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Effect of Particle Microstructure on Alkane Hydrogenolysis on Rh/SiO_2[1]

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Oxidation of supported Rh catalysts followed by low-temperature reduction in H_2 produces hydrogenolysis activities which are up to 10^5 times higher than those after high-temperature annealing the same catalyst in H_2. In this paper we examine the effects of treatment conditions and particle size and compare C_2H_6, C_3H_8, and C_4H_{10} hydrogenolysis. The alteration in activity is somewhat larger for larger particle sizes and for C_2H_6 than for C_3H_8 or C_4H_{10}. The selectivity of C_3H_8 and C_4H_{10} also changes with oxidation in that the freshly oxidized catalyst produces more CH_4 while the annealed catalyst produces larger alkanes. C_3H_8 and C_4H_{10} exhibit deactivation by a factor of ≤5 after many hours at 250°C in both the oxidized and the annealed states. It is also found that activation in O_2 begins even at 25°C and that H_2O is effective in partially activating the catalyst. These results are discussed in terms of crystal planes produced by these treatments and variations in carbon formation on different planes. © 1988 Academic Press, Inc.

INTRODUCTION

Reaction rates on supported metal catalysts can vary by orders of magnitude depending on metal loading, preparation method, treatment, support, and other as yet unquantified factors.

We have recently shown (*1*) that the rate of C_2H_6 hydrogenolysis on 5% Rh on SiO_2 can be altered by up to three orders of magnitude by treating in O_2 or in H_2 and that this process is reversible in that the high and low rates can be produced repeatedly on a given catalyst by oxidation and H_2 annealing. We also showed by TEM that ~100-Å-diameter particles form clusters of smaller 10- to 20-Å-diameter particles by oxidation and low-temperature reduction. XPS showed that H_2 treatment above 200°C produced completely reduced metal surfaces. These results suggested that the variation in catalytic activity was caused by morphology changes, with the high-index surfaces produced by oxidation and low-temperature reduction being much more reactive. Comparable studies of CO hydrogenation and of C_2H_6 hydrogenolysis on Ni on SiO_2 showed a change by a factor of ~3 upon oxidation and low-temperature reduction (*2–4*).

There have been many studies of alkane hydrogenolysis activities (*5–13*) on supported metals such as Rh, Ni, Pt, Ir, and Ru in which activities were shown to vary with preparation treatment (*14–18*). Ruthenium on titania shows low activities for butane hydrogenolysis after high-temperature reduction, and subsequent oxidation followed by low-temperature reduction gives much higher activities (*15, 16*), which Bond *et al.* ascribed to strong metal–support interaction (SMSI) and spreading of ruthenium oxide over the support. Other hydrocarbon reactions have also been considered structure sensitive (*19–24*) because in general small particles provide higher activities than large ones. However, very small particles have been reported to show the lower activity in the formation of multiple bonds, and lower hydrogenolysis activity as also observed (*19*). This subject has been re-

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viewed recently by van Broekhoven and Ponec (*25*).

In this paper we extend our previous studies (1) of C_2H_6 hydrogenolysis on Rh by examining C_3H_8 and C_4H_{10} hydrogenolysis reactions and by comparing several Rh metal loadings. Higher hydrocarbons of course have several hydrogenolysis products so that the effect of treatment on selectivity versus activity can also be examined.

EXPERIMENTAL

Samples of 1, 5, and 15% Rh on SiO_2 were prepared by impregnation of SiO_2 (Cab-O-Sil, 200 m^2/g) to incipient wetness with an aqueous solution of $RhCl_3 \cdot 3H_2O$, drying at 100°C, and heating in O_2 at 800°C for 4 h.

Reaction rates, O_2 and H_2 treatments, and H_2 chemisorption measurements were in a Pyrex flow microreactor at temperatures up to 650°C. Nitrogen (Air Products 99.998%) was purified by passing it over a molecular sieve and copper at room temperature, while hydrogen (Matheson, 99.99995%) was passed through a liquid N_2 trap. Oxygen (Matheson, 99.9%) and premixed reaction gases (5 mole% hydrocarbon, 35 mole% H_2, 60 mole% He) were used without further purification. In this study we examined only this hydrocarbon-to-hydrogen reactant ratio. Water was added by passing gas streams through a bubbler.

Samples were oxidized in flowing air at 500°C for 4 h and reduced in flowing H_2 at specified temperatures for 4 h. Reaction products were measured with an on-line gas chromatograph (GC) using a flame ionization detector. The GC sensitivity was calibrated with a known mixture of low-molecular-weight hydrocarbons.

Hydrogen chemisorption to determine metal surface areas was carried out using the flow desorption method (*26*). Results gave generally consistent values to within ±20% on a given sample, but values were occasionally very high or low. Table 1 lists H_2 uptake, calculated dispersion, and calculated average particle size for the three loadings. Particle sizes assume spheres with one hydrogen atom per surface Rh atom. It is seen that the dispersion decreases with increased metal loading as expected, but very high dispersion samples could not be obtained because of high-temperature treatment (800°C) initially and at 650°C repeatedly to produce the total annealed state.

Each sample was oxidized and reduced repeatedly as indicated by the following sequence,

$$\text{Preparation} \longrightarrow \xrightarrow[500^\circ\text{C}]{O_2} \xrightarrow[250^\circ\text{C}]{H_2} \xrightarrow[\text{Chemisorption}]{H_2} \xrightarrow[180\text{–}260^\circ\text{C}]{\substack{\text{alkane}\\+\\H_2}} \xrightarrow[650^\circ\text{C}]{H_2} \xrightarrow[\text{Chemisorption}]{H_2} \xrightarrow[180\text{–}260^\circ\text{C}]{\substack{\text{alkane}\\+\\H_2}} \qquad (1)$$

Except where noted, all oxidations were at 500°C in air for 4 h followed by reduction in H_2 at 250°C for 4 h. We shall refer to this as the "oxidized sample." The "annealed sample" refers to samples after treatment in flowing H_2 for 4 h at 650°C followed by H_2 chemisorption measurement. In the previous papers we examined the effect of H_2 annealing temperature on C_2H_6 hydrogenolysis activity, but in this paper we use mostly single low-temperature (250°C) and single high-temperature (650°C) conditions for H_2 treatment with the same support SiO_2 under the same pretreatment conditions.

The hydrogenolysis activity of the oxidized sample was quite reproducible, within a factor of 2 for repeated oxidation–reduction cycles, but the activity of the annealed sample was less reproducible. As will be shown later, this depended on the concentration of traces of H_2O in the H_2. The activity after treatment in the purest H_2 was, in fact, immeasurably small: more than 10^5 lower than that after O_2 treatment. The activities shown for the reduced catalyst are therefore upper bounds on the actual activity, which could be obtained only in the complete absence of H_2O.

RESULTS

Effect of Metal Loading

Figure 1 shows plots of rates of C_2H_6 hydrogenolysis on oxidized and annealed surfaces at 230°C with rates calculated on three bases: (a) rates per gram of catalyst, (b) rate per gram of metal, and (c) turnover frequency (TOF, molecules reacted per metal surface atom per second).

Two or three cycles of oxidation and reduction are shown for each sample. Each cycle represents treatments as sketched in Eq. (1). It is seen that the rate for each "oxidized" sequence and each "annealed" sequence drops by less than 20% after three cycles. This is an irreversible loss of activity which is probably associated with a decrease in metal surface area produced by high-temperature heating.

However, there is a large and reversible variation in rate between oxidized and annealed states. This variation is a factor of ~70 for 15% loading, ~30 for 5% loading, and ~15 for 1% loading. Previously we noted a variation of nearly 1000 for a 5% loading. The present variation is observed to be smaller, and this is associated with traces of H_2O or O_2 impurities in annealing treatments, different temperature calibrations, heating at different intermediate temperatures, or with other unknown differences between the samples.

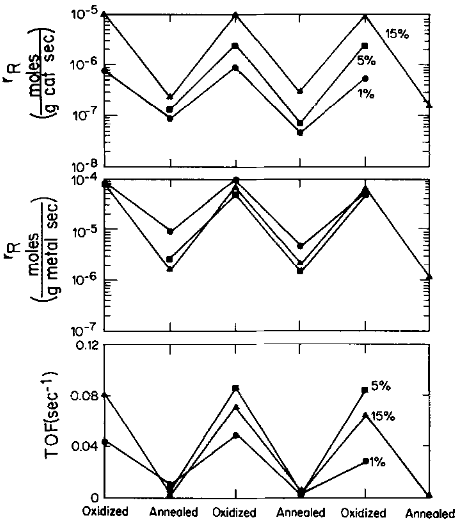

FIG. 1. Plot of reaction rate of C_2H_6 hydrogenolysis at 230°C after oxidizing and reducing the samples in H_2 at 250°C (oxidized) and at 650°C (annealed). The three sets of data show 1% (circles), 5% (diamonds), and 15% (triangles) Rh samples. Rates change reversibly by more than an order of magnitude, and the variation is largest on the 15% sample. The three panels show rate per gram catalyst, rate per gram metal, and turnover frequency (TOF), respectively.

Table 1 shows a comparison of the three catalysts. Column 2 shows the measured H_2 uptake on the annealed samples (heated in H_2 to 650°C). These values were averages obtained from 5 to 10 experiments involving oxidation–annealing treatments. The H_2 uptake after oxidation and low-temperature reduction was typically two to three times higher than values shown in Table 1. As discussed previously, this increase is cor-

TABLE 1

Comparison of Rh/SiO_2 Catalysts

Loading	μmole H_2/g cat.	Dispersion[b]	Particle diameter (Å)	C_2H_6 rate[a] (μmole/g metal)		TOF ($\times 10^3$ s^{-1})	
				Oxidized	Annealed	Oxidized	Annealed
1	6 ± 1.5	0.124	120	75	4.7	75	8.0
5	11 ± 3	0.045	320	44	1.4	118	6.4
15	24 ± 4	0.033	440	73	1.1	210	6.7

[a] Rates in μmole/g metal s.

[b] Based on the annealed state.

related with the formation of smaller particle clusters upon oxidation and low-temperature reduction.

The last columns of Table 1 and Fig. 1 show that the turnover frequency is approximately twice as high on the oxidized 15% catalyst as on the 1% catalyst, while after annealing the 1% catalyst has a somewhat higher TOF than the higher loadings.

From these experiments we conclude that both low and high loading exhibit large variations in activity, with a fairly small dependence on loading and particle size. The largest variations occur with the highest loading and the smallest with the lowest loading, but the difference between high and low loadings is not large. We could not examine a catalyst with close to 100% dispersion because the heat treatments required to produce activity changes also produced sintering low dispersions. We would, however, expect these changes to be somewhat smaller for higher-dispersion catalysts.

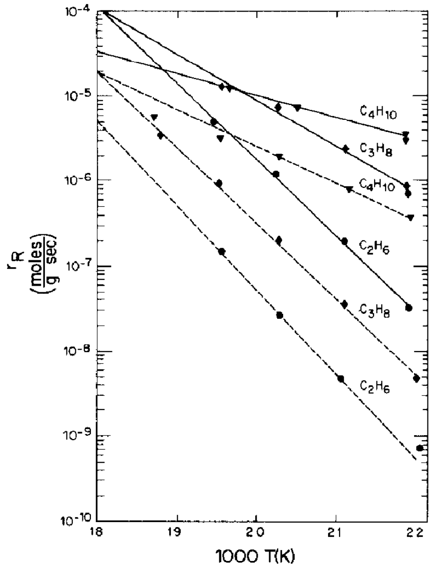

FIG. 2. Arrhenius plots of total rate of hydrogenolysis of C_2H_6, C_3H_8, and C_4H_{10} on Rh on 5% SiO_2 for oxidized (solid curves) and annealed (dashed curves) states. All rates are calculated on a carbon basis. Rates at 230°C and activation energies are shown in Table 2.

TABLE 2

Comparison of Rates on 5% Rh/SiO_2

Reactant	Products	Oxidized		Annealed	
		$r_{230°C}$[a]	E_R[b]	$r_{230°C}$[a]	E_R[b]
C_2H_6	CH_4	44	40	1.4	45
C_3H_8	All	200	30	15	40
	C_2H_6	124		10	
	CH_4	76		5	
C_4H_{10}	All	180	12	51	20
	C_3H_8	48		17	
	C_2H_6	74		24	
	CH_4	58		10	

[a] Rates in μmole/g metal s.

[b] In kcal/mole.

C_3H_8 and C_4H_{10} Hydrogenolysis

Rates in Fig. 1 were measured at 230°C. Rates were also measured at different temperatures, and Fig. 2 shows Arrhenius plots for total rates of C_2H_6, C_3H_8, and C_4H_{10} hydrogenolysis on 5% Rh/SiO_2. Table 2 lists effective activation energies from slopes of these curves. It is seen that E increases from ~25 kcal/mole to ~45 kcal/mole upon annealing the freshly oxidized surface. These activation energies have only qualitative significance since Arrhenius plots show definite curvature and strong dependence on annealing temperature. Figure 3 shows plots of total rates of C_4H_{10}, C_3H_8, and C_2H_6 hydrogenolysis at 230°C on the 5% catalyst in oxidized and annealed forms for two or three cycles of treatment.

Rates of formation of products and selectivities are calculated in Figs. 2–5 on a carbon basis rather than on a molecule basis because this permits a simpler calculation of selectivities which we define as

$$S_j = r_j/\Sigma\, r_j. \tag{2}$$

For example, complete cracking of C_4H_{10} to CH_4 creates four CH_4 molecules so that the rate on a carbon basis is one-fourth of that on a CH_4 molecule basis.

Rates of C_2H_6, C_3H_8, and C_4H_{10} hydrogenolysis at 230°C and activation energies

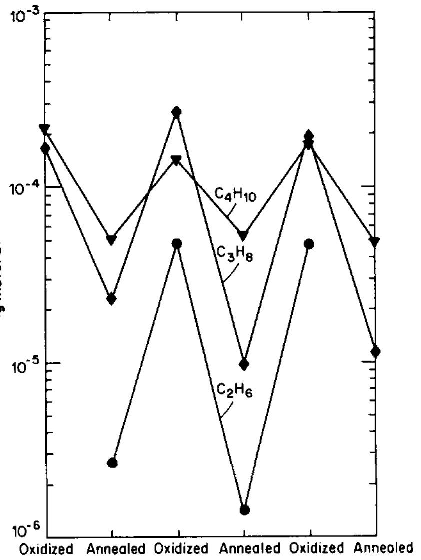

FIG. 3. Plot of total rates of hydrogenolysis of C_2H_6 (circles), C_3H_8 (diamonds), and C_4H_{10} (triangles) at 230°C on 5% Rh on SiO_2 on oxidized and annealed catalysts. C_4H_{10} has the highest rate while C_2H_6 has the lowest. The difference between oxidized and annealed catalysts is also largest for C_2H_6.

(from Figs. 2 and 3) are compared in Table 2. It is seen that $r_{C_2H_6}$ is 4 to 30 times smaller than $r_{C_4H_{10}}$ and that the reaction activation energy is significantly greater for C_2H_6 than for C_3H_8 or C_4H_{10}.

Figure 4 shows Arrhenius plots of C_4H_{10} hydrogenolysis rates on 1% Rh in oxidized (solid lines) and annealed (dashed lines) forms. Note that, while the total rates (upper curves) are approximately straight lines, rates of formation of individual products exhibit considerable curvature because selectivities are temperature dependent.

Figure 5 shows plots of selectivities of C_4H_{10} hydrogenolysis to C_3H_8, C_2H_6, and CH_4 on 5% Rh. The top and third panels are activities immediately after oxidation and after annealing, respectively, while the second and fourth panels show selectivities after deactivation after 20 h of reaction as discussed in the next section.

Figures 4 and 5 reveal significant variations in selectivities with temperature. In all cases C_3H_8 is the dominant product (on a carbon basis) at the lowest temperatures and the least favored product at high temperatures. The selectivity toward C_2H_6 production is nearly temperature independent, and therefore CH_4 always increases as temperature increases.

It should be noted that, while selectivities varied slightly between samples and with treatment conditions, this qualitative trend was observed in all of our experiments. Similar results were observed in C_3H_8 hydrogenolysis: mostly C_2H_6 at low temperatures and mostly CH_4 at high temperatures.

Effect of Gas and Temperature on Microstructure

We generally used H_2 at 650°C to "anneal" the sample and O_2 at 500°C to "oxidize" it, all for 4 h. We also used N_2 and

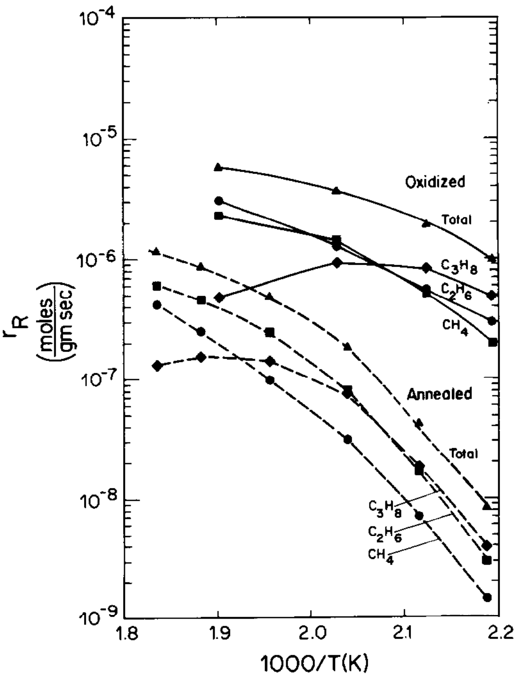

FIG. 4. Arrhenius plots of C_4H_{10} hydrogenolysis on 5% Rh/SiO_2 showing total rate and rates of formation of C_3H_8, C_2H_6, and CH_4 on the oxidized sample (solid line) and on the annealed sample (dashed lines). The total rate exhibits an approximately straight line but individual rates deviate considerably as reflected in selectivities shown in Fig. 5.

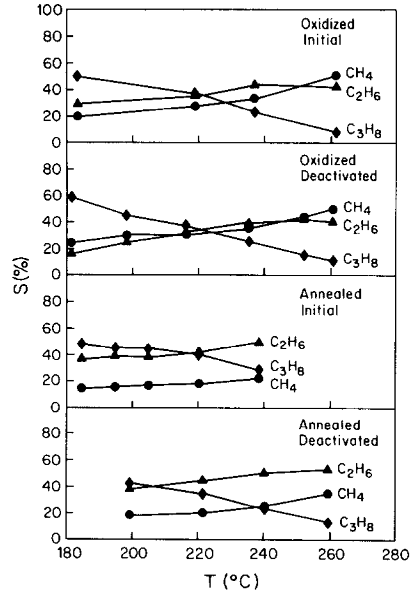

FIG. 5. Plot of selectivities of C_4H_{10} hydrogenolysis on 5% Rh on SiO_2 versus catalyst temperature. The upper panel is for initial activity after oxidation, the second is after reaction for 20 h, the third is initial activity after annealing, and the fourth is after reaction for 20 h on the annealed surface. Rates are calculated on a carbon basis.

H_2O and different times of treatment for these experiments.

Figure 6 is a plot of C_4H_{10} hydrogenolysis rate at 230°C on 15% Rh/SiO_2 versus treatment indicated at the bottom of the figure. All treatment times were for 2 or 4 h except where indicated. Points shown are for a single sequence of treatments of a sample over a 1-week period, but results were qualitatively repeated on several occasions.

For H_2 treatments in this sequence the H_2O and O_2 purifiers had been freshly installed so that oxidizing agents were totally removed. In this case the hydrogenolysis activity was unmeasurably small, from which we placed an upper bound on the activity of the annealed catalyst of 1×10^{-10} mole/g s. This shows that the ratio of activities in oxidized and annealed states is at least a factor of 700,000. Data in Ref. (*1*) and that shown previously in this paper employed less rigorous H_2 purification experiments, for annealing, and, therefore, ratios were between 50 and 10^3. However, careful purification of H_2 appears to produce a hydrogenolysis activity which is unmeasurably small.

This also suggests that traces of H_2O are effective in producing the active state of the catalyst. In treatments labeled 7, 8, and 11 in Fig. 6 the gases were bubbled through H_2O to saturation. Between treatments 6 and 7 it can be seen that the activity can be nearly restored by heating to 250°C in N_2 saturated with H_2O. This shows that H_2O is an effective oxidizing agent for Rh even at 250°C. Adding H_2O to a C_4H_{10} + H_2 mixture

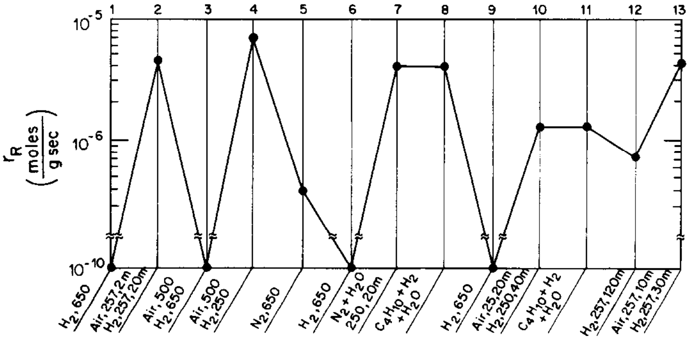

FIG. 6. Plot of rate of C_4H_{10} hydrogenolysis versus treatment conditions indicated. Data represent a single sequence of treatments on a single 15% Rh/SiO_2 sample. The rate after H_2 treatment at 650°C is less than 10^{-10} molecule/g s which is an upper bound on the rate. These results show that H_2O is an effective oxidizing agent, that oxidation begins even at 25°C, and that partial annealing occurs also in N_2.

does not significantly alter its hydrogenolysis activity, treatments 8 and 11.

We showed previously (*1*) that the reduction in activity produced by annealing the same catalyst in H_2 required a high temperature, 650°C, to become totally effective in deactivating C_2H_6 hydrogenolysis because heating to 300°C produced little deactivation, and 500°C produced only deactivation by a factor of 10.

Deactivation

All rates decreased somewhat with time, with the C_2H_6 hydrogenolysis rate exhibiting only a 10% decrease after 20 h in the reaction mixture at 230°C and C_4H_{10} exhibiting a fivefold decrease.

Initial activities reported here were measured by first attaining the desired temperature in flowing H_2, switching to the hydrocarbon mixture, and measuring the output gas composition by GC after 4 min. The flow was then switched to pure H_2 and the temperature was changed to a new value admitting the reactant mixture H_2. Therefore for a five-temperature Arrhenius plot, the hydrocarbon was on stream for only ~20 min for rates reported as initial values.

In the C_4H_{10}/H_2 mixture, with a sevenfold H_2 excess, there was a rapid drop of 30% of the total change in the first hour, followed by a slower decrease over the next 19 h. We of course would not observed any deactivation processes which occurred within the first 4 min of hydrocarbon mixture exposure. However, rapid deactivation processes did not appear to interfere with previously described rates in that good reproducibility was obtained within the accuracy required to characterize oxidized and annealed states.

Both freshly oxidized and annealed samples exhibited comparable decreases in activity. Deactivation was more rapid at higher catalyst temperatures, but there was no significant difference between annealed and oxidized states.

In the second and fourth panels of Fig. 5 are plotted selectivities of these products versus temperature on the deactivated catalysts. We also obtained almost identical selectivities on the 1% catalyst. The major conclusion from Fig. 5 is that deactivation produces little change in selectivity even though the total rates change by a factor of ~5.

Effect of Residence Time

For most of these experiments a flow rate was chosen such that the conversion of reactant was 1–10% to obtain accurate product analysis. We also examined the dependence of flow rate on conversions to determine its effect on selectivity in order to find whether hydrogenolysis products were formed by sequential reactions.

Figures 7 and 8 show selectivities versus residence time for C_3H_8 and C_4H_{10} hydrogenolysis on 15% Rh/SiO_2, respectively. The upper horizontal axes show the conversions corresponding to these times, which are nearly linear for low conversions. The conversion is of course higher

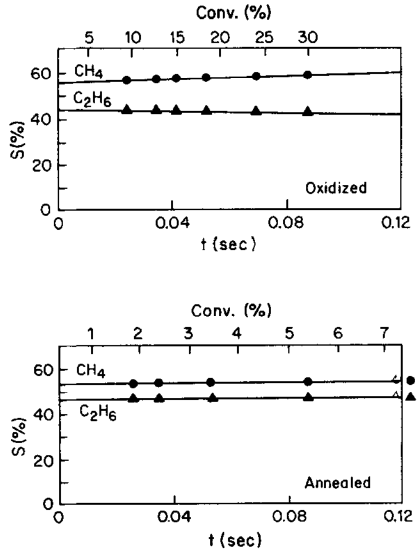

FIG. 7. Plot of selectivity of C_3H_8 hydrogenolysis versus residence time and conversion (upper axis) at 235°C for oxidized and annealed samples. Selectivities are nearly independent of residence time, showing that data yield essentially differential rates for each reaction.

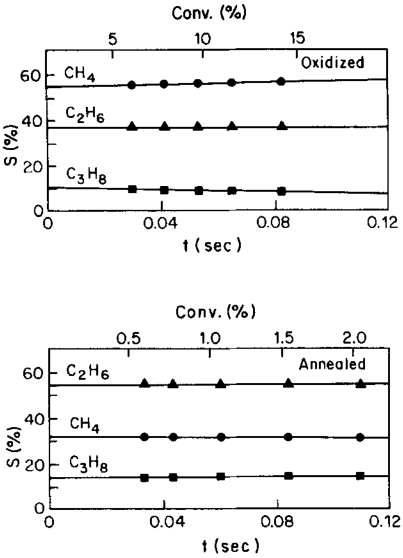

FIG. 8. Plot of selectivity of C_4H_8 hydrogenolysis versus residence time and conversion (upper axis) at 235°C for oxidized and annealed samples. Selectivities are nearly independent of residence time, showing that data yield differential rates of each reaction. Note that C_2H_6 formation is independent of residence time while C_3H_8 falls with increasing residence time and CH_4 rises.

for the oxidized sample than for the annealed samples. However, the conversions in both situations are sufficiently low that selectivities appear nearly independent of residence times and are therefore true selectivities of reaction of the parent species without interference from sequential decomposition.

For the high-activity samples the selectivities vary measurably with residence time, and it is clear that C_2H_6 is converted to CH_4 in C_3H_8 hydrogenolysis and that C_3H_8 is converted to and CH_4 and C_2H_6 in C_4H_{10}. From these data we can compute the C_2H_6 and C_3H_8 hydrogenolysis rates, and these are shown in Table 2. In C_4H_{10} hydrogenolysis the C_3H_8 decreases, the CH_4 increases, and the C_2H_6 is unchanged as the residence time increases.

DISCUSSION

To summarize these results, hydrogenolysis of all alkanes on Rh appears to exhibit a large, reversible change in activity which depends on whether the catalyst had been freshly oxidized or annealed at high temperatures. This variation is not a strong function of catalyst loading and is comparable for C_2H_6, C_3H_8, and C_4H_{10}.

The selectivities for production of CH_4, C_2H_6, and C_3H_8 from C_4H_{10} hydrogenolysis are different on oxidized and reduced catalysts, with freshly oxidized catalyst producing more CH_4 and the annealed catalyst producing more C_2H_6 and C_3H_8.

The intepretation of these results has been discussed previously (*1*, *2*) and will only be summarized here. TEM shows that particles are transformed from 100- to 200-Å-diameter crystals into clusters of 10- to 20-Å particles by oxidation and low-temperature reduction. XPS shows that particles are completely reduced in H_2 by 150°C so that all rates are on metal rather than on metal oxide particles (*2*). Hydrogen chemisorption confirms that metal surface areas increase by a factor of 2–3 in agreement with TEM results.

Basically these results suggest that the high-index crystal planes formed on small ~10-Å crystallites have a much higher specific activity in hydrogenolysis than do the predominantly (111) planes of the annealed catalyst. The particle size is too large to suggest strong support interactions or electronic changes in the Rh. We observed the opposite variation in activity in CO hydrogenation on Ni which suggests that each reaction in influenced differently by oxidation treatment.

Selectivities

There has been considerable discussion in the literature (*25*) concerning whether hydrogenolysis of higher alkanes occurs by a series process

$$C_4H_{10} \rightarrow C_3H_8 \rightarrow C_2H_6 \rightarrow CH_4 \tag{3}$$

or by parallel processes such as

$$C_4H_{10} \rightarrow C_3H_8 + CH_4 \tag{4.1}$$

$$C_4H_{10} \rightarrow 2C_2H_6 \qquad (4.2)$$

$$C_4H_{10} \rightarrow 4CH_4 \qquad (4.3)$$

Our results show clearly that C_2H_6 and CH_4 from C_4H_{10} are produced mostly by *decomposition of the parent molecules* and not significantly by series reactions, Eq. (3). That is, while the slopes in Fig. 8 show that C_3H_8 increases slightly and CH_4 decreases slightly as the residence time decreases, extrapolation to zero residence time yields approximately the selectivities shown. A similar argument holds for CH_4 from C_3H_8. Therefore, rates shown in Table 2 are at sufficiently low conversions that they represent true reaction rates of the parent molecules in the sense of Eq. (4).

We next inquire whether parallel rates can be regarded as specific processes such as

$$C_3H_8 \rightarrow C_2H_6 + CH_4 \qquad (5.1)$$

and

$$C_3H_8 \rightarrow 3CH_4 \qquad (5.2)$$

or whether they must be written as

$$C_3H_8 \rightarrow C_2H_6 \qquad (6.1)$$

$$\rightarrow CH_4 \qquad (6.2)$$

Stated otherwise, does an adsorbed C_3H_8 molecule retain its identity in unimolecular decomposition reactions as in Eq. (5) or is there a range of adsorbed complexes C_xH_y from which various products appear?

The mechanism of Eq. (5) requires a 2/1 ratio of C_2H_6/CH_4 by Eq. (5.1) (on a carbon basis) while reaction by Eq. (5.2) would produce more CH_4 and therefore a lower ratio. Since we observe $\leq 50\%$ CH_4 from Fig. 7, this is consistent with Eq. (5) is the rate of Eq. (5.1) were much larger than that of Eq. (5.2). At a lower temperature less CH_4 is produced than would be considered with Eq. (5.1). Similarly, in C_4H_{10} hydrogenolysis the unimolecular reaction to produce C_3H_8, Eq. (4.1), would yield a C_3H_8/CH_4 ratio of 3/1. Since other reactions also produce CH_4, reactions consisting only of unimolecular reactions would yield $C_3H_8/CH_4 < 3$. Since we exceed that selectivity ratio in Fig. 4 (by a slight amount), the results suggest that C_4H_{10} hydrogenolysis does not proceed exclusively by a sequence of unimolecular reactions.

SUMMARY

Reversible activation and deactivation of Rh catalysts occur for C_2H_6, C_3H_8, and C_4H_{10} hydrogenolysis. There is no strong influence of metal loading on the variation, although very high-dispersion catalysts could not be examined because high-temperature annealing unavoidably produces sintering. Annealing in N_2 is nearly as effective as that in H_2 in reducing activity as long as H_2O and O_2 are removed. The annealed state activity is very small and depends sensitively on traces of H_2O or other oxidizing agents. The "oxidized" state can be partially produced by treament in air even at room temperature and almost totally by air treatment at 250°C. H_2 is nearly as effective as air in restoring activity.

The selectivity of C_2H_6 formation from C_4H_{10} is a factor of 2 higher in the lower-activity annealed state. More CH_4 is produced on the oxidized sample, although the C_3H_8 changes only by ~30% between oxidized and annealed states. Self-poisoning effects are small on Rh, <10% for C_2H_6 and a factor of ~5 for C_4H_{10} over a 24-hour period under reaction conditions. The selectivity is nearly unchanged on fresh and deactivated samples.

In a later paper we will examine these variations on Ru, Ir, Pd, and Pt. These results show that Ru behaves such as Rh but that Ir, Pd, and Pt have much lower hydrogenolysis activities and smaller variations between oxidized and annealed states.

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