial steps are then followed by further hydrogenolysis to form lower hydrocarbons. Earlier, Boudart *et al.* (*1, 2*) found that both hydrogenolysis and isomerization occurred in all neopentane reactions over various Pt catalysts and that the selectivity for isomerization, defined as the percentage of isomerization in this study, depended on the pretreatment temperature of the catalyst. By varying the pretreatment temperature from 425 to 900°C, the selectivity at low conversion (<1%) increased from 26 to 96. This increase in isomerization selectivity has been explained as due to the increasing triadsorption of neopentane on triplets of Pt atoms such as does occur on Pt(111) faces and at point defects, edges, and steps which are formed on the Pt surface in the course of heating at high temperature (*2*). Recently, Foger and Anderson (*3*) found that the isomerization selectivity depends also largely on the particle size. By varying the particle size from 1 to 20 nm, the selectivity increased from 4.1 to 70.2. They suggested
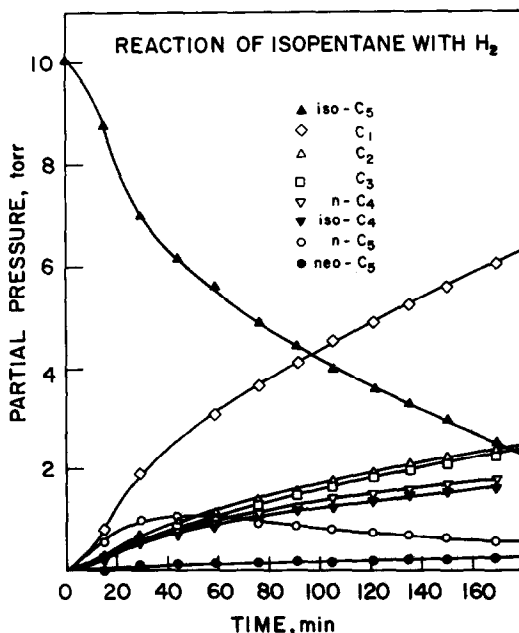
neopentane to isopentane and the subsequent hydrogenolysis of isopentane. For comparison with these results, the direct hydrogenolysis of isopentane over the same catalyst has been run and the products distribution for this reaction at 252°C is shown in Fig. 4. These results show that (i) isopentane is hydrogenolyzed to form methane, ethane, propane, *n*-butane, and isobutane at a rate comparable to that for neopentane, (ii) isopentane can also isomerize predominently to *n*-pentane and, to a smaller extent, to neopentane.

III. The Selectivity

In the previous studies of the reaction of neopentane with H_2 over a Pt catalyst, it has been generally assumed (*1–4*) that there are two parallel and simultaneous reaction paths: hydrogenolysis to form methane and isobutane and isomerization to form iso-

FIG. 4. Reaction of isopentane with H_2 over a 36.8-μmol Pt/m² (BET) catalyst at 252°C.

that isomerization of neopentane requires a surface site consisting of more than one platinum atom, at which the adsorbed intermediate consists of diadsorbed or triadsorbed neopentane, and the Pt(111) face in large particles appears to be particularly favorable for isomerization.

This work shows that the selectivity depends on the Pt-loading and the surface structure of the Pt/γ-Al$_2$O$_3$ catalysts. For the catalysts of Pt-loading lower than 2 μmol Pt/m^2 (BET), only a stepwise hydrogenolysis of neopentane to form isobutane, propane, ethane, and methane takes place. This indicates that the Pt in the two-dimensionally dispersed phase can catalyze only the hydrogenolysis reaction. For Pt/γ-Al$_2$O$_3$ catalyst of high Pt-loading (>2 γmol Pt/m^2) the hydrogenolysis is accompanied by an isomerization of neopentane to form isopentane. For the 2.8 μmol Pt/m^2 (BET) catalyst, where the surface Pt atoms are mainly in the dispersed phase, the hydrogenolysis still predominates. With increasing Pt-loading, the proportion of the surface Pt atoms in the particulate phase increases while that in the dispersed phase decreases. This shifts the reaction course toward the isomerization and the hydrogenolysis of isopentane (product of the isomerization) to form n-butane, isobutane, propane, ethane, and methane. Sintering of the catalyst by heating in H$_2$ at 500°C, or air at ≥600°C, which converts the dispersed phase into the particulate form, produces the same effect. As shown in Fig. 2, although the Pt-loading is the same, heating the catalyst in H$_2$ at 500°C lowers not only the activity for hydrogenolysis but also increases the activity for isomerization. Since only hydrogenolysis of isopentane produces n-butane, the amount of isopentane formed from the isomerization of neopentane can be estimated from the amount of n-butane produced. By comparing the n-butane formation in Fig. 4 with that in Fig. 3, an estimation for the "correct" isopentane

TABLE 3

Pt Catalysts of High Selectivity for Neopentane Reactions with H$_2$

Catalyst (wt% Pt)	Dispersion (%)	Selectivity (%)	Reference
Pt/μ-Al$_2$O$_3$ (1.96)	7.6	74	(1)
Pt/Spheron (1.0)	12	96	(1)
Pt(100)	0.028	90	(1)
Pt/Aerosil (0.9)	16	61, 48	(3)
Pt/Aerosil (0.9)	5.7	70, 60	(3)
Pt/γ-Al$_2$O$_3$ (61)	6	75	This study

formation is given in Fig. 3 (the broken line) and the selectivity is shown in Table 3. This selectivity is comparable to the values reported in Refs. (1) and (3) (see Table 3) for the catalysts of similar dispersion. Assuming an equal activity of Pt sites in the dispersed and in the particulate phase (see Table 1), these results indicate that about 75% of the surface Pt in this 36.8 μmol Pt/m^2 (BET) catalyst is in the particulate phase and the remainder is in the dispersed phase.

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