

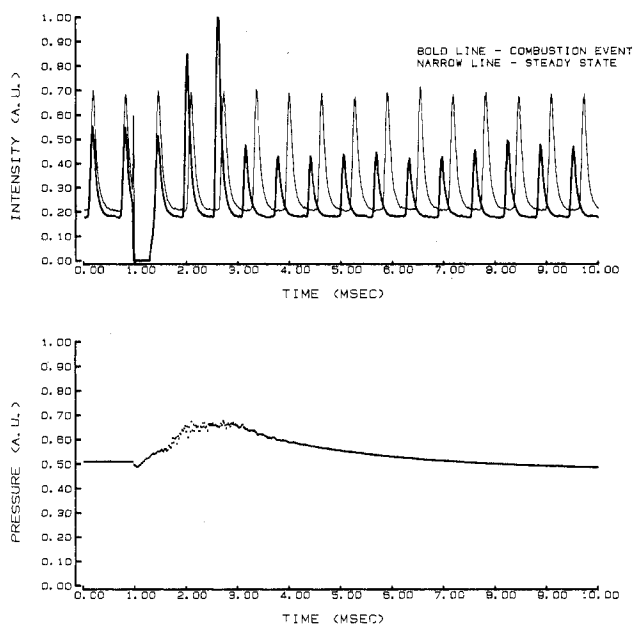


Figure 6. (a) Argon beam measured during combustion and noncombustion events. (b) Pressure trace recorded during combustion event.

they coincide with the room temperature peaks. We interpret the changes in the remaining argon peaks by assuming that a radical-enhanced combustion wave is propagating toward the sampling nozzle. The gases in front of the combustion wave are being compressed, but their temperature is not rising quickly. Thus the density, and the resulting signal intensity, increases. When the combustion wave passes the nozzle (between peaks 5 and 6), the

density drops sharply, and the temperature increases to its maximum value.

The temperature of the sampled argon molecules were estimated by assuming that the average mass and heat capacities of the molecules in the reacting mixture are essentially constant, and that the source Reynolds number was high enough to prevent pressure diffusion in the nozzle.¹⁴ Calculations of the peak arrival times yield temperatures for peaks 3 through 6 of 300 ± 25 , 475 ± 25 , 700 ± 100 , and 1900 ± 200 K. The remaining peaks are all near 1900 K. These results tend to confirm our assumption that the combustion wave passes the nozzle at ~ 3 ms.

Conclusions

We have shown that time-of-arrival curves from a chopped molecular beam system can be used to evaluate the quality of the resulting molecular beam, even for combustion systems in which the source conditions are rapidly varying. The half-width of the signal is not a strong function of the source conditions, and the time of arrival of the signal peak may be used to determine the source temperature. With proper design and characterization of the experimental apparatus, time resolution on the order of 100 μ s can be achieved throughout a combustion event.

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Registry No. Hydrogen, 1333-74-0; nitrogen dioxide, 10102-44-0.

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Novel Rh/TiO₂ and Ir/TiO₂ Catalysts for *n*-Butane Isomerization and Dehydrogenation

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An ion-exchange preparation of TiO₂-supported Rh and Ir which produces a 100% dispersed, low metal loading (0.3%) catalyst is described. When these catalysts are reduced at high temperature (773 K), they exhibit a unique activity for alkane isomerization and dehydrogenation. Hydrogenolysis, greatly suppressed on these catalysts, has an unusual positive order in hydrogen and a relatively high selectivity for terminal vs. central C-C bond breaking of *n*-butane compared to impregnated Rh and Ir catalysts. It is proposed that this behavior is the result of the strong metal-support interaction which results in a great depression and a change in the mechanism of hydrogenolysis, the mechanism being one where alkane isomerization competes with hydrogenolysis. Alkane dehydrogenation takes place on sites different from those where isomerization occurs. These sites may not involve zerovalent metal.

Introduction

In previous work¹ we have reported a large effect of the strong metal-support interaction (SMSI) on hydrogenolysis activity induced by reduction of Rh/TiO₂ catalysts at 773 K in contrast to a very modest influence on dehydrogenation activity. This clear difference would suggest that SMSI affects preferentially structure-sensitive reactions, of which hydrogenolysis is one example. We have also pointed out that the interaction occurring after high-temperature reduction appears to be localized at the periphery of small particles. From these observations we have drawn an analogy between group 8 metal-TiO₂ interaction and

group 8-group 1b metal-metal interaction with regard to the parallel effects observed on activity, selectivity, and reaction orders.² We concluded that some active sites were selectively deactivated, probably due to a migration of species from the support over the metal particles, while the rest retain their original properties. Small patches of TiO₂ may be expected to deactivate preferentially the large ensemble of atoms which constitute a site for hydrogenolysis. Therefore, a pronounced depression of the hydrogenolysis rate is observed after high-temperature reduction while relatively little change occurs for dehydrogenation activity. The suppression of the hydrogenolysis activity increases with the dispersion and becomes as great as six orders of magnitude for *n*-butane hydrogenolysis at 100% dispersion of Rh/TiO₂.

(1) (a) G. L. Haller, D. E. Resasco, and A. J. Rouco, *Faraday Discuss. Chem. Soc.*, **72**, 109 (1982). (b) D. E. Resasco and G. L. Haller, *Stud. Surf. Sci. Catal.*, **11**, 105 (1982).

(2) D. E. Resasco and G. L. Haller, *J. Catal.*, **82**, 279 (1983).

We describe here a study of *n*-butane reactions over highly dispersed Rh and Ir catalysts supported on TiO₂. These metals are normally poor isomerization catalysts but very active for hydrogenolysis, in contrast to Pt which is an excellent isomerization catalyst and shows relatively little hydrogenolysis activity. By suppressing the hydrogenolysis activity of Rh and Ir we may anticipate the observation of the nondestructive isomerization and dehydrogenation reactions, which may be otherwise masked by the dominant hydrogenolysis reaction.

Experimental Section

To obtain highly dispersed Rh and Ir on TiO₂ catalysts we used the following ion-exchange preparation method. A pH 11 solution of NH₄(OH) in distilled water was prepared. Titanium dioxide (Degussa P25) powder was added to obtain a concentration 16 mg of TiO₂ per cm³ of solution. This solution was stirred well and left at room temperature for 24 h, then centrifuged and washed until pH 7 was obtained. Rhodium and iridium solutions, 0.01 M, were prepared from Rh(NO₃)₃ and IrCl₃, provided by Alfa/Ventron. The Rh (or Ir) solution was added to the TiO₂ support in a ratio of 60 cm³ solution per gram of TiO₂. The resulting solution was stirred and left at room temperature for 24 h. It was then centrifuged and washed with distilled water 5 times. The liquid phase was colorless at this stage. The solid phase was washed with pure methanol, centrifuged, and left in air at room temperature until dry and then further dried in an oven at 403 K in air for 3 h. Subsequently, the standard reduction treatment¹ was carried out: initial reduction at 773 K in pure H₂ flow at a rate of 50 cm³/min, heating rate 3 K/min; oxidation at 673 K in pure O₂ (same flow, same heating rate). The final product was stored in a desiccator. Low- (473 K) and high- (773 K) temperature reductions were performed in situ before any activity or chemisorption measurement.

The metal loading of this ion-exchange preparation as measured by atomic absorption was 0.3% and the dispersion, measured by our standard hydrogen chemisorption procedure,¹ was 100%. To extract the metals from the support into a solution, for quantitative analysis by atomic absorption, we refluxed the catalysts in concentrated HCl solution for 48 h. Complete extraction was achieved, as determined by activity measurements.

The activity measurements were performed in a packed bed reactor which could be operated as a steady-state flow reactor or a pulse reactor and has been described elsewhere.¹ All specific rates are based on a site density measured by hydrogen chemisorption on a fresh catalyst reduced at 473 K. Justification and discussion for this procedure for catalysts which do not chemisorb hydrogen after reduction at 773 K is given in ref 2. The reactor was equipped with a Research Inc. programmable temperature controller, Model 73211, which allowed the control of reactor temperature to within 0.5 K. The reaction temperature was monitored by an iron-constantan thermocouple placed in the catalyst bed. The H₂, He, and hydrocarbon flows were measured by mass flowmeters placed in line, which allowed the estimation of partial pressures and precise measurements of total flows. In the measurements of reaction orders, each point was obtained by measuring the reaction rate at 688 K after 20 min of reaction. For the measurement of the order with respect to *n*-butane the partial pressure of *n*-butane was varied independently while keeping the partial pressure of H₂ constant. The total pressure was held constant at 1 atm by using He make up. To obtain the order in H₂ we varied both H₂ and *n*-butane partial pressures keeping 1 atm of total pressure. The order in H₂ was calculated from the slope of a plot of $\ln[(\text{rate})/(P(n\text{-butane}))^m]$ vs. $\ln[P(\text{H}_2)]$; where *m* is the order with respect to *n*-butane. A fresh catalyst was used in every run. The products were analyzed by gas chromatography using packed columns (Carbopack C/0.19% picric acid for *n*-butane reactions carried out in the flow reactor and Chromosorb 104 for hydrogenolysis reactions carried out in the pulse reactor) and a flame ionization detector. Hydrogen diffused through a Pd-Ag cell, helium passed through a molecular sieve trap at liquid nitrogen temperature, and MG Sci. Gases Inst. Grade *n*-butane were used as reactants or diluent.

TABLE I: Butane Reactions over Rh/TiO₂ Catalysts

catalyst	H/ Rh	reduc- tion temp, K	turnover freq, s ⁻¹		
			H ^a	I ^a	D ^a
impregnated 2 wt % Rh/SiO ₂	1.00	673	5000	0	0 ^b
impregnated 2 wt % Rh/TiO ₂	0.33	473	1600	0	0
	0.05	773	0.5	0	0
	0.76	473	3000	0	0
	0.02	773	0.07	0	0
ion-exchanged Rh/TiO ₂	1.00	473	400	0	0
	0.01	773	6×10^{-5c}	3×10^{-6c}	1×10^{-4c}
	1.00	473	4000 ^d	0	0
	0.01	773	0.007 ^d	0.001 ^d	NM ^e
blank TiO ₂		773	0	0	0

^a At 573 K. H = hydrogenolysis, I = isomerization, D = dehydrogenation. ^b The limit of detectability represents a turnover frequency $<10^{-9}$. This is the meaning of zero in the table. ^c Extrapolated from 688 K. ^d These results were obtained in a pulse reactor. They therefore are less affected by catalyst coking and were carried out at much higher average hydrogen to hydrocarbon ratio. ^e Not measured.

In order to determine the levels of coke formed during the reaction we performed the following experiment. After 20 min at the desired partial pressure the reaction was thermally quenched in the reacting mixture. Subsequently, the temperature was raised at a linear heating rate in a flow of pure H₂. The effluent stream was directly connected to a flame ionization detector and products of hydrogenation of coke were detected. Reduction at 773 K does not completely remove the coke formed. However, we assume that the amount removed as methane is proportional to the amount of coke present on the surface. Thus, this procedure gives a measure of a relative coking rate, which is sufficient for calculating the reaction orders.

Results and Discussion

The activity and selectivity of these catalysts were measured in a steady-state flow reactor after reduction at 773 K (high-temperature reduction (HTR)) and 473 K (low-temperature reduction (LTR)). Table I lists turnover frequencies of *n*-butane reactions on the Rh ion-exchanged catalysts as compared to other Rh catalysts. Note that only the ion-exchange prepared catalysts, when reduced at high temperature, exhibit isomerization and dehydrogenation activity. The suppression in hydrogenolysis activity for the ion-exchanged catalysts after reduction at 773 K is six orders of magnitude. Once the normal hydrogenolysis activity of Rh has been lost, the catalysts are able to display isomerization and dehydrogenation activities, masked while the hydrogenolysis capability was high. Even though the turnover frequencies for these reactions are very low and at the temperature used it takes about 1 h before the integral turnover per site exceeds one, the reaction was followed for 4 days to ensure its catalytic nature. By adjusting the temperature to work at total conversions higher than 1%, site time yields (turnover per site per resident time) greater than 100 were achieved.

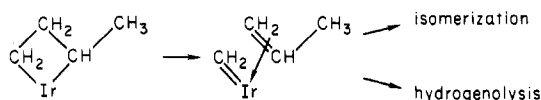
Table II shows a comparison between the catalytic behavior of some Ir catalysts reported in the literature and our Ir ion-exchanged catalysts. Again, only these novel catalysts show unique isomerization and dehydrogenation activities. An interesting trend can be noticed in Table II by comparing the fraction of ethane in the products, a measure of the selectivity for central vs. terminal bond rupture in the hydrogenolysis of *n*-butane. There is a clear decrease in the fraction of ethane in the products when going from low- to high-temperature reduction for the TiO₂-supported catalysts. A similar change in product distribution has been observed when Au was added to SiO₂-supported Ir catalysts.⁵ This is yet another example of the analogy between group 8-group 1b and group 8-TiO₂ interactions recently proposed by us.² Our Ir/TiO₂ ion-exchange catalysts after LTR exhibit the characteristic ethane

TABLE II: Butane Reactions over Ir/TiO₂ Catalysts

catalyst	H/Ir	reduction temp, K	ethane in products	E, kJ/mol	turnover freq, s ⁻¹			ref
					H ^a	I ^a	D ^a	
Ir/SiO ₂ ^b	1.00	673	0.73	172	61	0	0	3
Ir-Au/SiO ₂ ^b	0.10	673	0.57	163	2	0	0	4
Ir/TiO ₂ ^b	1.00	473	0.72	167	16	0	0	16
		773	0.55	NM ^f	0.001	0	0	16
Ir/TiO ₂ ^c	1.00	473	0.71	NM ^f	50	0	0	g
	<0.01	773	0.33 ^d	NM ^f	2 × 10 ^{-5 d}	3 × 10 ^{-6 d}	3 × 10 ^{-5 d}	g
	1.00	473	0.73	167	45 ^e	0	0	g
	<0.01	773	0.42	202	2 × 10 ^{-3 e}	5 × 10 ^{-4 e}	NM ^f	g

^a At 575 K. H = hydrogenolysis, I = isomerization, D = dehydrogenation. ^b Prepared by impregnation. ^c Prepared by ion exchange. ^d Extrapolated from 688 K. ^e These results were obtained in a pulse reactor. ^f Not measured. ^g This work.

selectivity of highly dispersed Ir catalysts, i.e., around 70%. The decrease in the central vs. terminal bond rupture selectivity is much more pronounced for the ion exchanged than for impregnated Ir/TiO₂ catalysts. This clear changeover in selectivity may suggest a change in hydrogenolysis mechanism. Fogar and Anderson³ have distinguished two types of hydrogenolysis modes on Ir catalysts, the C₂- and the iso-unit modes. The former has a lower activation energy and requires a larger ensemble of atoms to constitute the active site. For the latter, every exposed Ir atom is equally active. In Ir-Au catalysts⁴ the activation energies of both the C₂-unit mode and the iso-unit mode are independent of the Au content although they differ. The frequency factor for the iso-unit mode is also constant but decreases dramatically for the C₂-unit mode as the Au content is varied. From these observations Anderson has concluded that the critical reaction site for the iso-unit mode reaction is a single Ir atom. *n*-Butane hydrogenolysis normally proceeds through the C₂-unit mode. However, it would not be surprising that, in the case of our ion-exchanged Ir/TiO₂ catalysts, as the C₂-unit mode is suppressed, the reaction may proceed through the iso-unit mode on atoms isolated by SMSI. In addition to the change over in selectivity, we cite the increase in activation energy from 167 to 202 kJ/mol (see Table II) as evidence for a change over from C₂- to iso-unit hydrogenolysis mode in as much as these activation energies agree with those measured by Fogar and Anderson⁴ for the respective mechanisms. This hydrogenolysis mode is accompanied by bond shift isomerization and would proceed via the following C₃ carbocyclic intermediate:



Hydrogenolysis occurs by hydrogenation of the methylene and the π -bonded olefin. Isomerization requires rotation about the olefin π -bond, re-formation of the C₃ cycle, and desorption by addition of hydrogen. From this mechanism it follows that the main hydrogenolysis products will be propane and methane, which would explain the drastic change in ethane selectivity when going from low- to high-temperature reduction.

We have studied the variation of central/terminal bond rupture selectivity (ethane selectivity) over ion-exchanged Ir/TiO₂ catalysts as the hydrogenolysis activity was progressively suppressed by the SMSI. The extent of interaction and hence the decay in hydrogenolysis activity was varied by using different temperatures and times of reduction. The measurements were carried out in a pulse reactor to minimize the effect of coking. The hydrogenolysis activity started to decrease at reduction temperatures as low as 523–573 K dropping monotonically as the reduction temperature was increased. However, as shown in Figure 1 there is not much decay in the ethane selectivity up to 673 K and, in fact, there is a slight increase after reduction at 573 K. Only after long reduction times does the ethane selectivity begin to decay. At the same time, isomerization selectivity does not become evident until reduction at about 673 K and it reaches its maximum fol-

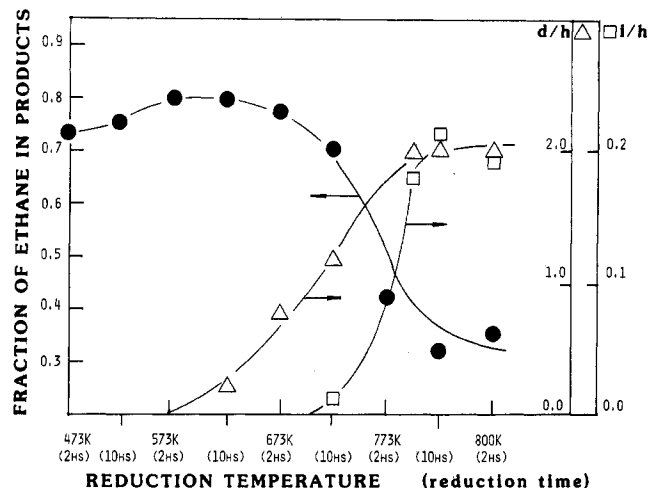


Figure 1. Left axis: Fraction of ethane in products of *n*-butane hydrogenolysis as a function of temperature and time of reduction. Right axis: Isomerization (squares) and dehydrogenation (triangles) selectivities expressed as ratios of these reactions to hydrogenolysis rate. Reaction temperature was 575 K.

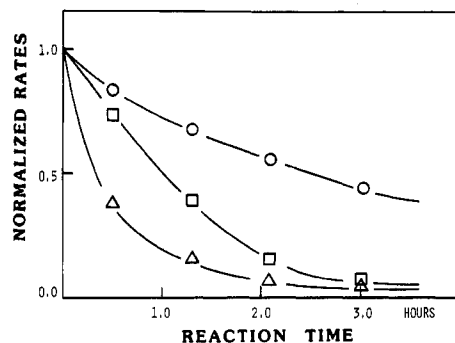


Figure 2. Normalized rates of hydrogenolysis (Δ), dehydrogenation ($\circ$), and isomerization ($\square$) of *n*-butane over Rh/TiO₂ as a function of reaction time at 688 K. The rates were normalized to their initial value.

lowing reduction at 773 K. The onset of isomerization coincides with the sharp decrease in hydrogenolysis selectivity. Thus, it appears that the proposed iso-unit mode mechanism operates over our ion-exchanged Ir/TiO₂ catalysts after HTR. By way of contrast, the dehydrogenation activity, also shown in Figure 1, becomes detectable following much lower reduction temperatures than isomerization, which would suggest that it proceeds through a different reaction path unrelated to the intermediate involved in iso-unit mode hydrogenolysis and isomerization.

Figure 2 shows turnover frequencies for *n*-butane hydrogenolysis, isomerization, and dehydrogenation over ion-exchanged Rh/TiO₂ catalysts after HTR as a function of reaction time measured in the flow reactor at 688 K (H₂ partial pressure = 0.5 atm, *n*-butane partial pressure = 0.5 atm). The observed deactivation may be associated with coke formation during the reaction. The activity was almost completely restored by oxidation at 673

(3) K. Fogar and J. R. Anderson, *J. Catal.*, **59**, 325 (1979).

(4) K. Fogar and J. R. Anderson, *J. Catal.*, **64**, 448 (1980).

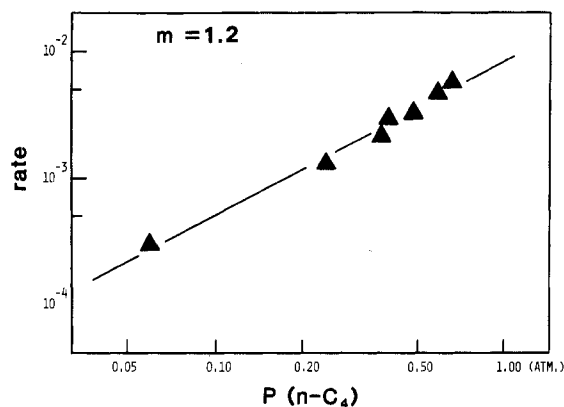


Figure 3. Turnover frequency (s^{-1}) for *n*-butane hydrogenolysis as a function of *n*-butane partial pressure at constant H_2 partial pressure = 0.30 atm and 688 K. Rate $\propto P(n\text{-butane})^m$, $m = 1.2$.

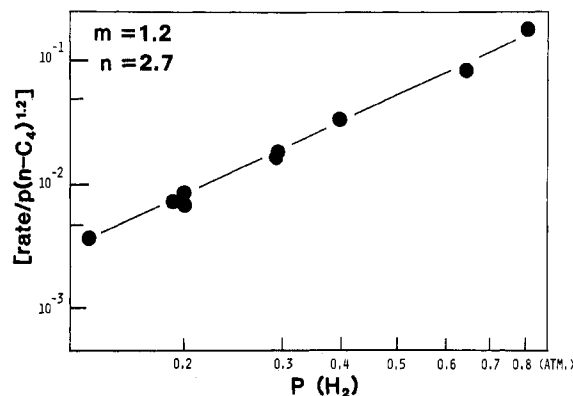


Figure 4. Turnover frequency/ $P(n\text{-butane})^{1.2}$ as a function of H_2 partial pressure at 688 K. Rate $\propto P(n\text{-butane})^{1.2}P(H_2)^n$, $n = 2.7$.

K followed by reduction at 773 K, while it was only partially restored when the oxidation step was not performed. The activity loss was most pronounced for the hydrogenolysis reaction. Thus, although the total rate decreases, the selectivity for isomerization and dehydrogenation is improved as the reaction proceeds.

The *n*-butane and hydrogen reaction orders for *n*-butane hydrogenolysis over Rh/TiO₂ reduced at 773 K were calculated from the slopes of the straight lines in Figures 3 and 4. The reaction orders for *n*-butane hydrogenolysis were 1.2 with respect to *n*-butane and 2.7 with respect to H_2 . The order in hydrocarbon is about what one expects for Rh/SiO₂. However, the normal order in H_2 would be -2.2 . The unusual positive order in H_2 is probably due, in part, to the effect of the carbon deposited on the surface during the reaction. Some evidence for this is provided by comparison to ethane hydrogenolysis where coking is not significant. Here the order in H_2 becomes less negative (-1.5) but does not become positive.² Coke acts as a poison of the metal surface. Thus, the ability of H_2 to remove hydrocarbon residues, which probably causes large apparent positive orders in hydrogenolysis (because residues deposited on one atom might deactivate the whole ensemble⁵), may overcome the negative effect that H_2 usually has in hydrogenolysis reactions by competing with the hydrocarbon for the adsorption sites. This also occurs on normal Rh catalysts but the balance between the inhibiting effect of strongly held H_2 and the positive effect on coke removal must, in that case, lie on the side of H_2 inhibition of hydrocarbon adsorption.

A typical spectrum of coke removal as methane as a function of temperature is shown in Figure 5. It can be observed that reduction at 773 K is not enough to remove all the carbon residues. Thus, the areas under the peaks between 423 and 673 K were used

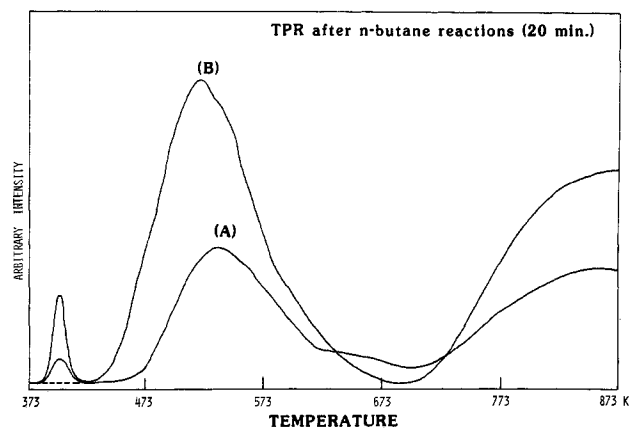


Figure 5. Typical spectrum from thermal-programmed reaction of H_2 with coke deposits after 20 min of *n*-butane reactions at 688 K: (A) $P(n\text{-butane}) = 0.5$ atm, $P(H_2) = 0.5$ atm; (B) $P(n\text{-butane}) = 0.5$ atm, $P(H_2) = 0.2$ atm.

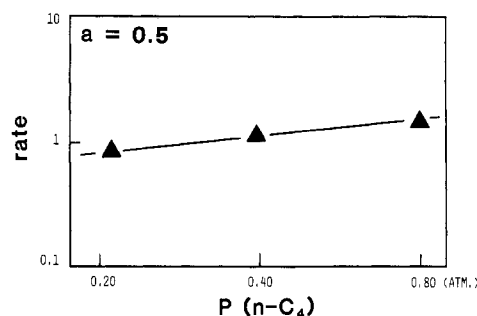


Figure 6. Relative coking rate as a function of *n*-butane partial pressure at constant H_2 partial pressure = 0.20 atm and 688 K. Rate $\propto P(n\text{-butane})^a$, $a = 0.5$.

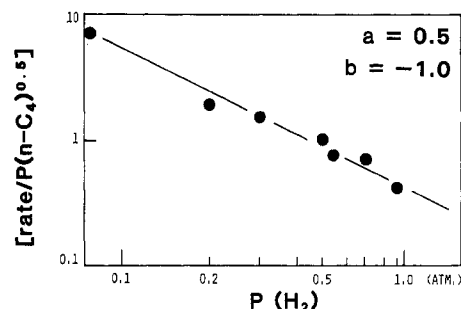


Figure 7. Coking rate/ $P(n\text{-butane})^{0.5}$ as a function of H_2 partial pressure at 688 K. Rate $\propto P(n\text{-butane})^{0.5}P(H_2)^b$, $b = -1.0$.

to quantify the relative rate of coke formation at the various partial pressures of *n*-butane and hydrogen. The partial pressure dependences for coke formation were then obtained, resulting in an order of -1.0 with respect to H_2 and 0.5 with respect to *n*-butane, as calculated from Figures 6 and 7.

Quantitative measurements of coke formation using a microbalance are now in progress. Preliminary results have shown that under our reaction conditions, i.e., at 688 K and a H_2 :*n*-butane ratio of 1.0, the amount of carbon deposited per surface Rh atom during 20-min reaction was $C/Rh = 1.2$. This number rules out the possibility that hydrogenolysis products were solely derived from coke precursors. If that were so, the number of molecules undergoing hydrogenolysis would be equal to or lower than the number of carbon atoms left on the surface. However, the integrated number of reacted molecules in the 20-min period was about 60 times greater than the number of C on the surface.

As pointed out previously, there is a clear analogy between the localized metal-support interaction observed when a TiO₂-supported group 8 metal is reduced at high temperatures and the effect of alloying group 8 metals with group 1b. In most of the group 8-group 1b bimetallic systems studied so far (Os-Cu,

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Ru-Cu, Pt-Au, Ir-Cu, Ni-Cu, Pd-Au, Ir-Au⁶) alloying leads to a sharp decrease in hydrogenolysis activity. The large ensemble required for hydrogenolysis appears to be the cause of this large effect compared to that observed for other reactions, whose requirements in terms of ensemble size are less demanding. Foger and Anderson,⁴ studying skeletal reactions over supported Ir-Au catalysts, have no evidence for isomerization of *n*-butane for any Ir-Au composition. However, selectivity for isomerization of neopentane increases from 0 to 6% when 50% Au is added. They have also pointed out that, although *n*-butane isomerization is not observed up to a Au/Ir ratio of about six, isobutane isomerization has been observed over evaporated films of this composition.⁷ The surface of the film was surmised to be much richer in Au than the supported catalyst and so the decrease of C₂-unit hydrogenolysis activity would be more marked, perhaps to an extent that may allow the reaction to proceed through an iso-unit mode. It has been found that Au by itself showed some activity for neopentane isomerization.⁸ However, as noted by Anderson,⁹ it is possible that the observed isomerization activity is due to a transition-metal impurity segregated to the surface. Van Schalk et al.,¹⁰ investigating the reactions of *n*-pentane and *n*-hexane on Pt-Au/SiO₂ catalysts, found that isomerization was most favored on low Pt content catalysts and it decreased as the Pt/Au ratio was increased. They explained this trend by assuming that isomerization can occur on the smallest ensembles of Pt atoms (perhaps on a single Pt atom) while hydrogenolysis requires a larger ensemble. In highly diluted catalysts, the number of Pt ensembles is strongly reduced, thus an enhancement in the selectivity to isomerization vs. hydrogenolysis can be expected.

An alternative explanation of these unique features might be considered, at least for the case of the ion-exchanged Rh/TiO₂ catalysts. Recently Hulzinga and Prins¹¹ have detected Pt⁺ by ESR on reduced Pt/TiO₂ catalyst and suggested that the oxidized Pt exists at the metal-oxide interface. If a similar circumstance prevails for Rh, then the extremely small particles (or even isolated atoms) may be in an oxidation state different than zero. From infrared of chemisorbed CO it certainly appears that Rh⁺ can survive a hydrogen reduction of 673 K¹² on Rh/TiO₂ even when the loading is relatively high and the dispersion is relatively low compared to our catalysts. However, in view of recent EXAFS studies of CO chemisorption on rhodium catalysts,¹³ which show that Rh-Rh bonding is disrupted by CO adsorption itself, we cannot ensure that species present upon CO addition are also present under reaction conditions.

An experimental observation we have made which would support the hypothesis of nonzero oxidation state of Rh is an unusually high amount of CO chemisorption relative to H₂ chemisorption on the Rh catalysts. The observed CO/H chemisorption ratio was about 3. We assume that conversion of Rh⁰

to Rh⁺ will suppress H₂ chemisorption more than CO although H₂ chemisorption on Rh⁺ must certainly occur, e.g., Wilkinson's catalyst for olefin hydrogenation.¹⁴ In fact, these homogeneous catalysts may be good analogies for our highly dispersed ion-exchanged Rh on TiO₂. They are highly active for olefin hydrogenation but are not known to catalyze hydrogenolysis. Our catalysts are not nearly so selective but because of their low activity our reaction temperatures are high and very likely there is at least some portion of the Rh in the zerovalent state. The homogeneous catalysts have not been reported to catalyze dehydrogenation but this is because they are thermally unstable at temperatures where these reactions are thermodynamically feasible. However, Crabtree¹⁵ has demonstrated that stoichiometric dehydrogenation of cyclic alkanes can be accomplished by certain Ir complexes at modest temperatures using *tert*-butylethylene as a hydrogen acceptor. While the coupling of the dehydrogenation of an alkane with the hydrogenation of another olefin makes the overall reaction about thermally neutral, *tert*-butylethylene is apparently unique in that it does not strongly compete with the unhindered cyclic alkane as a potential ligand for Ir, but still acts as a hydrogen acceptor.

It cannot be expected that a Rh or Ir oxidized species will either be active for hydrogenolysis (as noted above) nor interact with the support in the same way as metallic Rh would, i.e., it may not show SMSI because a surface support reduction catalyzed by the same metal is necessary to induce this type of interaction. Therefore, the oxidized Rh may remain unaltered while most of the Rh⁰ particles are being deactivated by the SMSI, resulting in a catalyst which has a very low hydrogenolysis activity but still exhibit activity for dehydrogenation, which may occur on isolated Rh⁺ species. The effect of coking may also be explained by this scheme, since coke formation will occur mainly on the metallic Rh particles, where hydrogenolysis takes place. Thus, this reaction will be more affected than dehydrogenation.

Conclusions

Titanium oxide supported Rh and Ir catalysts which have a unique activity for alkane dehydrogenation and isomerization have been discovered. Dispersion of 100% is necessary but not sufficient to produce these catalysts which are formed by ion exchange. We believe that the alkane dehydrogenation and isomerization activity may already exist on the catalysts reduced at low temperature but only becomes evident after high-temperature reduction because this process deactivates normal Rh and Ir particles for hydrogenolysis reactions by SMSI. Because the sites for dehydrogenation are only formed by ion exchange where the support effectively becomes a ligand and because these sites exhibit unusually high CO/H₂ chemisorption ratios and are apparently not active for hydrogenolysis, we suggest that they may involve Rh and Ir as isolated atoms which are not zerovalent.

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Registry No. TiO₂, 13463-67-7; Rh, 7440-16-6; Ir, 7439-88-5; *n*-butane, 106-97-8.

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