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Reactions of *n*-Butane and 2,2-Dimethylpropane on Silica-Supported Rh–Pt Bimetallic Catalysts

TEIK CHEN WONG,* LOUIS C. CHANG,* GARY L. HALLER,*
JAMES A. OLIVER,† NORMAN R. SCAIFE,† AND CHARLES KEMBALL†

**Department of Chemical Engineering, Yale University, New Haven, Connecticut 06520, and †Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, Scotland*

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Two series of highly dispersed Rh–Pt bimetallic catalysts supported on high-area silica have been prepared, characterized by adsorption of H_2 and CO and used in pulse, flow, or static reactor systems for the hydrogenolysis of *n*-butane and 2,2-dimethylpropane. Activity decreased markedly with increase of the Pt content of the catalysts by factors of 200 to 600 for the hydrogenolysis of 2,2-dimethylpropane and by factors of 4×10^3 to 10^4 for the reaction of *n*-butane. Both series of catalysts showed the same trends in the selectivity of the reactions with metal composition but exhibited some minor differences in absolute activity. The types of selectivity noted were the relative extent of multiple-bond cleavage to single-bond cleavage, the preferred position of bond cleavage with *n*-butane and the relative rates of isomerization and hydrogenolysis. Some comments are made on probable mechanisms of the reactions.

INTRODUCTION

We suggest that Rh–Pt bimetallic catalysts merit more attention than they have received so far for reactions of hydrocarbons related to reforming processes. First, the fact that Rh has an activity many orders of magnitude greater than Pt (*1*) for the hydrogenolysis of ethane indicated that a substantial variation in activity with metal composition is to be expected for the hydrogenolysis of other hydrocarbons. Consequently, such studies should be helpful in determining the relative importance of ensemble effects and electronic interactions in the catalytic behavior of the bimetallic catalysts. Second, Pt shows high activity for alkane isomerization (*2*) but Rh only exhibits such activity in special preparations where the hydrogenolysis activity has been severely suppressed (*3*). These very dissimilar catalytic properties of Rh and Pt make this bimetallic system of interest because of the additional mechanistic handle of variable selectivity across the composition series as well as the large change in activity.

In any study of bimetallic catalysts the possibility of some variation in properties due to different methods of preparation has to be considered. In the present work we have deliberately set out to study two independent preparations of the SiO_2-supported catalysts—one made at Yale, the other at Edinburgh—in order to determine what features were common to the two sets and which varied. The reactants selected were *n*-butane and 2,2-dimethylpropane and a number of different reactor systems were used again to see the extent to which common behavior was found in the different systems.

Much of the previous work on Rh–Pt catalysts has involved oxidation reactions since these catalysts are used commercially for the air oxidation of ammonia and the control of automobile exhaust (*4*). Two recent characterizations of Rh–Pt catalysts should also be noted. Wang and Schmidt (*5*) used X-ray photoelectron spectroscopy to examine the surface composition of Rh–Pt on planar amorphous SiO_2 following oxidation–reduction cycling. A similar study us-

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ing extended X-ray absorption fine structure has been made for Al_2O_3-supported catalysts by Broach *et al.* (*6*).

EXPERIMENTAL

Catalyst Preparation

Two series of Rh–Pt/SiO_2 catalysts, labeled the 100 and 500 Series, respectively, were prepared. Essentially all preparation variables were identical except for the Rh salt used which was $RhCl_3$ (Fischer Sci.) and $Rh(NO_3)_3 \cdot 2H_2O$ (Ventron Corp.) for the 100 and 500 Series, respectively. The Pt salt was $H_2PtCl_6 \cdot 6H_2O$ for all catalysts and was supplied by Ventron. For all catalysts the total molar metal loading was constant and equal to 10^{-4} mol/g silica. The silica support used was Davison grade 923 with a particle size between 100 and 200 mesh and a BET surface area of 600 m^2/g.

Catalysts were prepared by incipient wetness impregnation using 1 cm^3 solution per gram of silica. In a flat dish, the salt solutions (0.2 *M*) were pipetted into sufficient distilled water to provide approximately 1.0 cm^3/g silica. The solutions were stirred while adding the silica support. The impregnated silica was air-dried in the dark for 48 h and oven-dried at 383 K for 8 h. The primary reduction to metals was carried out in flowing H_2 (15 cm^3/min). Catalysts were purged with H_2 and the temperature was raised to 373 K for 1 h and then a high-temperature reduction at 723 K was maintained for 12 (100 Series) or 16 (500 Series) h. For the 100 Series adsorbed H_2 was removed by purging with He at the reduction temperature; the catalysts were cooled in He and slowly exposed to air at ambient temperature. The same procedure was used for the 500 Series except flowing He was replaced by evacuation. Hydrogen used for the 100 Series reduction was purified by diffusion through a Pd–Ag thimble; hydrogen for the 500 Series reduction was purified by a Deoxo unit (room temperature), molecular sieve trap (room temperature), and a liquid-N_2 trap in series.

Chemisorption and Activity Measurements

The chemisorption and pulse reactor experiments have been previously described in (*7*) and in more detail in the thesis of Wong (*8*). Several of the experiments were repeated using a flow reactor as described by Rouco and Haller (*9*). In order to approximate the partial pressures of the pulse reactor, a H_2 : hydrocarbon ratio of 19 : 1 was used, this being approximately the ratio obtained in the pulse reactor at the peak of the pulse. The H_2 : hydrocarbon ratio used in the static reactor was 10 : 1. Background pressures of 10^{-6} Torr were obtained with liquid-N_2-trapped Hg diffusion pumps. A hydrocarbon charge of 1.93×10^{19} molecules was expanded into a reactor of 185 cm^3 and the reaction followed by periodic sampling of 0.2 cm^3 (Carle valve) analyzed by flame ionization gas chromatography. Hydrocarbon separation was accomplished on a 3-m column of *n*-octane on Porasil "C" operated at ambient temperature with H_2 carrier gas. For each experiment in the static reactor an amount of 10–150 mg fresh catalyst sample was purged under flowing H_2 and reduced *in situ* at 673 K for 1 h. The catalyst was then evacuated at 673 K for 1 h and cooled under vacuum to the reaction temperature. The *n*-butane and 2,2-dimethylpropane used in the static reactor were supplied by Cambrian Chemicals (99.5%); they were degassed by freeze–pump–thaw cycles before use. Hydrogen was purified by diffusion through a heated Pd thimble.

RESULTS

Catalyst Characterization

The numbering of the catalyst in the two series and the H_2 and CO chemisorption results, H/M and CO/M, are presented in Table 1 and the CO/H ratios are compared for the two series of catalysts in Fig. 1. The CO/H ratios are 1.23 (average) and 0.93 on pure Rh in the 100 and 500 Series, respectively, and 0.79 and 0.71 on the pure Pt in

TABLE 1

Hydrogen and Carbon Monoxide Chemisorption

Catalyst No.	% Rh	H/M	CO/M
100	100	0.61	0.78
110	100	0.77	0.91
120	87.5	0.69	0.92
130	75	0.74	0.87
140	62.5	0.75	0.87
150	50	0.84	0.83
160	37.5	0.88	0.80
170	25	0.84	0.77
180	12.5	0.85	0.72
190	8.0	1.0	0.77
200	4.0	0.98	0.75
210	0	0.67	0.54
220	0	0.78	0.61
500	100	0.92	0.86
510	90	0.85	0.75
520	80	0.63	0.62
530	60	0.90	0.83
540	40	1.1	0.83
550	20	0.90	0.75
560	15	0.94	0.69
570	10	0.92	0.64
580	5	0.92	0.63
590	0	0.98	0.69

the 100 and 500 Series, respectively. If one assumes that the individual CO/H stoichiometries of Pt and Rh are retained in the bimetallics and attempts to estimate a surface composition, as we were able to do for Rh–Ir (*7*), we find that the surface and bulk compositions estimated in this manner are the same within a rather large experimental error. The errors are larger for the 500 Series because the pure Rh and Pt of this series have very similar CO/H ratios. The difference in the CO/H ratio and dispersion (percentage exposed based on H_2 chemisorption) is believed to be the result of the different anion of the Rh salt used in the two preparations. As we have previously noted in a study of Rh/SiO_2 (*10*), the CO/H chemisorption ratio is generally greater than 1 for Cl^- preparations and about 1 for NO_3^- preparations in agreements with our observations here for the bimetallic catalysts.

Catalytic Measurements with the Pulse and Flow Reactors

Rates of reaction of 2,2-dimethylpropane at 538 K and of *n*-butane at 465 K determined by the pulse system on the 100 Series of catalysts are shown in Fig. 2. The rate of reaction of 2,2-dimethylpropane was not significantly reduced by increases in the Pt content of the catalysts up to 40% but thereafter fell by more than a factor of 400; with *n*-butane the rate declined by 10^4 from Rh to Pt and again its decrease was more marked at the Pt-rich end of the series. Activation energies were determined for both reactants on all of the 100 Series catalysts by the pulse reactor and the values obtained

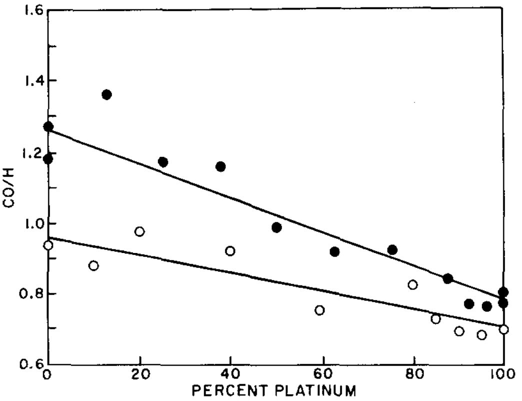

FIG. 1. Ratio of CO/H chemisorption: ●, 100 Series; ○, 500 Series.

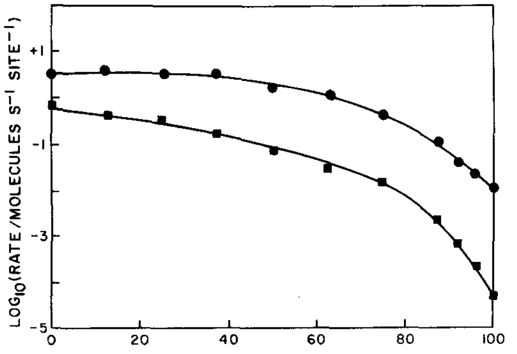

FIG. 2. Rates of reaction on the 100 Series of catalysts determined by the pulse reactor: ●, reaction of 2,2-dimethylpropane at 538 K; ■, reaction of *n*-butane at 465 K.

which showed little significant variation with catalyst composition are given in Table 2.

Data on the selectivities of the reaction followed by the pulse reactor are shown in Fig. 3. Some isomerization of 2,2-dimethylpropane to 2-methylbutane was observed on all catalysts but the amounts rose dramatically on the catalysts containing more than 90% Pt. With *n*-butane the main reaction on most of the catalysts was central-bond cleavage to form ethane and the percentage of propane in the product resulting from terminal-bond cleavage rose slowly as the Pt content was increased but again the major change occurred with more than 90% Pt.

The flow system was used to determine the rates and selectivities of the reactions of 2,2-dimethylpropane (538 K) and of *n*-butane (465 K) on the catalysts 100, 130, 180, 200, and 220. The absolute rate of reaction for 2,2-dimethylpropane was lower by a factor of about 8 in the flow system compared with the pulse system and a corresponding reduction by a factor of about 5 was observed for *n*-butane. But the relative rates on the various catalysts determined by the two systems agreed within a factor of 2 and furthermore the selectivities of the reactions were the same within experimental error for both systems. The activation energies found by the flow system are given in Table 2.

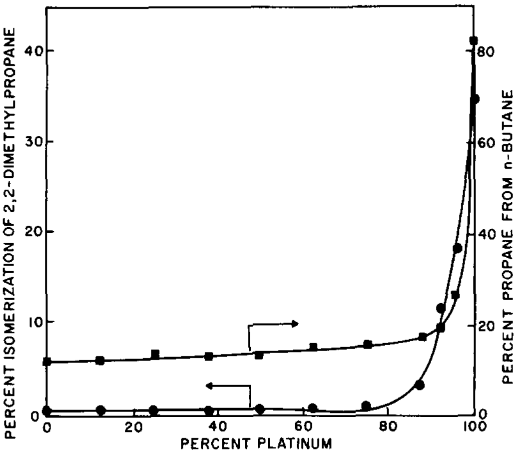

FIG. 3. Selectivities across the 100 Series of catalysts determined by the pulse reactor: ●, percentage isomerization of 2,2-dimethylpropane to 2-methylbutane at 538 K; ■, percentage propane from *n*-butane at 465 K.

TABLE 2

Activation Energies in kJ mol^{-1}

(Rh/Pt)	100 Series of catalysts				(Rh/Pt)	500 Series of catalysts	
	2,2-Dimethylpropane		*n*-Butane			2,2-Dimethylpropane static	*n*-Butane static
	Pulse	Flow	Pulse	Flow			
(100/0)	190	180	190	175	(100/0)	152 ± 5	174 ± 21
(87.5/12.5)	190		175				
(75/25)	205	185	200	170			
(62.5/37.5)	210		200				
(50/50)	210		190				
(37.5/62.5)	220		200				
(25/75)	225		210		(20/80)		135 ± 16
(12.5/87.5)	220		215	200	(15/85)		144 ± 34
(8/92)	220		200				
(4/96)	215	190	200	205			
(0/100)	190	175	180	(145)[a]	(0/100)	144 ± 5	136 ± 9

[a] Error ±40 kJ mol^{-1}.

Catalytic Measurements with the Static Reactor

Rates of reaction of 2,2-dimethylpropane at 463 K on both the 100 and 500 Series of catalysts are shown in Fig. 4. The variation in rate with catalyst composition was almost 600 with the 100 Series but only 200 with the 500 Series; both series showed more similar activity with Pt-rich catalysts than with Rh-rich catalysts. The variation in the rate of reaction of *n*-butane at 398 K with the 500 Series is also included in Fig. 4 and for this system there was a reduction in rate by 4 × 10^3 with increasing Pt content. Such activation energies as were determined are given in Table 2.

In the static system the selectivities of the reactions were measured as molecules of each product formed for each molecule of reactant used up and in each case it was possible to extrapolate the ratios back to zero conversion. Thus the selectivities reported in Tables 3 and 4 were initial values uncomplicated by any contributions from sequential reactions of the products first formed. The results for *n*-butane at 398 K in Table 3 again show the marked preference for central-bond cleavage as opposed to terminal-bond cleavage and also that this preference was not greatly reduced on catalysts with up to 85% Pt. But with pure Pt both terminal and central bonds appeared to cleave at identical rates leading to equal

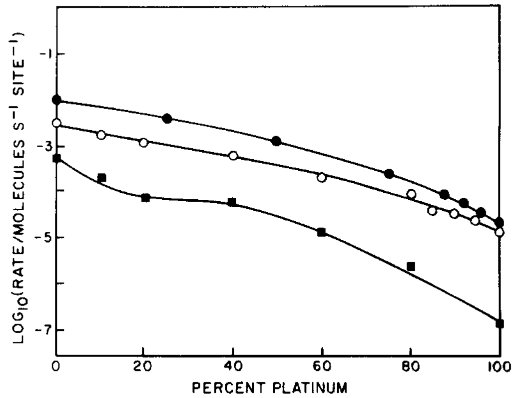

FIG. 4. Rates of reaction determined by the static reactor: ●, reaction of 2,2-dimethylpropane at 463 K on the 100 Series of catalysts; ○, reaction of 2,2-dimethylpropane at 463 K on the 500 Series; ■, reaction of *n*-butane at 398 K on the 500 Series.

TABLE 3

Selectivities for the Reactions in the Static Reactor on the 500 Series of Catalysts

Catalyst	(Rh/Pt)	Molecules product/molecule reactant used						
		2,2-Dimethylpropane at 463 K				*n*-Butane at 398 K		
		CH_4	C_2H_6	C_3H_8	C_4H_{10}[a]	CH_4	C_2H_6	C_3H_8
500	(100/0)	1.42	0.15	0.17	0.69	0.23	1.60	0.18
510	(90/10)	1.17	0.08	0.08	0.71	0.28	1.48	0.24
520	(80/20)	1.16	0.09	0.07	0.81	0.28	1.51	0.24
530	(60/40)	1.14	0.07	0.06	0.85	0.26	1.54	0.22
540	(40/60)	1.03	0.07	0.05	0.86	0.24	1.56	0.24
550	(20/80)	0.98	0.06	0.04	0.91	0.23	1.58	0.23
560	(15/85)	0.96	0.07	0.04	0.91	0.20	1.61	0.18
570	(10/90)	0.97	0.08	0.04	0.91			
580	(5/95)	0.92	0.10	0.05	0.88[b]			
590	(0/100)	0.85	0.02	0.04	0.82[c]	0.67[d]	0.67[d]	0.67[d]

[a] 2-Methylpropane.

[b] Also 0.03 2-methylbutane.

[c] Also 0.08 2-methylbutane and 0.05 *n*-butane.

[d] Extrapolated from results at higher temperatures.

TABLE 4

Selectivities for the Reaction of 2,2-Dimethylpropane at 463 K in the Static Reactor on the 100 Series of Catalysts

Catalyst	(Rh/Pt)	Molecules product/ molecules reactant used			
		CH_4	C_2H_6	C_3H_8	C_4H_{10}[a]
100	(100/0)	1.64	0.21	0.15	0.60
130	(75/25)	1.26	0.15	0.16	0.73
150	(50/50)	1.19	0.11	0.11	0.86
170	(25/75)	1.06	0.09	0.06	0.95
180	(12.5/87.5)	1.07	0.10	0.08	0.87
190	(8/92)	0.92	0.13	0.07	0.87[b]
200	(4/96)	0.89	0.18	0.08	0.88[c]
220	(0/100)	0.82	0.04	0.04	0.77[d]

[a] 2-Methylpropane.
[b] Also 0.02 2-methylbutane.
[c] Also 0.05 2-methylbutane.
[d] Also 0.07 2-methylbutane and 0.05 *n*-butane.

amounts of all three hydrogenolysis products.

There is good general agreement between the selectivities for the reaction of 2,2-dimethylpropane at 463 K on the 500 Series of catalysts (Table 3) and on the 100 Series (Table 4). The main reaction on all catalysts was a single-bond cleavage to give methane and 2-methylpropane but on Rh and Rh-rich catalysts some multiple-bond cleavage occurred and the relative amount of methane increased as the Pt content of the catalysts decreased. Small but significant amounts of ethane and propane were found on nearly all the catalysts but isomerization products were only observed over the Pt-rich members of the two series of catalysts.

DISCUSSION

The absence of any evidence for surface enrichment of the catalysts from the H_2 and CO chemisorptions is in agreement with results reported by Wang and Schmidt (*5*). No enrichment of the surface by Rh was detected by them on catalysts subjected to an initial reduction at 873 K although enrichment by as much as a factor of 3 was found with a (48/52) (Rh/Pt) catalyst but only after oxidation at 873 K and, once established, enrichment was not easily reversed by subsequent heating in H_2. We therefore assume that the overall composition of our catalysts is an adequate measure of their surface composition and we base our estimate of the number of metal sites on the data for hydrogen adsorption.

Turning to the catalytic results, a notable feature is the good agreement in the character of the results on the two series of catalysts and the minor differences in absolute activity found for the hydrogenolysis of 2,2-dimethylpropane at 463 K. The latter is probably attributable to the different Rh salts used in the preparation of the two series of catalysts. The activities of the Pt catalysts in the two series are the same and both were made from $H_2PtCl_6 \cdot 6H_2O$. The difference in activity between the two series of bimetallics increases up to a factor of 3 with increasing Rh content of the catalysts as shown in Fig. 4. A broadly similar effect has been noted for Ru catalysts prepared from different salts and used for the hydrogenolysis of ethane (*11*). A catalyst made from Davison 923 SiO_2 and $RuCl_3$ was some 2 to 3 times more active than a catalyst resulting from the impregnation of the same SiO_2 with solutions of $Ru(NO)(NO_3)_3$. Some of the factors which are important in the preparation of dispersed metal, oxide-supported catalysts have been discussed by Brunelle (*12*) and on the basis of his work it is perfectly reasonable to attribute differences in catalytic performance to the nature of the salts used in their preparation. The exact nature of the difference in metal particle surface resulting from Cl^- compared to NO_3^- anions of Rh^{3+} in the impregnation has not been identified. Phenomenologically the Cl^- preparation (100 Series) exhibits a weakening in Rh–H bonding relative to Rh–C bonding when compared to the NO_3^- preparation (500 Series). This is reflected in a higher CO/H ratio (Fig. 1) and possibly less hydrogen inhibition and hence higher hydrogenolysis activity (Fig. 4) on the 100 Series compared to the 500 Series.

We suggest that the greater variations in catalytic activity across the series for *n*-butane hydrogenolysis of 4×10^3 and 10^4 compared with the somewhat lower factors of 200, 400, or 600 for the reaction of 2,2-dimethylpropane may be associated with different mechanisms for the two reactions. Foger and Anderson (*13*) have distinguished two modes of hydrogenolysis on Ir catalysts, the C_2-unit and the iso-unit modes. The former has a lower activation energy but requires a larger ensemble of atoms to form the active site whereas the latter has a higher activation energy but may occur on a single Ir atom. The preferential cleavage of the central carbon–carbon bond in *n*-butane is some supporting evidence for a C_2-unit mechanism of hydrogenolysis for this reactant because the rate of this reaction is expected to be greater with a pair of secondary carbon atoms than with a primary and a secondary carbon atom. The marked decrease in activity, particularly with catalysts containing more than 85% Pt, suggests that Pt is not a very effective catalyst for the C_2-unit mechanism and also that an ensemble incorporating 2 or more Rh atoms may be required. A curious feature of the selectivity results for *n*-butane is that preferential central-bond cleavage is not appreciably influenced by Pt content until it exceeds 85–90%. Thus we have evidence that over a composition range from pure Rh down to only 15 to 10% of that metal the character of the reaction is not changing although the activity is falling by factors of more than 100. In general terms such results could be interpreted as the C_2-unit mechanism requiring an ensemble of, say, 4 metal atoms and ensembles consisting of only Rh atoms having greater activity than mixed ensemble containing one or more Pt atoms. In this way the character of the reaction would remain Rh-like over a considerable range of composition while the rate of reaction fell substantially.

Because of the nature of the molecule, the hydrogenolysis of 2,2-dimethylpropane cannot involve a C_2-unit mechanism but must occur by the iso-unit mode. Platinum is apparently a relatively more active catalyst for this type of mechanism than for the C_2-unit mechanism although it is still much less active than Rh. The consequence is that the overall fall in activity with catalyst composition is less dramatic with 2,2-dimethylpropane than with *n*-butane and the decrease for the Pt-rich catalysts is less marked. The shapes of the activity–composition curves in Figs. 3 and 4 are not consistent with the idea of a single metal atom of Rh as the active site but they may indicate that a smaller ensemble size is required for the iso-unit mechanism than for the C_2-unit process.

Several aspects of the selectivity results for the reaction of 2,2-dimethylpropane given in Tables 3 and 4 are worthy of comment. The good agreement between the data from the two series of catalysts has already been noted. The main reaction on the majority of the catalysts is the cleavage of one carbon–carbon bond to give as products a molecule of 2-methylpropane and a molecule of methane. But there is also some multiple carbon–carbon bond cleavage because the production of methane is always greater than the production of the C_4-molecule and this type of reaction is of increasing importance with catalysts containing 50% or more Rh and is particularly marked for the pure-Rh catalysts. Put another way, the methane to 2-methylpropane ratio is 1.1 on the pure-Pt catalysts and rises sharply on the Rh-rich catalysts to 2.1 and 2.7 on the pure Rh-catalysts in the 500 and 100 Series, respectively. This suggests that the higher activity of the 100 Series is mostly a result of greater activity for multiple-bond cleavage in the 100 Series.

The origin of ethane and propane as initial products from the reaction of 2,2-dimethylpropane on all catalysts except pure Pt is worth discussing. One possibility is that these smaller hydrocarbons arise by successive demethylation of the adsorbed species. If this process operated it follows that the minimum amount of methane would be given by $C_1 = C_4 + 2C_3 + 3C_2$, where C_n refers to the number of molecules of hydrocarbon with *n* carbon atoms produced from each 2,2-dimethylpropane molecule reacting. This mechanism might apply to the pure-Rh catalysts where the calculated minimum numbers of methane molecules on the 100 Series and the 500 Series are 1.53 and 1.48, respectively, and the experimental ratios are 1.64 and 1.42. But on some of the other catalysts, the experimental amounts of methane are not sufficient to support the suggestion of successive demethylation as the origin of ethane and propane. For example, the required minimum values of 1.50 and 1.53 would be needed for the 130 and 150 catalysts (Table 4) but the experimental values for methane were only 1.26 and 1.19, respectively.

We believe that a more probable source of the ethane and propane is from the cleavage of a carbon–carbon bond in an isomerized C_5 molecule on the catalysts surface and the first fact which supports this hypothesis is that the amounts of ethane and propane are about equivalent on the great majority of the catalysts. Our proposal is that all of the catalysts are capable of bringing about the isomerization of 2,2-dimethylpropane to other C_5 molecules but in the static reactor these products are only seen on those catalysts which are relatively inefficient at hydrogenolysis, i.e., the Pt-rich catalysts. On all the other catalysts, the isomerized C_5 species on the surface suffers carbon–carbon bond cleavage before it can desorb as an isomerized C_5 molecule. The results in Fig. 3 for the percentage isomerization of 2,2-dimethylpropane at the higher temperature used in the pulse reactor are consistent with these ideas. At 538 K some isomerized products are detected but only in trace amounts for catalysts containing less than 87.5% Pt. Thus the results for the pulse and static reactors are in broad agreement in that appreciable isomerization products are only detected from Pt-rich catalysts.

The results in Table 2 indicate that there is rather more variation in the value of activation energies determined by different techniques than on catalysts of different composition by the same technique. We suggest that much of the variation in the apparent activation energies with technique may be attributable to the different H_2 : hydrocarbon ratios under the operating conditions. The lowest ratio of 10 : 1 obtained in the experiments in the static reactor; the ratio of 19 : 1 applied for the flow reactor but the value in the pulse reactor was indeterminate and always exceeded 19 : 1 which corresponded to the approximate ratio at the maximum of the hydrocarbon pulse. Our results suggest that higher H_2 : hydrocarbon ratios lead to increased apparent activation energies in agreement with the generally accepted concept that increase of H_2 pressure gives some inhibition of hydrogenolysis reactions on many metals.

In conclusion we believe that we have produced two series of supported Rh–Pt catalysts of similar character. Both show large variations in activity with catalyst composition. The manner in which the selectivities of the reactions of *n*-butane and 2,2-dimethylpropane depend on catalyst composition together with the related activity patterns have some potential for the determination of probable mechanisms and possible ensemble sizes of the catalytically active sites. Some preliminary discussion has been given in this paper mainly in terms of the C_2-unit mechanism for the hydrogenolysis of *n*-butane and the iso-unit mechanism for the reactions of 2,2-dimethylpropane. Further discussion will be given when the results for a wider range of hydrocarbons has been obtained.

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