Activity and Selectivity of Bifunctional Platinum Catalysts in Hydrocarbon Reactions

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Conversions of a number of C_6–C_8-alkanes, naphthenes, and aromatics on bifunctional platinum/carrier catalysts, on Pt-black, and on the acidic carriers of the bifunctional catalysts are investigated in the temperature range 300–500°C and at hydrogen partial pressures of 0–45 bars in a continuously operated fixed-bed reactor and in microcatalytic pulse reactors. Three activity and selectivity levels of the platinum in bifunctional Pt/acidic carrier catalysts may be broadly recognized: (1) temperatures below 350°C where mainly platinum-catalyzed reactions contribute to the measured product distributions, (2) a temperature region around 400°C where platinum drastically changes its activity and selectivity in hydrogenolysis and isomerization reactions due to removable carbonaceous deposits, and (3) a region above about 400°C where due to irreversible carbiding platinum only displays (de)hydrogenation activity. The product distributions from conversions of the model compounds on irreversibly carbided Pt/carrier catalysts are mainly governed by acid-catalyzed interconversions through nonclassical carbonium ion intermediates.

INTRODUCTION

Bifunctional Pt or Pt-alloy catalysts play an important part in basic petroleum refining processes such as catalytic reforming and C_8-aromatic isomerization. Following Mills *et al.* (*1*) and Weisz and Swegler (*2*), the concept of bifunctional catalysis consists in combining two different functions in one catalyst. The catalyst contains a metal which catalyzes (de)hydrogenation reactions of paraffins into olefins or naphthenes into aromatics and the reverse reactions and an acidic function which catalyzes skeletal rearrangements of the olefins formed on the metal through carbocation mechanisms. This picture seems to be consistent with the macroscopic phenomena observed in catalytic reforming. However, dehydrocyclization, skeletal isomerization, closure and opening of five- and six-membered rings, as well as hydrogenolysis of n-alkanes, can be catalyzed by the metallic function only. Similarly, the acidic function alone can catalyze ring opening, ring closure, isomerization, and ring expansion re-

actions. Thus, the species over bifunctional catalysts are interconverted by a large number of consecutive or parallel elementary reactions (*3, 4*). A kinetic analysis of such reaction systems with respect to supplying data for catalyst screening, reactor modelling, or process optimization should concern the following three steps (*5*): first, the underlying reaction mechanism should be examined; second, on the basis of the reaction network the dynamic model equations should be constructed; and in the third step the model parameters should be evaluated by fitting to experimental conversion versus reaction time plots. The examination of the underlying reaction network is a difficult task. The different approaches may be divided into kinetic and nonkinetic methods.

Considering the large number of elementary reactions occurring at elevated temperatures in the system H_2–hydrocarbons–Pt/acidic carrier the application of non-stationary kinetic methods (*6*) for evaluating the reaction network seems not very promising. Therefore nonkinetic methods

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are usually adopted. One of these which is widely used is the comparison of product distributions from model compounds with product distributions expected assuming certain mechanisms. If this does not allow distinction between rival mechanisms, isotope labelling of the reactants is a useful tool. Nonkinetic methods may even supply indications on rate-determining steps (rds), which are useful for the kinetic analysis of reaction networks.

With respect to the reaction system under consideration the examination of the underlying reaction network is further impeded by changing activity and selectivity during operation of the catalyst, by which, for example, the hydrogen partial pressure dependences of individual hydrocarbon conversion rates or the portions by which certain reactions contribute to the measured overall conversions are drastically changed.

In the present investigation a number of earlier and new experimental results of the authors on C_6–C_8-hydrocarbon conversions over Pt, Pt/acidic carrier, and acidic carrier catalysts are summed up in order to clarify in more detail the complex reaction network by which hydrocarbons are interconverted on bifunctional Pt/carrier catalysts.

EXPERIMENTAL

(a) *Materials*. Kali-Chemie AG provided 0.35 wt% Pt/Al$_2$O$_3$ (RD150C), 0.5 wt% Pt/Al$_2$O$_3$, 0.5 wt% Pt/Y-zeolite, and the acidic carriers of the last two catalysts. The unsupported Pt-black was reduced from H$_2$PtCl$_6$ by means of HCHO in the presence of concentrated KOH solution at 20–25°C (7).

The C_6–C_8-alkanes, cycloalkanes, and aromatics were purchased from Fluka AG and Merck, and some of the cycloalkenes were produced by Grignard reactions followed by dehydration. Hydrogen was dried over molecular sieves to a content of less than 0.5 vpm.

(b) *Apparatus and operation conditions*.

The experiments were carried out in a pulse microreactor (inner diameter 6 mm) and a continuously operated fixed-bed reactor described earlier (8, 9). Reaction conditions with the pulse microreactor for supported catalysts were: particle diameter 0.1–0.3 mm, carrier gas velocity 100–200 ml/min (STP), input pulses 0.02–0.2 μl reactant, 150 mg catalyst. Various hydrogen partial pressures were obtained by applying mixtures of He and H$_2$ as the carrier gas. Conditions with the fixed-bed reactor were: particle diameter 0.4–0.5 mm, 2–10 g catalyst, 420–450°C, 4–54 bars, H$_2$/HC mole ratio 10–40, space velocity 2–70 h^{-1}. Products were analyzed by gas chromatography with a 100-m squalane capillary column. The reactions were performed over catalysts only heated up to the reaction temperature chosen, these are designated "fresh" catalysts. In order to reduce isomerization, cyclization, and hydrogenolysis activity of the platinum function the bifunctional Pt/Al$_2$O$_3$ catalysts were pretreated at 530°C under H$_2$ flow with twenty 5-μl pulses of methylcyclopentane and these are termed "partially deactivated" catalysts. Bifunctional zeolite catalysts were heated no further than to the reaction temperature chosen because the acidic function also lost its activity at 530°C. Special attention was given to achieving an activity and selectivity level of the catalyst which was constant during a series of experiments and the same for different catalyst charges. Differences in product concentrations obtained over various charges of the individual catalysts were below 5% of the actual conversion.

The pulse microreactor used for studies with unsupported Pt-black has been described earlier (10). The 3-μl pulses were introduced into a carrier gas stream of 60 ml min^{-1}; two columns were alternatively used for analysis: a polar column containing triethylene glycol dibutyrate and a nonpolar column containing squalane over Chromosorb P. The catalysts were regenerated between hydrocarbon pulses by air and subsequent hydrogen slugs; omitting this

procedure it was possible to study the behavior of partly deactivated catalysts (11).

RESULTS

The results are divided into three sections. First, the actions of the two catalyst functions are shown in detail and some reactions are presented which give indications on the contribution of "bifunctional" and "monofunctional" reactions to the measured overall conversions. In the second section, reaction sequences in which only acidic sites are involved are presented with special emphasis on nonclassical carbonium ion- and carbenium ion-type mechanisms and in the last part it is demonstrated in the case of some selected reactions how partial deactivation of the platinum affects measured product distributions.

1. Platinum-Catalyzed and "Bifunctional" Reactions

(a) Transformations of alkanes. In addition to product distributions from conversions of model compounds indications on the underlying reaction network may be obtained from partial and total pressure dependences of reaction rates. In the following figures partial and total pressure
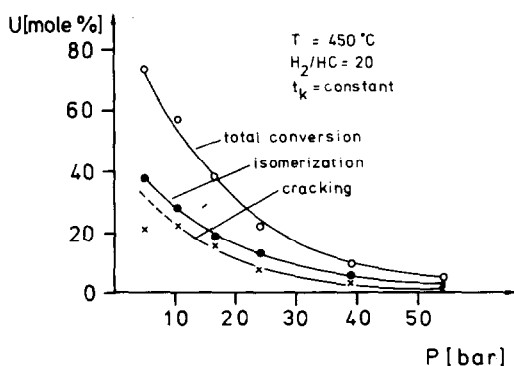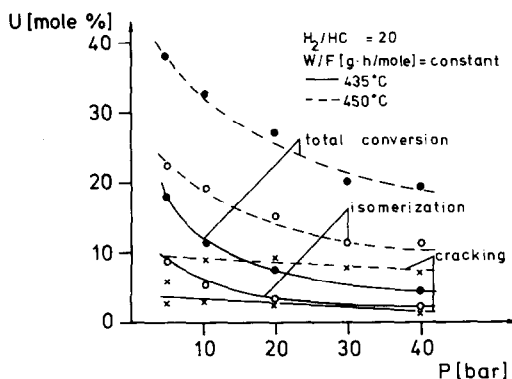
FIG. 1. Dependence of total, isomerization, and cracking conversions (U) from total pressure at constant hydrogen/hydrocarbon mole ratio and constant reaction time t_K (the total conversion includes dehydrocyclization products). Apparatus: continuously operated fixed-bed reactor. Reactant: n-hexane. Catalyst: fresh 0.35 Pt/Al$_2$O$_3$.

FIG. 2. Dependence of total, isomerization, and cracking conversions (U) from total pressure at constant hydrogen/hydrocarbon mole ratio and constant space velocity W/F [g · h/mole] (the total conversion includes dehydrocyclization products). Apparatus: continuously operated fixed-bed reactor. Reactant: n-hexane. Catalyst: fresh 0.35 Pt/Al$_2$O$_3$.

dependences of isomerization and cracking rates of n-hexane on fresh (Figs. 1–4) and partially deactivated (Fig. 5) 0.35 Pt/Al$_2$O$_3$ are plotted (9).

Figures 1 and 2 reveal that total conversion and isomerization and cracking conversion decrease with increasing total pressure (varied from 5 to 54 bars) when the hydrogen/hydrocarbon mole ratio and the reaction time or the space velocity (vol reactant (STP)/reaction vol × time), respectively, are kept constant. This signifies
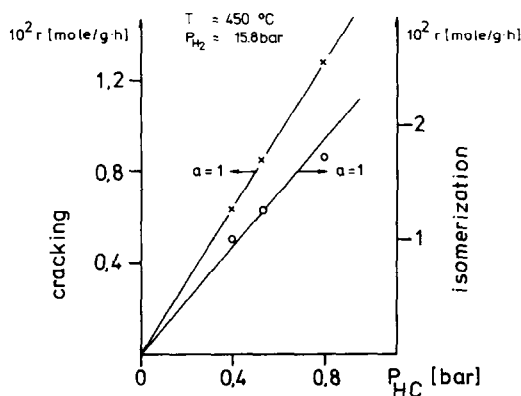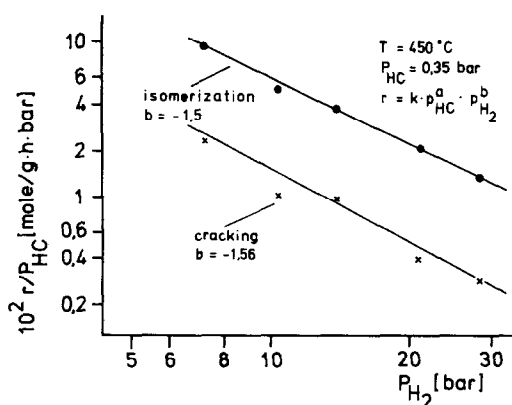
FIG. 3. Dependence of isomerization and cracking rates r [mole/g · h] of n-hexane from n-hexane partial pressure. Apparatus: continuously operated fixed-bed reactor. Catalyst: fresh 0.35 Pt/Al$_2$O$_3$.

FIG. 4. Dependence of isomerization and cracking rates r [mole/g · h] of n-hexane from hydrogen partial pressure. Apparatus: continuously operated fixed-bed reactor. Catalyst: fresh 0.35 Pt/Al$_2$O$_3$.

rates were obtained at conversions < 15% by $r = dn/Wdt = \Delta u/\Delta(W/F)$ (W = catalyst weight [g], F = molar feed rate [mole/h])). The plots indicate that hydrocarbon partial pressure dependencies of n-hexane isomerization and cracking rates are +1, a result which is in agreement with data from Hosten and Froment (12) and Voorhies and Bryant (13), whereas hydrogen partial pressure dependences are ca. −1.5. Hydrogen partial pressure dependences drastically change on the Pt/Al$_2$O$_3$ catalyst which was pretreated at 530°C (Fig. 5) and take now values of ca. −1, whereas hydrocarbon pressure dependences are still +1. This means that in the case of pretreated Pt/Al$_2$O$_3$ catalysts the overall reaction orders of cracking and isomerization rates toward hydrogen and hydrocarbon partial pressures are zero, a result which confirms those of Ciapetta and Hunter (14) and Sinfelt et al. (15). A possible interpretation of these experimental results is the following: hexane isomers and cracking products are either formed via the classical bifunctional mechanism or mainly the platinum function is involved in the skeletal rearrangements.

that within the used reaction conditions, isomerization and cracking rates of n-hexane on fresh Pt/Al$_2$O$_3$ have a negative overall reaction order with respect to the partial pressures of hydrogen and hydrocarbons when modelling these rates by a simple power law expression:

$$r = k \, p_{HC}{}^a \, p_{H_2}{}^b.$$

In Figs. 3 and 4 isomerization and cracking rates of n-hexane are plotted against n-hexane and hydrogen partial pressures (the

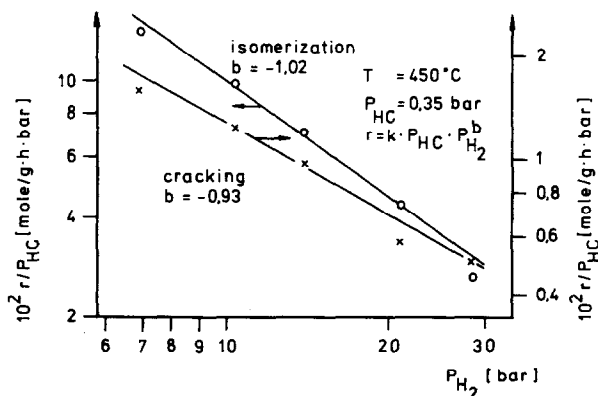The extent to which both mechanisms contribute to the observed conversions de-

FIG. 5. Dependence of isomerization and cracking rates r [mole/g · h] of n-hexane from hydrogen partial pressure. Apparatus: continuously operated fixed-bed reactor. The 0.35 Pt/Al$_2$O$_3$ catalyst (Rd150C) has been thermally pretreated at 530°C for 12 h followed by conversion of n-hexane at this temperature for 1 h and a total pressure of 10.5 bars, hydrogen hydrocarbon mole ratio of 20, and a space velocity of 15 h^{-1}.

pends on the actual activity and selectivity state of the catalyst. As long as a bifunctional mechanism is operative the reactions are endowed with an overall reaction order of zero. In the case of platinum-catalyzed isomerization and hydrogenolysis of alkanes, Garin and Gault (*16*) on the other hand reported a reaction order of +1 with respect to the hydrocarbon partial pressure and −1 to −3 with respect to hydrogen partial pressure for *n*-pentane reaction on platinum. The foregoing considerations are further confirmed by means of methylcyclopentane ring opening product distributions which are discussed later.

As opposed to the results reported so far at low hydrogen partial pressures positive and zero reaction orders of alkane isomerization, ring closure, and hydrogenolysis rates versus hydrogen partial pressures have been found (*17, 18*). In Fig. 6 isomerization and cracking conversions of *n*-hexane obtained in the microcatalytic pulse reactor are plotted against the hydrogen content of the carrier gas. On the fresh 0.35 Pt/Al$_2$O$_3$ catalyst isomerization and crack-
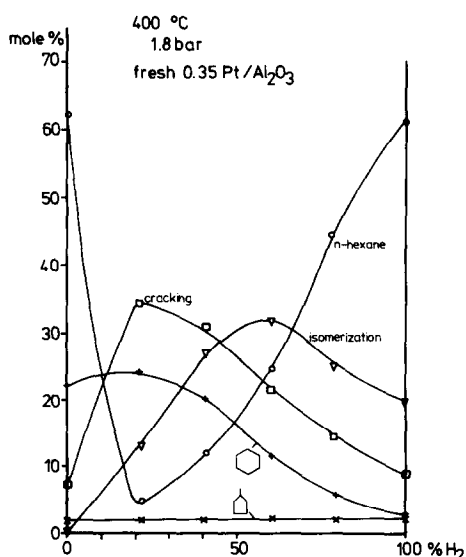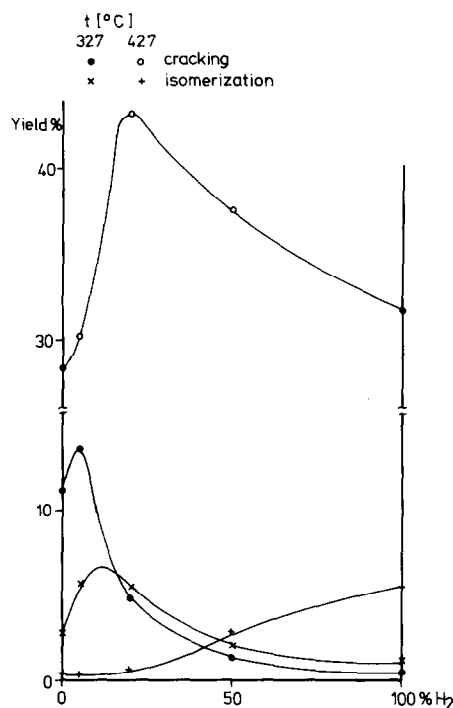

FIG. 7. Effect of hydrogen partial pressure on isomerization and cracking conversions of *n*-hexane on platinum black. Apparatus: pulse microreactor. Carrier gas: He/H$_2$ mixture.

ing conversions pass through a maximum, indicating that at low hydrogen partial pressures in the range of several hundred Torr the order of isomerization and cracking rates versus hydrogen partial pressure is positive. These maximum rates again indicate platinum-catalyzed reactions as the results which are given in the following two figures reveal. In Fig. 7 isomerization and cracking conversions from *n*-hexane reaction on Pt-black at different temperatures are replotted as a function of the hydrogen partial pressure after Ref. (*19*). The hydrogen pressure corresponding to maximum yields is shifted towards higher hydrogen pressures as the temperature increased.

No such effects occur with a partially deactivated Pt/Al$_2$O$_3$ catalyst (Fig. 8), although due to the reduced activity of this catalyst the conversions are very low.

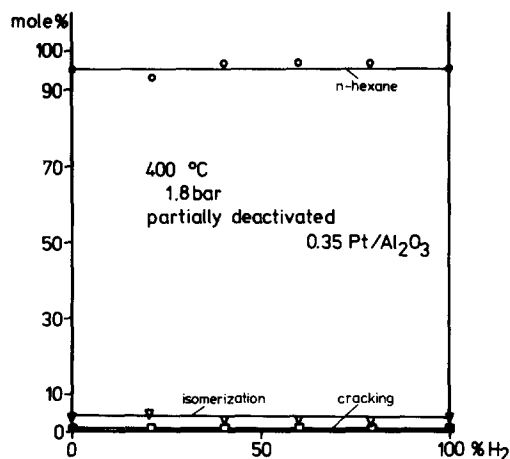(*b*) *Transformations of methylcyclopentane.* It has been shown previously that

FIG. 6. Effect of hydrogen partial pressure on isomerization and cracking conversions of *n*-hexane on fresh 0.35 Pt/Al$_2$O$_3$ catalyst. Apparatus: pulse microreactor. Carrier gas: He/H$_2$ mixture.

FIG. 8. Effect of hydrogen partial pressure on isomerization and cracking conversions of n-hexane on partially deactivated 0.35 Pt/Al$_2$O$_3$ catalyst. Apparatus: pulse microreactor. Carrier gas: He/H$_2$ mixture.

methylcyclopentane ring opening yields selectively n-hexane on acidic catalysts (20), n-hexane/2-methylpentane/3-methylpentane in a ratio of 2:2:1 on small platinum crystallites and selective ring opening producing methylpentanes only over large platinum crystallites (21). In Fig. 9 are plotted pulse technique results on product distributions from methylcyclopentane reactions on a laboratory 0.5 Pt/Al$_2$O$_3$ catalyst which has the same carrier as the 0.35 Pt/Al$_2$O$_3$ catalyst, on the acidic carrier of this catalyst, and also on unsupported Pt-black. Over the fresh supported catalyst the primary ring opening products n-hexane, 2-methylpentane, and 3-methylpentane are formed nearly in the ratio 2:2:1, whereas over the partially deactivated catalyst and the Al$_2$O$_3$-carrier n-hexane is the main product. Thus over the fresh catalyst mainly platinum reactions contribute to the measured ring opening products, while on partially deactivated catalysts mainly the acidic sites of the carrier catalyze the ring opening reactions. On platinum black with rather large crystallites mainly selective ring opening occurs.

The results of methylcyclopentane conversions on differently pretreated Pt/Al$_2$O$_3$ catalysts clearly indicate that by the employed pretreatment the platinum function is partially deactivated inasmuch as it has lost its isomerization and hydrogenolysis activity while the (de)hydrogenation activity remained unchanged.
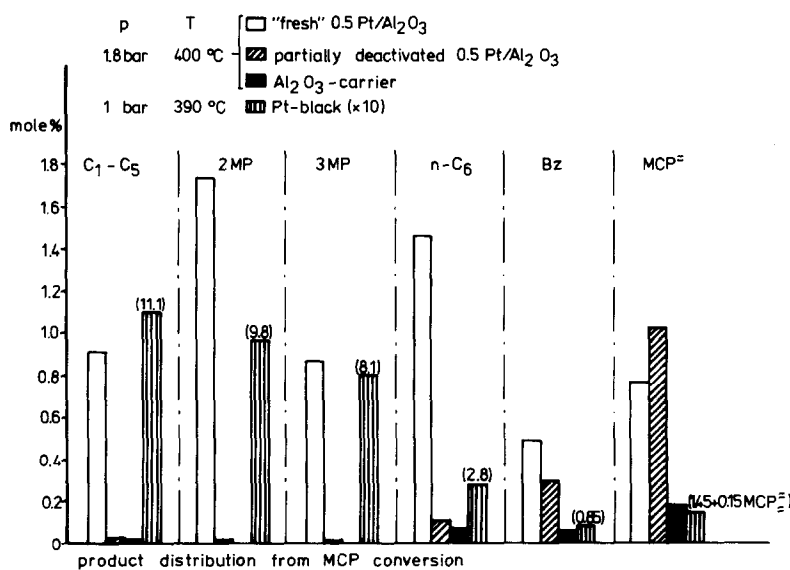

FIG. 9. Catalytic activity and selectivity of 0.5 Pt/Al$_2$O$_3$ and Pt-black in methylcyclopentane conversions. Apparatus: pulse microreactor. Carrier gas: H$_2$.

The transferability of the microcatalytic pulse reactor results to those obtained in continuously operated fixed-bed reactors is demonstrated in Table 1, where product distributions from methylcyclopentane conversion over fresh and partially aged RD150C are given. Again n-hexane is the main product of methylcyclopentane ring opening in the case of pretreated catalysts.

2. Reactions on the Acidic Sites

According to Olah (22) protonolysis of a C–C or C–H bond, by which 2-electron-three-center linkages are formed, is the first step in isomerization or C–C bond scission of alkanes on acidic centres. Protonolysis of a C–C bond results in C–C bond scissions with formation of a smaller alkane and a carbenium ion, whereas protonolysis of a C–H bond is followed by splitting off hydrogen and formation of a carbenium ion. The carbenium ions react either with other C–C or C–H bonds or undergo skeletal isomerizations via C–C or C–H delocalizations. The most important differences between mechanisms in which carbenium ions and carbonium ions are involved and the classical formulations of carbenium ion mechanisms are direct scission of protonolyzed C–C bonds and the formation of nonclassical protonated cyclopropanes in the transition state of carbenium ion rearrangements, which are more stable than primary carbenium ions (23). While nonclassical carbocations have been identified in superacids, their existence has not been proved up to now in heterogeneous catalytic gas

reactions, although in a number of papers mechanisms with carbonium ion intermediates have been postulated to account for measured product distributions (24, 25).

Indications of carbonium ion-type intermediates may be obtained from product distributions of conversions of C_5-ring naphthenes. The experimental result of n-hexane being the main product of methylcyclopentane ring opening on acidic centres has been interpreted by Brandenberger et al. (20) in terms of a mechanism where a C–C-ring bond is protonolyzed by a hydrogen ion. Due to the stabilizing effect of the methyl group the most probable transition state is the following:
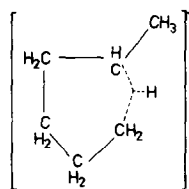
This further reacts yielding a secondary carbenium ion with n-hexane structure. This carbenium ion either stabilizes through proton abstraction by which n-hexene is formed or through hydride ion abstraction from an alkane by which n-hexane is formed. On the other hand, Donnis (26) demonstrated that the above experimental findings fit also with a mechanism which is formulated in classical carbenium ions and β-scissions. Assuming, that (i) the rate-determining step is C–C bond scission and that (ii) C–C bond ruptures by which secondary and tertiary carbenium ions are

TABLE 1

Product Distributions from Methylcyclopentane Conversion in a Continuously Operated Fixed-Bed Reactor.

Catalyst[a]	Product distribution[b] (mole%)						
	<C_6	2MP	3MP	nH	DMB	MCP^{2-} + Bz	MCP
Fresh	0.29	11.4	5.5	8.9	0.2	2.2	71.6
Deact.	—	0.27	0.17	1.6	—	3.7	94.3

[a] Catalyst: 4 g RD150C; 420°C; 10.5 bars; hydrogen/hydrocarbon mole ratio = 20; W/F = 4.56 g h mole^{-1}.
[b] M = methyl, P = pentane, H = hexane, C = cyclo, Bz = benzene, D = di, B = butene, P^{2-} = pentene.

transformed into primary ones are energetically unfavoured, out of the six possible ring ruptures only two yielding n-hexane are energetically favoured. This means both mechanisms supply an interpretation for the experimental result that n-hexane is the main product of acid-catalyzed methylcyclopentane ring opening.

Indications of a protonolysis of methylcyclopentane ring bonds may be obtained from the following results. Product distributions from conversions of methylcyclopentene and methylcyclopentane on pretreated 0.5 wt% Pt/Al$_2$O$_3$ and the Al$_2$O$_3$-carrier (Table 2) reveal that the main reaction of methylcyclopentene is isomerization yielding C$_6$-ring naphthenes, whereas ring cleavage products are only formed in small amounts. Methylcyclopentane undergoes mainly ring rupture reactions and is only converted to a small extent yielding skeletal isomerization products. This signifies that the dominating reaction of cyclic carbenium ions formed from methylcyclopentene by proton addition is iomerization, by which six-membered rings are formed, while protonolysis of methylcyclopentane ring bonds results in ring

FIG. 10. Ring opening products from 1,2-dimethylcyclopentane conversion on 0.35 Pt/Al$_2$O$_3$. Apparatus: pulse microreactor. Carrier gas: H$_2$.

opening and not in formation of cyclic carbenium ions.

The two rival acid-catalyzed C–C bond scission mechanisms can be distinguished on the basis of product distributions from 1,2-dimethylcyclopentane ring opening (8). If the classic carbenium ion mechanism is the operative mechanism for ring cleavage, then with the above assumptions for methylcyclopentane ring opening similar amounts of n-heptane and 3-methylhexane are expected from 1,2-dimethylcyclopentane ring opening. Direct protonolysis of 1,2-dimethylcyclopentane C–C bonds should result on the other hand in ring rupture yielding mainly n-heptane, because the transition state is thermodynamically favoured in which the C–C bond between the two methyl groups is protonolyzed. As the results in Fig. 10 reveal, n-heptane is the main product of acid-catalyzed ring cleavage of 1,2-dimethylcyclopentane which indicates a carbonium ion-type intermediate followed by direct C–C bond scission. Further evidence for the existence of nonclassical carbocations follows from experimental results of ethylbenzene isomerization yielding o-xylene as the main product on weakly acidic Pt/Al$_2$O$_3$ (24, 25). From individual conversions of possible intermedi-

TABLE 2

Product Distributions of Methylcyclopentane and Methylcyclopentene Conversions on Partially Deactivated 0.5 Pt/Al$_2$O$_3$ and the Pretreated Al$_2$O$_3$ Carrier of this Catalyst

Catalyst:	0.5 wt% Pt/Al$_2$O$_3$ partially deactivated		Al$_2$O$_3$ carrier pretreated	
Reactant: Product	MCP	MCP$^=$	MCP	MCP$^=$
C$_1$–C$_5$	0.03	0.08	0.02	0.82
Σ hexanes	0.15	0.09	0.08	0.02
MCP	98.4	97.3	99.65	6.5
Benzene	0.3	1.3	0.07	0.4
MCP$^=$	1.03	0.8	0.18	89.1
Σ cyclohexane and cyclohexene	0.08	0.46		3.21

Note. Reaction conditions: 400°C, 1.8 bars H$_2$ carrier gas, 0.3-μl pulses, 120 mg catalyst, carrier gas velocity 100 ml/min, pulse microreactor.
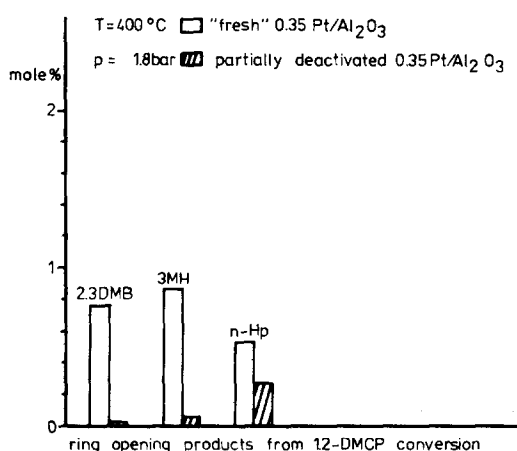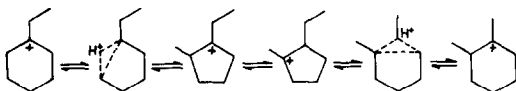
ates the following reaction sequence was postulated by which ethylbenzene is converted yielding o-xylene:

This reaction path is the only one in the total C_5- and C_6-ring system in which only skeletal rearrangements of tertiary carbenium ions through nonclassical bridged cyclopropane ring structures are involved.

In the foregoing we have preferentially treated the nature of the intermediates through which alkanes and alkenes undergo skeletal rearrangements on acidic centres. In the following some product distributions from various C_8-alkane conversions on the 0.35 Pt/Al$_2$O$_3$ and 0.5 Pt-zeolite catalyst are given in order to show particularly the action of the acidic carrier in bifunctional catalysts. In Figs. 11 and 12 dehydrocyclization products from n-octane, 2-methylheptane, and 3-ethylhexane conversions are plotted. The results of Fig. 12 reveal that only C_8-aromatics are formed from the indi-

vidual reactants which are expected from 1,6-ring closure. C_5-ring naphthenes which are also formed will not further react yielding C_6-ring naphthenes under the applied reaction conditions on the Pt/Al$_2$O$_3$ catalyst (Fig. 13). On the Pt-zeolite catalyst (Fig. 12), one the other hand, with n-octane, 2-methylheptane, and 3-ethylhexane always the same C_8-aromatic distribution is obtained which corresponds to the thermodynamic equilibrium concentrations and no C_5-ring naphthenes could be detected among the dehydrocyclization products. Opposite to the Al$_2$O$_3$-carrier the zeolite carrier due to its much higher activity sets up thermodynamic equilibrium among C_5- and C_6-ring naphthenes. Since the zeolite carrier of the Pt/zeolite catalyst exhibits no ring closure activity (4) the rate-determining steps in the reaction sequence should be 1,5- and 1,6-ring closures on platinum sites. Due to the high (de)hydrogenation activity of the platinum by which C_6-ring naphthenes are immediately dehydrogenated no C_5-ring naphthene intermediates will occur among the products.
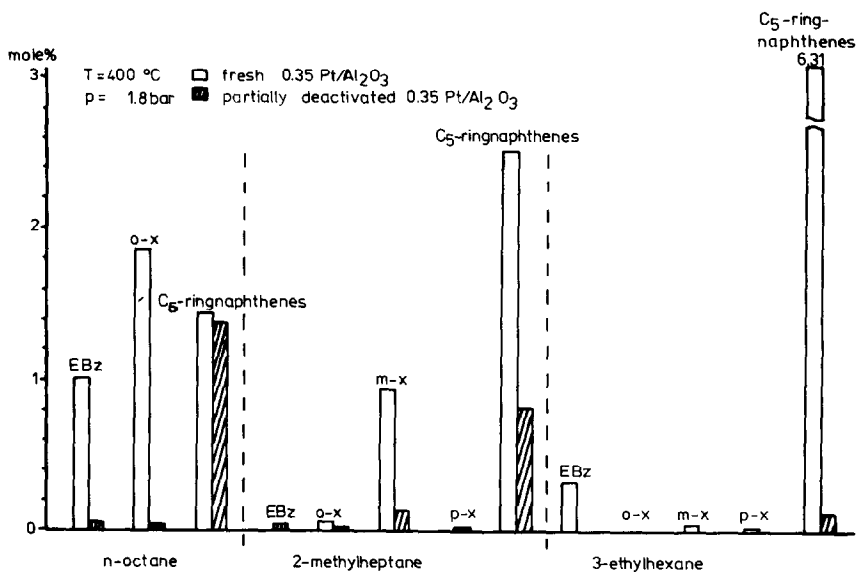

FIG. 11. Dehydrocyclization of C_8-alkanes on fresh and partially deactivated 0.35 Pt/Al$_2$O$_3$ (EBz = ethylbenzene, x = xylene). Apparatus: pulse reactor. Carrier gas: H$_2$
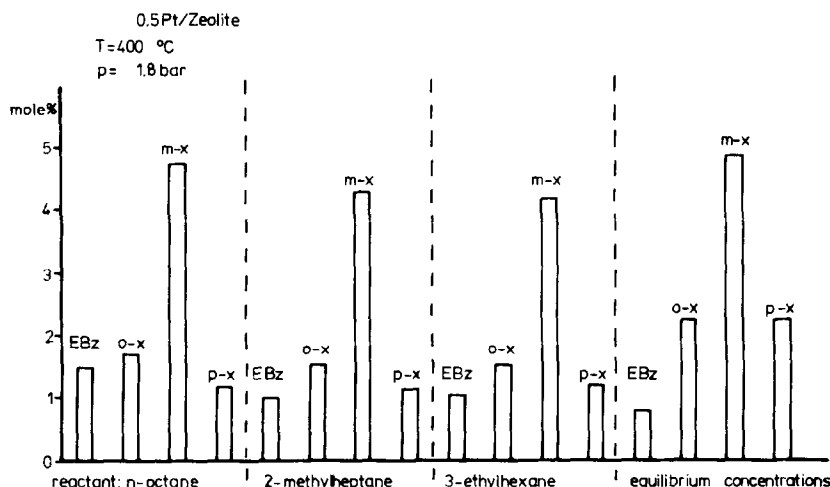
FIG. 12. Dehydrocyclization of C_8-alkanes on fresh 0.5 Pt/zeolite. Apparatus: pulse microreactor. Carrier gas: H_2.

3. Experiments with Partially Deactivated Catalysts

Deactivation of the catalysts is in most cases selective, i.e., various functions are suppressed to different extents. Some results have already been incorporated into previous sections, but another feature is represented by the variation of the distribution of cracked products. Figure 14 shows that in the presence of hydrogen statistical scission of the bonds of the n-hexane molecules occurs, whereas helium favours splitting of the end methyl group. C_1 and C_5 and C_2 and C_4 fragments are formed in complementary amounts over fresh catalysts indicating single hydrogenolysis. On deactivating catalysts however, multiple fragmentation to give methane in excess amounts occurs. An explanation of this phenomenon may be found in the work of
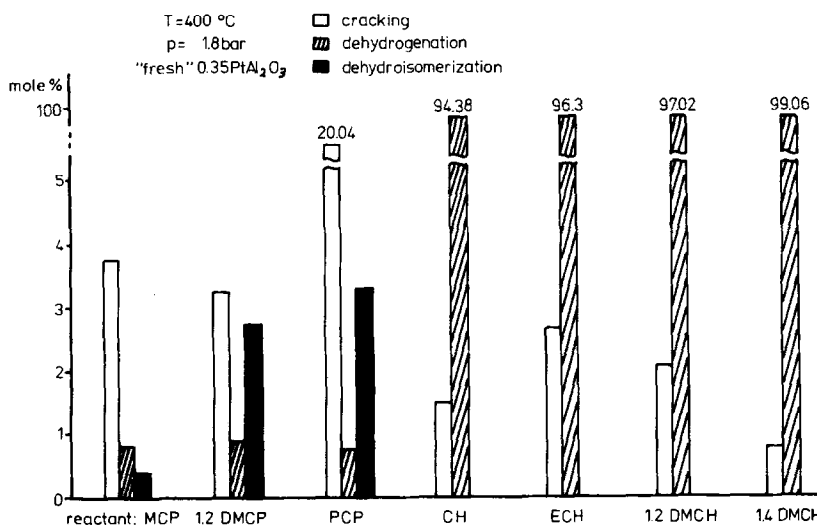

FIG. 13. Reactions of naphthenes on fresh 0.35 Pt/Al_2O_3 (PCP = propylcyclopentane, E = ethyl). Apparatus: pulse microreactor. Carrier gas: H_2.
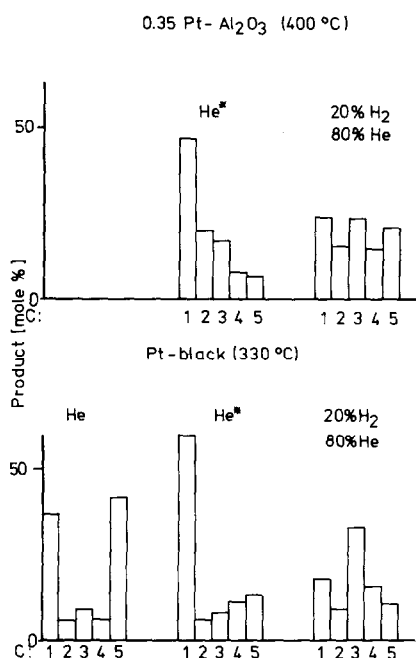
0.35 Pt- Al₂O₃ (400 °C)

FIG. 14. Distribution of hydrogenolysis products obtained over Pt/Al₂O₃ and Pt-black in various carrier gases. The asterisk (*) denotes a catalyst after several pulses without regeneration. Apparatus: pulse microreactor. Carrier gas: He, H₂, He/H₂ mixture.

Clarke and Rooney (27) who, based on the experiments of Paál et al. (17), proposed a predominant internal adsorption of alkanes over "clean" metal surfaces whereas they claimed a favoured terminal adsorption over partially carbonized metals. The presence of hydrogen gas prevents deactivation of the metallic function. The importance of end demethylation (as expressed by the ratio $CH_4/\Sigma(C_2-C_5)$) gradually increases with decreasing hydrogen content in the carrier gas (Table 3). When the gas is switched again to hydrogen (without any other regenerating treatment) a very high demethylating effect is observed, confirming that the combined effect of hydrogen and carbon on the surface may change entirely the catalyst selectivity. The original selectivity of the Pt/Al₂O₃ catalyst is restored after pretreatment in hydrogen for several hours at reaction temperature, which is observed from the $C_1/\Sigma(C_2-C_5)$ ratio, which decreases for following pulses (Table 3). Like the $C_1/\Sigma(C_2-C_5)$ ratio, the 2-methylpentane/3-methylpentane mole ratio from n-hexane conversion changes drastically from a value of 1.9 to 1.3 when switching from hydrogen carrier gas to helium carrier gas. The composition of methylcyclopentane ring opening products at the same time remains unchanged, indicating platinum-catalyzed reactions.

TABLE 3

Hydrogenolysis Product Distribution and 2-Methylpentane/3-Methylpentane Ratio from n-Hexane Conversion as Function of Hydrogen Partial Pressure

Catalyst	Carrier gas (vol%)	Feed pulse	$C_1/\Sigma(C_2-C_5)$ (mole%/mole%)	2-MP/3-MP
Pt/Al₂O₃ fresh	H₂	MCP	0.6	n-C₆/2-MP/3-MP 1.6/1.8/1
	H₂	n-C₆	0.3	1.9
	80% H₂–20% He	n-C₆	0.32	1.86
	60% H₂–40% He	n-C₆	0.35	1.7
	40% H₂–60% He	n-C₆	0.4	1.55
	20% H₂–80% He	n-C₆	0.5	1.5
	He	n-C₆	0.9	—
	H₂[a]	n-C₆[b]	5.7/4.4/3.6	1.27
		MCP[b]	12.8/9.4/8.5	n-C₆/2-MP/3-MP 1.75/1.9/1

[a] n-Hexane and methylcyclopentane conversions after switching from H₂/He mixtures and He carrier gas to H₂ carrier gas.
[b] $C_1/\Sigma(C_2-C_5)$—ratio from the first three pulses after switching from He to H₂ carrier gas.

DISCUSSION

In deriving a general reaction network for interconversions of a mixture or single classes of hydrocarbons on bifunctional platinum catalysts as a basis for kinetic modelling with respect to the aims claimed above, the main difficulties stem from a large number of different effects which may drastically change the observed actual activity and selectivity level of the catalyst. Most of the literature work on platinum catalysts has been accomplished at low pressures and reaction temperatures at 250–350°C, whereas typical hydrocarbon reforming conditions are elevated H_2 partial pressures and reaction temperatures of 480–520°C. Ring closure of alkanes on platinum catalysts in the presence of hydrogen at temperatures <400°C gives mainly C_5-cyclic products (3, 27). This has been explained with a six-membered ring (30), which is formed by a 1,5 diadsorbed hydrocarbon species with one platinum adsorption site. At typical hydrocarbon reforming reaction temperatures, however, evidence for direct six-membered ring closure has been reported (3, 28, 29). The present results (Fig. 11) for n-octane, 2-methylheptane, and 3-ethylhexane cyclization on weakly acidic Pt/Al₂O₃ also clearly indicate a direct 1,6-ring closure. At the applied reaction temperature of 400°C C_5-ring naphthenes undergo ring expansion reactions on platinum only to a very small extent as the results in Fig. 13 reveal. Furthermore, at 400°C reactions on the acidic carrier will contribute to the measured product distributions only to a small extent. Thus, the observed product distributions from the individual C_8-alkane conversions cannot be described in terms of a five-membered ring closure on platinum sites and consecutive ring expansion either on platinum or acidic sites.

Possible explanations for direct 1,6-ring closure are (i) a change of the preferred platinum-catalyzed metal–carbene/metal-alkyl insertion mechanism to a metal-olefin/metal–alkyl mechanism (1,6-clo-

sure) on carbided platinum surfaces (27) or (ii) a stepwise cyclization mechanism via equilibrated dehydrogenation reactions on Pt and alkatriene/cyclohexadiene ring closure, either catalytic or thermal, in the homogeneous phase (3). The latter mechanism is more or less uncertain due to the various reaction possibilities of the intermediate hexadienes and hexatrienes which up to the present are far from being fully understood. Moreover, from thermodynamic calculations only very small amounts of hexadienes and hexatrienes should be formed under the present reaction conditions. Indications for the metal–olefin/metal–alkyl mechanism are found in the work of Davis and Venuto (29) and the present work. The experiments of Davis and Venuto, who reported evidence for direct 1,6-ring closure for C_8-alkane dehydrocyclization on nonacidic supported platinum, were performed under conditions (no hydrogen carrier gas, 482°C) where rapid carbiding of the platinum surface occurs. Thus, their catalyst was not a platinum but a Pt/C catalyst. The same will hold for the present catalyst. From the data given in Table 3 and Fig. 14 it is obvious that decreasing hydrogen partial pressures result in increasing methane formation, a reaction which occurs on carbided platinum surfaces. As the results of Table 3 further reveal, methane formation is the dominating hydrogenolysis reaction of n-hexane conversions when switching from helium as carrier gas to hydrogen again. The formation of carbonaceous overlayers at this reaction temperature, however, seems to be a reversible reaction because the original hydrogenolysis and isomerization activity and selectivity of the Pt/Al₂O₃ catalyst are totally restored when the catalyst is treated in hydrogen atmosphere at the same reaction temperature for around 10 h. As opposed to this reversible platinum deactivation, the platinum is irreversibly deactivated when pretreated at 530°C in hydrogen followed by alkane conversion at this temperature. According to the results of methylcyclopentane ring opening on fresh and partially

deactivated Pt/Al$_2$O$_3$, the platinum loses nearly completely its isomerization and hydrogenolysis activity whereas the (de)hydrogenation activity remains unchanged. Thus, a Pt/Al$_2$O$_3$ catalyst which has been exposed to severe carbiding conditions displays nearly ideal bifunctionality. On a rough scale, therefore, three activity and selectivity levels of platinum in bifunctional Pt/acidic carrier catalysts may be separated:

(1) at temperatures <400°C where platinum-catalyzed reactions mainly contribute to the measured product distributions,

(2) at temperatures around 400°C where platinum drastically changes its activity and selectivity due to reversible carbonaceous deposits;

(3) at temperatures above about 430°C where platinum is irreversibly carbided and only displays (de)hydrogenation activity.

Aside from deactivation of platinum resulting from deposition of carbonaceous residues, bifunctional Pt/Al$_2$O$_3$ catalysts will change their activity and selectivity with the water and chloride content of the feed. This deactivation is caused by the Al$_2$O$_3$-carrier which is usually chlorided with the purpose of increasing its acidity and this is easily circumvented by adapting certain water and chloride concentrations in the feed. A distinction between ideal bifunctional and platinum-catalyzed reactions follows from hydrogen partial pressure dependences of alkane isomerization and cracking rates and methylcyclopentane ring opening products. With hydrogen partial pressure dependences, assuming adsorption of the reactant not being the rds, the underlying sets of elementary reactions in both cases differ in the number of equilibrated reactions in which gas-phase hydrogen is involved. This is unity for ideal bifunctional reactions and more than unity for platinum-catalyzed processes. The corresponding kinetic expressions yield hydrogen orders of −1 and less than −1, respectively. In the low hydrogen pressure range maxima in hydrocarbon conversion rates as a function of hydrogen partial pressure only

occurred with platinum-catalyzed hydrocarbon transformations. With the partially aged Pt/Al$_2$O$_3$ catalyst no influence of hydrogen partial pressure on conversion was observed. The results of methylcyclopentane ring opening are consistent with the mechanistic considerations on the basis of the observed formal hydrogen pressure dependences. On fresh Pt/Al$_2$O$_3$ catalyst nonselective ring opening occurs, yielding n-hexane, 2-methylpentane, 3-methylpentane in 2:2:1 mole ratio, whereas on severely carbided bifunctional catalysts ring opening product distributions are observed which correspond to predictions from an ideal bifunctional mechanism.
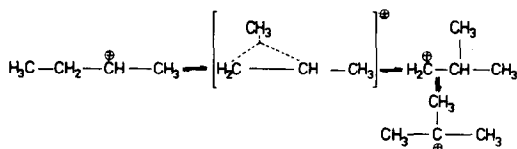
The 2-methylpentane/3-methylpentane ratio from n-hexane conversion is indicative for the actual "deactivation" state of the platinum. As long as the underlying mechanism is "bifunctional" the 2-methylpentane/3-methylpentane ratio from n-hexane conversion amounts to 1.3 (31). According to the "cyclic" isomerization mechanism on clean platinum surfaces this ratio should amount to 2. The results of Table 3 reveal that on fresh Pt/Al$_2$O$_3$ the 2-MP/3-MP ratio is nearly 2, indicating isomerization via a methylcyclopentane intermediate. On carbided platinum surfaces this ratio, however, drops down and reaches values of 1.3, although platinum reactions still mainly contribute to the measured conversions as the n-C$_6$/2-MP/3-MP ratios from methylcyclopentane ring opening illustrate. This implies that the methylpentanes are no longer formed from n-hexane through a C$_5$-cyclic intermediate but more likely through a bond shift mechanism via cyclopropane rings (27).

These bond shift mechanisms are very similar to mechanisms which have been considered for isomerization on acidic centres.

Platinum:
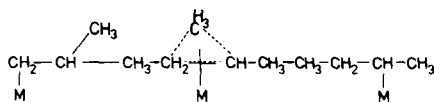
Acidic sites:

The value of 1.3 for the 2-MP/3-MP role ratio approximates to the ratio of the thermodynamic equilibrium concentrations of 2- and 3-methylpentane. As the rate of equilibration between the methylpentanes has the same order of magnitude as hexane isomerization, the cyclopropyl structured intermediate through which the methylpentanes are formed should be present in concentrations which correspond to the methylpentane equilibrium concentrations. The observed differences in the 2-MP/3-MP ratio on fresh and carbided catalysts may be interpreted as follows. C_5-ring closure and opening, i.e., the C_5-cyclic mechanism of isomerization, requires ensembles consisting of at least two platinum atoms and containing also hydrogen. Bond shift can occur on single metal atoms which may or may not be attached to carbon atoms. The formation of carbonaceous overlayers thus favours skeletal rearrangement via bond shift which corresponds to results of Van Schaik et al. (32) obtained with Pt-alloy catalysts with varying surface platinum concentrations. To this end it does not matter whether carbon or inactive metal atoms "dilute" the platinum surface. Bond shift and C_5-cyclic isomerization can be separated as a function of the hydrogen pressure (33): the former occurs selectively but with a much lower overall rate in the region of low hydrogen pressures.

Gradual accumulation of carbonaceous deposits deactivates most rapidly C_5-cyclic reactions (11). Supported and unsupported platinum thus exhibited the same general trends of behavior as far as hydrogen and carbon effects are concerned.

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