JOURNAL OF CATALYSIS **111**, 397–408 (1988)

A Kinetic and Mechanistic Study of Cyclohexene Disproportionation: An Example of Irreversible Hydrogen Transfer

DAVID M. REBHAN AND VLADIMIR HAENSEL

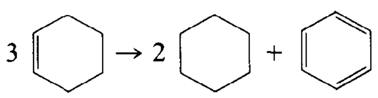
Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

Received October 6, 1987; revised January 4, 1988

The kinetics and mechanism of cyclohexane disproportionation, as well as its structure sensitivity, have been studied over a variety of Group VIII metal catalysts (i.e., Pt, Pd, and Ni). The goal of this work was to better understand how hydrogen transfer occurs in heterogeneous catalysis. Three reactions were studied: cyclohexene disproportionation, cyclohexene hydrogenation, and benzene hydrogenation. A gas-phase, microcatalytic reactor was used to obtain the data. The results were analyzed in terms of their activities, apparent activation energies, and selectivities. It was found that all the catalysts (except 0.001% Pt/Al_2O_3) were active catalysts for benzene hydrogenation. The apparent E_a's were between 42 and 50 kJ/mole. The activities decreased in the following manner, Pt > Ni > Pd. In contrast, during cyclohexene disproportionation, the apparent E_a's varied among catalysts (Pt ≈ 84, Pd ≈ 50, and Ni ≈ 25 kJ/mole), but their activities at 100°C were similar (except 0.01 and 0.001% Pt/Al_2O_3). During cyclohexene disproportionation, it was also found that the selectivity was a function of temperature. There existed a transition temperature below which the correct stoichiometry for cyclohexene disproportionation was observed, and above which the selectivity (measured as moles cyclohexane produced/moles benzene produced) decreased with temperature. This transition temperature varied with type of metal (T was ≈60°C for Ni, ≈90°C for Pd, and ≈110°C for Pt). The results can be explained as a competition between two reactions, intermolecular hydrogen transfer among cyclohexene molecules and cyclohexene dehydrogenation. The idea of reaction occurring over a carbonaceous overlayer was used to explain the observed similar activities at 100°C, and also the varying apparent E_a's among catalysts. Furthermore, the catalysts' capacity for hydrogen storage seems to be a fundamental part of the mechanism. If the capacity for hydrogen storage is impaired, then activity and selectivity are greatly altered.

INTRODUCTION

The disproportionation of cyclohexene is one of the most interesting examples of hydrogen transfer. Hydrogen redistributes among the three cyclohexene molecules to form two molecules of cyclohexane and one of benzene:



The reaction is exothermic and has a negative free energy change at room temperature. From early work (*1–5*), it was observed to occur irreversibly and quantitatively over a variety of Group VIII metal catalysts (i.e., Pt, Pd, and Ni). For this reason, cyclohexene disproportionation was called "irreversible catalysis."

Since the early work concerning this reaction, few investigations have been made to study its nature. Hence, the reaction mechanism is still largely speculative.

Perhaps the most interesting question to be answered in regard to cyclohexene disproportionation is how the hydrogen transfer occurs. Does it occur intermolecularly, or is hydrogen first transferred to the catalysts' surface in a dehydrogenation step to be used subsequently for hydrogenation? Also, is the hydrogen storage capacity of the catalyst linked to its ability to transfer hydrogen?

Many mechanisms have been proposed. Balandin and Brusow (*6*) hypothesized that

0021-9517/88 $3.00

the reaction occurred termolecularly. Germain (*7*) proposed that upon cyclohexene adsorption a rapid equilibrium is formed among all the cyclic C_6 hydrocarbons and that only cyclohexane and benzene could desorb. Carra *et al.* (*8, 9*) have concluded that the reaction proceeds through a bimolecular surface reaction in which hydrogen is directly transferred between reactants. Davis and Somorjai (*10*) have suggested that the hydrogen transfer occurs over a carbonaceous overlayer which covers the catalysts' surface. Cyclohexene disproportionation has also been accomplished in the liquid phase using homogeneous catalysts (*11, 12*). This supports the idea that intermolecular hydrogen transfer is possible.

The goal of our study was twofold. First, we wanted to investigate the mechanism and kinetics of cyclohexene disproportionation. Second, we wanted to study its structure sensitivity. To this end, we have studied cyclohexene disproportionation, cyclohexene hydrogenation, and benzene hydrogenation in a gas-phase, microcatalytic reactor with a series of Pt, Pd, and Ni catalysts. The information we have gathered has allowed us to evaluate cyclohexene disproportionation in terms of its mechanism, apparent kinetics, and structure sensitivity.

METHODS

Materials

The catalysts were chosen such that some catalysts had a high concentration of large ensembles (e.g., 66% Ni/kieselguhr, 5% Pd/alumina, and 0.8% Pt/alumina) while others had mostly small ones (e.g., 0.1, 0.05, 0.01, and 0.001% Pt/alumina). Our basic concept was that if the catalyst had large enough ensembles, it could accommodate intermolecular hydrogen transfer or hydrogen storage. On the other hand, if one reduces the metal loading by some five orders of magnitude, then the possibility of retaining large enough ensembles for intermolecular hydrogen transfer or hydrogen storage is greatly reduced.

Five platinum catalysts were tested—0.8, 0.1, 0.05, 0.01, and 0.001% Pt by weight. These were all supplied to us by UOP in the reduced form. The 0.8–0.01% Pt/alumina catalysts were prepared using the wet impregnation of chloroplatinic acid on γ-alumina. After impregnation the catalysts were steamed, dried, calcined in air, and reduced in hydrogen. This method of preparation produces catalysts with predominantly two-dimensional (2D) ensembles (raft-like) of Pt and very high dispersions. The 0.001% Pt/alumina was prepared via vapor phase deposition of platinum. All the Pt catalysts measured 100% dispersion of platinum by H_2 chemisorption and had surface areas of $\approx$170 m^2/g. The 66% Ni/kieselguhr catalyst was produced by Harshaw and had a surface area of 30 m^2/g. If one assumes that the surface of this catalyst is completely covered by Ni, then its dispersion corresponds to approximately 10%. The 5% Pd/alumina catalyst was produced by Grace (SMR 7-2229) and had a surface area of 100 m^2/g. We have assumed that its dispersion was 50%.

The cyclohexene used in this study was Aldrich, 99%. Before reaction, it was passed through activated alumina in order to remove any peroxides. Benzene was Fisher spectranalyzed grade and was stored over 3-Å molecular sieves to keep it dry. Tank hydrogen was purified with a Deoxo unit followed by a molecular sieve/drierite trap. Helium was purified using a 3-Å molecular sieve trap followed by an oxygen trap.

Reactor

Kinetic studies were performed in a vapor-phase, microcatalytic reactor operated at $\approx$1–2 psig. A schematic diagram is given in Fig. 1. Liquid reactants were fed via a syringe pump into a preheater/vaporizer operated at 130°C and mixed with He and/or H_2. This mixture was then passed into an

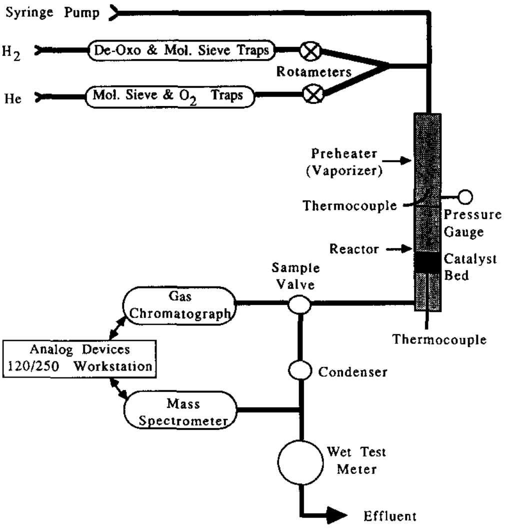


FIG. 1. Schematic diagram of microcatalytic reactor.

isothermal Pyrex reactor of 8 mm i.d. (When more than 1 g of catalyst was used, a 13-mm-i.d. reactor was used.) The catalyst bed was supported by quartz wool and a thermocouple was placed in its center. All empty sections of the reactor and preheater were filled with glass beads to improve mixing and heat transfer. Gauge pressure was measured through a port located above the bed. The hydrocarbon products were analyzed using on-line gas chromatography and the net hydrogen make was determined using on-line mass spectrometry. The reactor, Hewlett–Packard 5890A gas chromatograph, and UTI quadropole mass spectrometer were interfaced to an Analog Devices 120/250 work station.

Catalyst Bed

The catalyst bed generally consisted of $\approx$50 to 1000 mg of catalyst depending on its activity and metal loading. It was ground and sieved to sizes between 125 and 500 μm in order to minimize internal diffusion effects. When working with small quantities of catalyst ($\leq$150 mg) about 1 g of α-alumina was mixed with the bed in order to keep it of sufficient size to prevent flow channeling. Also, approximately 200 mg of γ-alumina was used as a guard bed in order to remove any poisons still present in the cyclohexene feed. (Experiments with only γ-alumina present in the reactor showed that it is not active for cyclohexene conversion.) These were also ground and sieved to the same size range.

Catalyst Reduction

The catalysts were reduced *in situ* prior to reaction. Since they were all prereduced, only a light reduction treatment was necessary. The Pt and Pd catalysts were reduced for 2 h at 300°C in 75 cc/min. H_2 flow and the Ni catalysts were treated similarly except at 350°C. An exception was made for 0.001% Pt/Al_2O_3 catalyst. Even though this catalyst was prereduced, it was felt that the very small Pt aggregates on this catalyst could spontaneously oxidize in air at room temperature (i.e., under normal storage conditions). Therefore, it was reduced for 2 h at 520°C prior to reaction.

Typical Experiment

A typical disproportionation experiment was performed as follows. After reduction the bed was cooled in hydrogen to $\approx$100°C. At that time, the H_2 was replaced by He at 150 cc/min and cooled to the initial reaction temperature, 60°C. After purging the reactor for 1 h the He flow rate was adjusted to the desired rate (usually 280 cc/min STP) and the cyclohexene feed was introduced (usually 13 gaseous cc/min STP). We estimated that external diffusion effects were negligible at these rates. After allowing time for the reactor to reach steady state ($\approx$5 min), the effluent was sampled and analyzed. Now, the reactor temperature was increased in 10°C intervals, with the effluent being sampled at each point, up to approximately 150°C. After taking samples in a temperature-increasing sense, the temperature was decreased and another set was taken. This allowed us to evaluate the effect and magnitude of deactivation which had occurred during the experiment. Generally, the whole procedure lasted about 2 h and the extent of deactivation was small.

Cyclohexene and benzene hydrogenation experiments were performed similarly. After reduction, the bed was cooled in H_2 to 60°C. Then the flow rates were adjusted (usually 6 gaseous cc/min STP benzene and 140 cc/min STP H_2 for benzene hydrogenation or 26.5 gaseous cc/min STP cyclohexene and 520 cc/min STP H_2 for cyclohexene hydrogenation) and samples were taken as with disproportionation.

Catalyst Deactivation

Deactivation is an unavoidable aspect of catalytic kinetics. Usually, the amount of deactivation can be minimized by operating with high partial pressures of hydrogen (as for hydrogenation) and/or by operating at temperatures where the rate of deactivation is small (as for disproportionation).

In these experiments, cyclohexene caused faster deactivation of the catalyst than benzene. This is understandable since cyclohexene is more reactive than benzene. Also, as expected, deactivation was faster when He was used as a carrier gas (i.e., cyclohexene disproportionation) as compared to hydrogen (i.e., cyclohexene hydrogenation). This could be due to the faster buildup of carbonaceous material on the catalysts' surface (*16*).

In addition, there existed specific temperature regimes—corresponding to changes in the adsorbed state of hydrocarbon—where deactivation occurred to different extents. For example, during cyclohexene disproportionation, deactivation was negligible at temperatures less than 100°C. In this region, cyclohexene is mainly associatively adsorbed (*13, 14*). Between 100 and 150°C, adsorption starts to become dissociative in nature and consequently a small amount of deactivation "by coking" occurs. Above 150°C, decomposition occurs readily and deactivation occurs quickly. During cyclohexene hydrogenation deactivation occurred in the same temperature regimes but more slowly. For benzene hydrogenation, deactivation was negligible at temperatures less than 150°C.

For these reasons, only data collected between 50 and 100°C was used in the calculation of kinetic parameters for cyclohexene disproportionation and cyclohexene hydrogenation, the only exception being the 0.01% Pt/Al_2O_3 catalyst, which had appreciable conversion only in the temperature range between 90 and 150°C. Data collected between 50 and 150°C were used in the calculation of kinetic parameters for benzene hydrogenation and the net hydrogen make during cyclohexene disproportionation.

RESULTS

Active Hydrogenation Catalysts

The hydrogenation of benzene has been the subject of numerous investigations and reviews. Therefore, it is often used to compare the activity levels of catalysts. It is a rather complex reaction and and normally gives values of the apparent activation energy between 42 and 50 kJ/mole over Group VIII metals (*15*).

Table 1 lists the apparent activation energies and Table 2 gives the turnover frequencies at 100°C for the various catalysts during both benzene hydrogenation and cyclohexene disproportionation. As expected, it was found that the apparent activation energy for benzene hydrogenation remained relatively constant regardless of the type of metal or support used, 42–50 kJ/mole. When the specific activities of the Pt, Ni, and Pd catalysts were compared it was found that the rate on Pt was about an order of magnitude faster than that on Ni, which was about an order of magnitude faster than that on Pd. (The only exception was the 0.001% Pt/Al_2O_3 catalyst. It was active for cyclohexene hydrogenation, but not for benzene hydrogenation.) Also, the observed levels of activity were consistent with other results (*15*). Hence, all the catalysts used in this study were active hydrogenation catalysts.

TABLE 1

Apparent Activation Energies (kJ/mole) Calculated from the Zero-Order Rate Expression, Rate = $A\{\exp(-E_a/RT)\}$

Catalyst	Benzene hydrogenation (50–150°C)	Cyclohexene conversion[a] (50–150°C)	Net H_2 make[b] (50–150°C)
66% Ni/kieselguhr	53	26	84
		26	69
5% Pd/alumina	51	49	77
0.8% Pt/alumina	44	77	71
0.01% Pt/alumina	42	89	90
		85	77

[a] Cyclohexene conversion refers to the sum of conversions to benzene and cyclohexane.

[b] Net H_2 make was determined from mass spectrometry as the integrated area under the $m/e = 2$ peak.

Kinetics of Cyclohexene Disproportionation

Many insights into the nature of cyclohexene disproportionation can be gained from a general overview of the data. At low temperatures (≤70°C for Ni, ≤90°C for Pd, and ≤110°C for Pt), the observed products were only cyclohexane and benzene. At higher temperatures, the observed products were cyclohexane, benzene, and hydrogen. This indicates the complex nature of the disproportionation reaction. A comparison of the turnover frequencies at 100°C (Table 2) showed that the rate of cyclohexene disproportionation was similar for all the catalysts (0.25–0.75/s) except the 0.01 and 0.001% Pt/Al_2O_3 catalysts.

Other aspects of the kinetics (i.e., selectivity and apparent E_a) varied not only with the type of metal but also with the method of preparation. Figure 2 shows Arrhenius plots based on the conversion of cyclohexene for different catalysts. The apparent E_a for cyclohexene conversion changed de-

TABLE 2

Turnover Frequencies[a] Calculated at 100°C

Catalyst	Benzene hydrogenation TOF ca. 100°C	Cyclohexene conversion TOF ca. 100°C
66% Ni/kieselguhr	0.019	0.38
5% Pd/alumina	0.001	0.74
0.8% Pt/alumina	0.28	0.24
0.05% Pt/alumina	0.37	0.3
0.01% Pt/alumina	0.18	0.07
		0.04
0.001% Pt/alumina	0.0	0.0

[a] TOF is defined as molecules C_6H_{10} converted per assumed metal surface atom per second. Ten percent dispersion is assumed for 66% Ni/kieselguhr, 50% dispersion is assumed for 5% Pd/alumina, and 100% dispersion is used for the Pt catalysts.

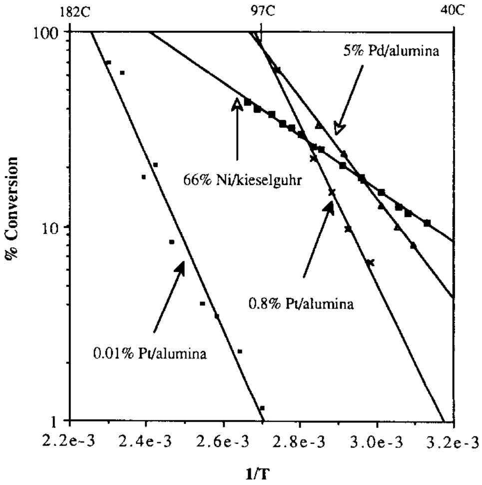


FIG. 2. Arrhenius plots (based on cyclohexene conversion) for cyclohexene disproportionation over various catalysts.

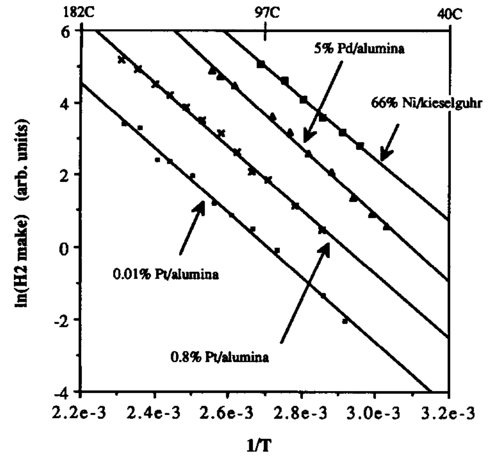


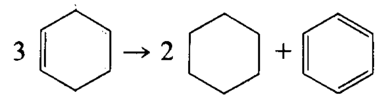
FIG. 3. Arrhenius plots (based on net H_2 make) for cyclohexene disproportionation over various catalysts.

pending on the type of metal used. Ni gave a value of 25 kJ/mole, Pd gave 50, and Pt was between 75 and 84. This seemed to indicate that hydrogen transfer occurred in different ways over different metals, but in fact seems to be linked with the varying buildup of carbonaceous residue on, and the hydrogen storage capability of, each catalyst (see discussion). Figure 3 shows Arrhenius plots based on the net H_2 make as measured by mass spectrometry. Contrary to disproportionation, these values did not vary much among catalysts. They fell between 67 and 80 kJ/mole (Table 1 gives the value for individual catalysts).

Another pertinent point is that while all the catalysts had similar specific activities at 100°C for disproportionation, the specific activities at the same temperature for benzene hydrogenation dropped by approximately two orders of magnitude as the type of metal was changed from Pt to Ni to Pd (Table 2). This behavior can be explained as reaction occurring over a carbonaceous overlayer (see under Discussion). The benzene hydrogenation experiments were performed with a large excess of H_2, thus preventing the buildup of carbonaceous residue. Therefore, the observed rates were characteristic of relatively clean metal surfaces. However, for cyclohexene disproportionation, formation and buildup of carbonaceous residue were very likely (*16*). In this scenario the individual natures of the metals would be "shielded," thus explaining the observed similar rates (i.e., rates characteristic of reaction occurring over a carbonaceous overlayer).

Selectivity during Cyclohexene Disproportionation

Figures 4 and 5 show the percentage conversion to cyclohexane and benzene with temperature for the 66% Ni/kieselguhr catalyst. At low temperatures, the amount of conversion to cyclohexane parallels that of benzene. However, as temperature is increased the conversion to benzene keeps increasing, but the conversion to cyclohexane goes through a maximum. Now, if one plots the selectivity expressed as moles cyclohexane produced/moles benzene produced vs temperature, as shown in Fig. 6, it is seen that at low temperatures the correct stoichiometry for cyclohexane disproportionation is observed:



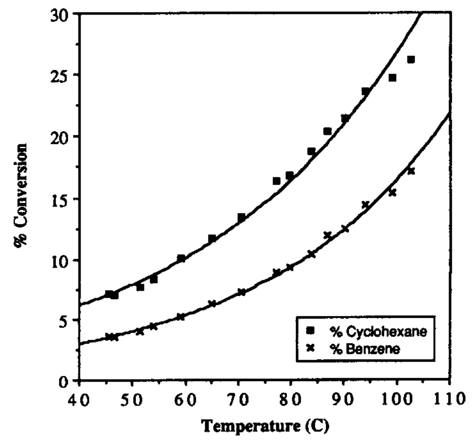


FIG. 4. Product distribution at low temperatures during cyclohexene disproportionation over 66% Ni/kieselguhr (61 Torr cyclohexene, 916 Torr helium, WHSV = 292).

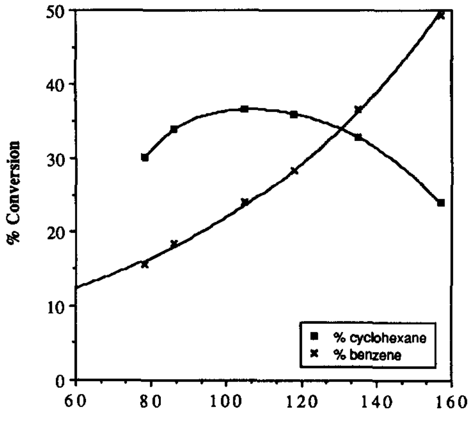
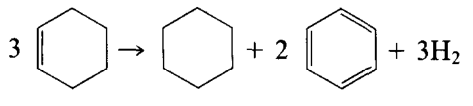


FIG. 5. Product distribution at low temperatures during cyclohexene disproportionation over 66% Ni/kieselguhr (86 Torr cyclohexene, 803 Torr helium, WHSV = 233).

At higher temperatures, however, the selectivity ratio falls in conjunction with the formation of H_2. At 160°C, the stoichiometry becomes



It is important to note that the results shown in Fig. 6 include those in which the catalyst has undergone deactivation with accompanying reduced total conversion. Nevertheless, the selectivity ratio appears to be a function only of temperature rather than conversion—an indication that hydrogen storage is important during cyclohexene disproportionation.

Moreover, this effect varied with both type of metal and catalyst preparation. Thus, it seems that the varying ability to store hydrogen among catalysts influences the reaction. The selectivity–temperature behavior for three catalysts (0.8% Pt/Al_2O_3, 5% Pd/Al_2O_3, and 66% Ni/kieselguhr) is compared in Fig. 7. It is seen that the selectivities continued with the correct stoichiometry until a transition temperature was reached. This temperature was different for different catalysts. (For the 66% Ni/kieselguhr catalyst, $T \approx 60°C$; for 5% Pd/Al_2O_3, $T \approx 90°C$; and for 0.8% Pt/Al_2O_3, $T \approx 110°C$.)

The difference between the two apparent activation energies $\{E_a$ (C_6H_{10} conversion) $- E_a$ (net H_2 make)$\}$ can be correlated with the rate at which the selectivity decreases with temperature (see Table 1 and Fig. 7). In general, the larger the difference, the steeper is the descent in selectivity. Catalysts which had similar values of apparent activation energy for disproportionation and net H_2 make had selectivities which were roughly constant with temperature.

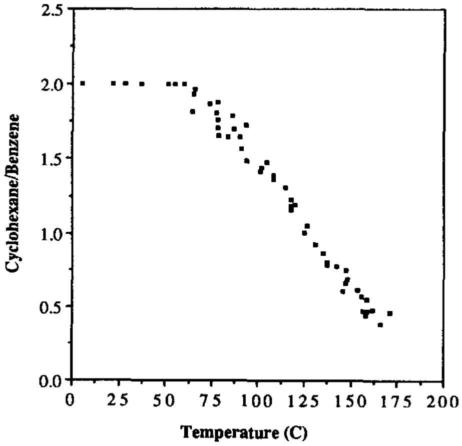


FIG. 6. Selectivity vs temperature during cyclohexene disproportionation over 66% Ni/kieselguhr.

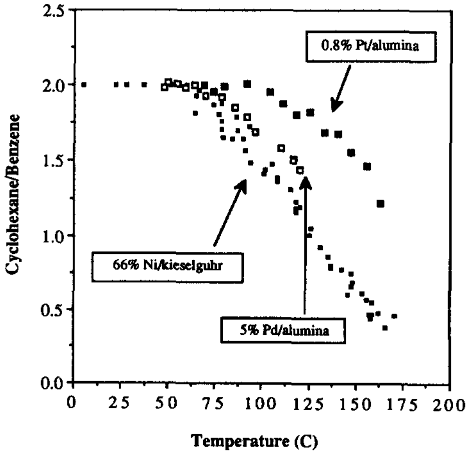


FIG. 7. Selectivity vs temperature during cyclohexene disproportionation over Ni, Pd, and Pt catalysts.

Two Competing Reactions

We postulate that this behavior is best explained as a competition between two reactions, intermolecular hydrogen transfer among cyclohexene molecules and cyclohexene dehydrogenation. The intermolecular hydrogen transfer, in this sense, would not be true transfer among molecules, but a kind of coupled transfer aided by the diffusion of hydrogen through/across a carbonaceous overlayer. The hydrogenation of cyclohexene is also a thermodynamically favorable reaction at these temperatures. However, it seems to be inhibited because of the low concentration of adsorbed hydrogen. (Note that hydrogenation reactions are normally one-half order in hydrogen concentration.) Thus, the apparent E_a based on cyclohexene conversion—at low temperatures—can be thought of as corresponding to disproportionation (i.e., intermolecular hydrogen transfer). The apparent E_a based on net hydrogen production—at higher temperatures—would then correspond to cyclohexene dehydrogenation.

This, however, is not the only explanation. The results can also be rationalized in terms of a sequential mechanism in which the adsorption–desorption equilibrium of hydrogen controls the product distribution. Below some critical temperature, hydrogen would absorb irreversibly and be utilized to the fullest extent. Above the critical temperature, hydrogen adsorption would occur reversibly and be in equilibrium with the gas phase. Thus, with increasing temperature, the utilization of hydrogen would drop in concert with the coverage of hydrogen.

Nevertheless, many of the experimental observations support the claim that the change in selectivity is due to the presence of two competing reactions, cyclohexene disproportionation and dehydrogenation (see under Discussion).

Hydrogen Storage

Regardless of how hydrogen transfer occurs, the catalysts' capacity for hydrogen storage figures to be an fundamental part of the mechanism. As shown by Davis *et al.* (*16*), the adsorption of hydrocarbons on metal surfaces, in the absence of H_2, is accompanied by the formation of high concentrations of carbonaceous material, the composition of which changes with temperature (i.e. the H/C ratio decreases with increasing temperature).

In the case of intermolecular hydrogen transfer, this layer could serve as a conduit for the diffusion of hydrogen among molecules (*17, 18*). Its composition would determine the ease and speed of transfer. Thus, the activity and activation energy measured during cyclohexene disproportionation would be determined in part by the extent and composition of the carbonaceous overlayer. Also, the onset of dehydrogenation, marked by the transition temperature, would correspond to the temperature at which the H/C ratio in the overlayer starts to decrease (see Ref. (*16*)).

For the case of a sequential reaction mediated by the adsorption/desorption equilibrium of hydrogen, the overlayers' capacity for hydrogen storage would greatly affect the extent to which cyclohexene could be hydrogenated.

An effect of hydrogen storage is clearly illustrated in Fig. 8. It shows the conver-

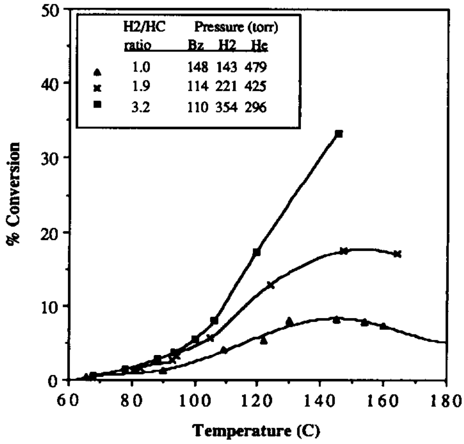


FIG. 8. Benzene hydrogenation over 66% Ni/kieselguhr with less than stoichiometric amounts of H_2 (WHSV = 48).

sion vs temperature behavior for benzene hydrogenation over 66% Ni/kieselguhr and less than stoichiometric amounts of H_2 (H_2 : HC = 1 : 1, 2 : 1, and 3 : 1). As seen, the percentage conversion to cyclohexane goes through a maximum at a temperature close to 150°C. It is important to note that at this temperature there are no equilibrium constraints based on gas-phase calculations. Also, at the maximum, the level of conversion is much lower than the stoichiometric amount based on the limiting reactant. As one increases the H_2 : benzene ratio at constant temperature from 1 : 1 to 2 : 1 and finally to 3 : 1, the maximum conversion also increases, suggesting an effect of hydrogen availability. Thus, even though H_2 was present in the reactor, it was not available on the surface for reaction.

Structure Sensitivity

Another fact which points to the complex nature of cyclohexene disproportionation is its "apparent structure sensitivity." As postulated by Boudart, both hydrogenation and dehydrogenation reactions are structure insensitive (*19*). If that is the case, then the mere dehydrogenation of cyclohexene and the subsequent use of the hydrogen produced to hydrogenate the remaining cyclohexene should also be structure insensitive. If, on the other hand, intermolecular hydrogen transfer or the catalysts' hydrogen storage capability were involved, larger ensembles of atoms would be required to form a "site," and the reaction would be structure sensitive. Recently, Boudart and Cheng (*20*) working with supported Ni catalysts have obtained evidence that cyclohexene disproportionation is indeed structure sensitive. Their evidence suggests that disproportionation occurred over Ni ensembles of size greater than or equal to 2.9 nm, but did not occur over Ni ensembles of size 1.5 nm. Hence, by systematically varying the average metal ensemble size among catalysts, the mechanism could be probed.

We have studied a number of different kinds of catalysts with widely varying ensembles sizes (i.e., 66% Ni/kieselguhr, 5% Pd/Al_2O_3, 0.8%, 0.1%, 0.05%, 0.01%, and 0.001% Pt/Al_2O_3). All of the platinum catalysts, through the formation of two-dimensional ensembles, showed 100% accessibility of Pt by hydrogen chemisorption. However, one would expect their average ensemble sizes to decrease with metal loading.

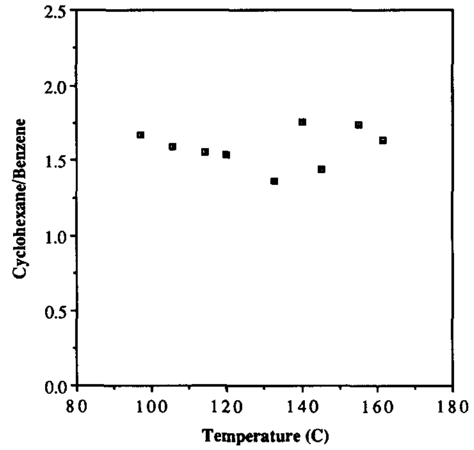


FIG. 9. Selectivity vs temperature for 0.01% Pt/alumina (37 Torr cyclohexene, 884 Torr helium, WHSV = 0.81).

When the specific activities calculated at 100°C were compared (Table 2), it was seen that all the catalysts except the 0.01 and 0.001% Pt/Al_2O_3 catalysts gave approximately the same activity. The 0.01% Pt catalyst was an order of magnitude slower, and the 0.001% Pt catalyst had no activity. (Note that these catalysts were active hydrogenation catalysts. The 0.001% Pt catalyst, however, was active for cyclohexene hydrogenation but not for benzene hydrogenation.)

Also, as seen from Fig. 2, reasonably high total conversions were obtained for the 0.01% Pt/Al_2O_3 catalyst. However, we were unable to obtain the typical disproportionation behavior. The selectivity vs temperature behavior of this catalyst (Fig. 9) was quite variable and indicated that that we were dealing with a sequential dehydrogenation–hydrogenation reaction rather than intermolecular hydrogen transfer (i.e., the hydrogen storage capability appears to be destroyed at very low metal loadings). Thus, it appears that cyclohexene disproportionation requires a minimum ensemble size.

DISCUSSION

Thus far, we have discussed the kinetics and structure sensitivity of cyclohexene disproportionation. Little, however, has been postulated about its mechanism. The question whether disproportionation occurs via intermolecular hydrogen transfer or by a "sequential" dehydrogenation–hydrogenation mechanism has not been fully answered.

We have postulated that intermolecular hydrogen transfer does occur for various reasons. First, at low temperatures, the correct stoichiometry for disproportionation is obtained regardless of the conversion level, 2 or 100%. If the reaction were sequential in nature, dehydrogenation followed by hydrogenation, one would expect to observe an excess of benzene in the effluent at 100% conversion, or at high space velocities. This has not occurred. Also, in other experiments, we have found that cyclohexene conversion proceeds at temperatures as low as 4°C. Furthermore, the observed apparent activation energies suggest that the sequential mechanism does not operate in this case. For example, if dehydrogenation of cyclohexene were the first step in cyclohexene disproportionation, then one should observe the characteristic high apparent activation energy for dehydrogenation. Instead, one observes 25 kJ/mole for 66% Ni/kieselguhr, 50 kJ/mole over 5% Pd/Al_2O_3, and 84 kJ/mole over Pt/Al_2O_3. Finally, the "apparent" structure sensitivity of cyclohexene disproportionation suggests that it differs from the structure-insensitive dehydrogenation and hydrogenation reactions.

It is interesting to speculate why the apparent activation energies for disproportionation change so much among the different catalysts. On the surface, it would seem that the mechanism is changing. However, this behavior can be explained in terms of a reaction occurring over a carbonaceous overlayer. As the reaction proceeds, it is likely that an overlayer of carbonaceous material is deposited on the metal surface. This would create new adsorption sites and serve as a conduit for the diffusion of hydrogen among molecules. Thus, the overlayer would serve as a hydrogen storage device determining the ease and speed of hydrogen transfer. With increasing temperature it is likely that the composition of the overlayer changes (i.e., the H/C ratio decreases), and the degree of change is different among catalysts.

This would affect intermolecular hydrogen transfer as follows. Let us postulate that hydrogen transfer takes place more readily on overlayers with high H : C ratios (e.g., 2 : 1) and less readily on ones with low H : C ratios (e.g., $\leq 1:1$). Then, for catalysts which form more polynuclear overlayers with low H/C ratios, the diffusion of hydrogen through the layer would be rate limiting and low apparent activation energies would be observed (i.e., Ni catalysts). Conversely, high apparent activation energies would be observed for catalysts which form less dense overlayers with higher H/C ratios (i.e., Pt catalysts). Catalysts which have ensembles so small that they are not able to store hydrogen via a carbonaceous overlayer would not be able to support hydrogen transfer reactions.

Also, since the hydrogen concentration in the overlayer decreases with increasing temperature, the activation energy for hydrogen transfer should decrease as temperature increases. Thus, for catalysts in which the H/C ratio in the overlayer decreases quickly with temperature, low apparent activation energies would be observed. For catalysts whose H/C ratio decreases more slowly with temperature, higher apparent activation energies would be observed.

Further evidence to support the idea that

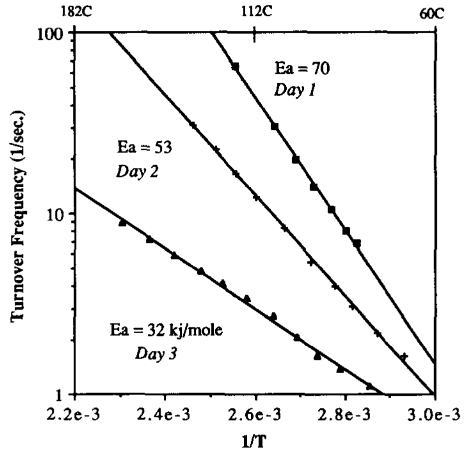


FIG. 10. Arrhenius plots for cyclohexene hydrogenation over 0.01% Pt/alumina showing change in activity and apparent E_a with time (42 Torr cyclohexene, 873 Torr H_2, WHSV = 29).

hydrogen transfer occurs by the diffusion of hydrogen through a carbonaceous overlayer comes from our cyclohexene hydrogenation experiments. Arrhenius plots for cyclohexene hydrogenation over a 0.01% Pt/Al_2O_3 catalyst showing that the apparent activation energy changed with time are given in Fig. 10. These experiments were performed such that all three were made using the same catalyst bed, reaction conditions, and with the catalyst being reduced between each experiment. The first experiment, on fresh catalyst gave a high apparent activation energy for hydrogenation, 70 kJ/mole, and very high turnover frequencies (roughly two orders of magnitude faster than cyclohexene disproportionation). This was also accompanied by some deactivation. During the second experiment, the catalysts' activity was less and also yielded a lower apparent activation energy, 53 kJ/mole. For the third experiment, the activity and apparent activation energy (32 kJ/mole) dropped again. It is interesting to note that this last result is close to what has been reported in the literature (*10, 20*).

Since cyclohexene hydrogenation is generally thought of as a structure-insensitive reaction (*20*), these results were very striking. However, the data can easily be explained in terms of a reaction occurring over a growing carbonaceous overlayer. With fresh catalyst, the metal surface was relatively clean and hydrogenation proceeded without diffusional resistances. With time of hydrocarbon exposure, it is likely that an overlayer of carbon was deposited on the metal surface. This layer would create new adsorption sites for cyclohexene. If one now postulates that H_2 must be activated on the metal surface, then it would have to diffuse through this layer in order to become activated. Subsequently, H atoms aided by the carbonaceous overlayer would diffuse back out to the adsorbed cyclohexene in order to react. Furthermore, as the overlayer becomes denser and/or thicker, the diffusional resistances would increase. In this way, the reaction becomes progressively more limited by the diffusion of hydrogen through a carbonaceous overlayer covering the surface of the metal. Hence, with time, one would expect to observe a lowering both of the activity and also of the apparent activation energy.

This idea is not new. The transfer of H atoms from a Pt surface through a layer of irreversibly adsorbed ethylene has been postulated to occur during the vapor-phase hydrogenation of ethylene (*21*). In general, it seems that because cyclohexene hydrogenation is much faster than other hydrogenation reactions, this effect is more easily seen. For example, during benzene hydrogenation the rate-limiting step could be the addition of H atoms instead of the diffusion of H atoms through/across an overlayer.

We have begun experiments (pulse reaction and temperature-programmed reduction) to elucidate the extent and chemistry of initial cyclohexene adsorption on various catalysts. Preliminary results for the 66% Ni/kieselguhr catalyst at 75°C indicate that ≈1 monolayer (based on total surface area) is rapidly adsorbed. This results in an unsaturated residue on the catalyst since the initial pulse reaction product is essentially pure cyclohexane. After a number of small pulses, we began a temperature-programmed reduction and found the sequential appearance of cyclohexane at 155°C, propane at 220°C, and finally methane and ethane at 250°C. No other products were detected as the temperature was raised to 400°C. These results are indicative of the formation of various adsorbed species during the initial pulse reaction.

Since the commercial nickel on kieselguhr catalyst is composited with 6–8% graphite during the manufacturing process, we believe that any oxidative determination of the C/H ratio of the carbonaceous residue may be questionable, particularly at higher temperatures. For future work we have planned to perform a number of isotopic studies, including the use of perdeuterocyclohexene in order to investigate the amount of hydrogen (H or D) in the overlayer. Such experiments would be particularly interesting as we change the metal loading of the platinum catalysts.

CONCLUSIONS

Our present conclusions are that we are dealing with two competing reactions, intermolecular hydrogen transfer among cyclohexene molecules and cyclohexene dehydrogenation. At lower temperatures, disproportionation prevails, but gives way to dehydrogenation as temperature is increased. The reaction changeover depends on type of catalyst and its ensembles which in turn are dependent upon metal concentration. The catalysts' capacity for hydrogen storage seems to be a fundamental part of the mechanism. If the capacity for hydrogen storage is impaired, then activity and selectivity are greatly altered. Also, the idea of reaction occurring over a carbonaceous overlayer explains both the observed similar reaction rates at 100°C and the varying apparent activation energies among catalysts.

ACKNOWLEDGMENTS

We thank UOP for providing the Pt catalysts used in this study. We also recognize the contributions of Wm. C. Conner, Hertha Skala Haensel, and Timothy R. Lynn for their discussions, insights, and comments pertaining to this work.

REFERENCES

1. Zelinskii, N. D., *J. Russ. Phys. Chem. Soc.* **43,** 1222 (1911).
2. Zelinskii, N. D., and Glinka, N., *Ber. Dtsch. Chem. Ges.* **44,** 2305 (1911).
3. Zelinskii, N. D., and Pavlov, *Ber. Dtsch. Chem. Ges.* **56,** 1249 (1923).
4. Zelinskii, N. D., **57,** 2055 (1924).
5. Corson, B. B., and Ipatieff, V. N., *J. Amer. Chem. Soc.* **61,** 1056 (1939).
6. Balandin, A. A., and Brusow, J. J., *Z. Phys. Chem.,* **34,** 96 (1936).
7. Germain, J. E., "Catalytic Conversion of Hydrocarbons." Academic Press, London/New York, 1969.
8. Carra, S., Beltrame, P., and Ragaini, V., *J. Catal.* **3,** 353 (1964).
9. Carra, S., Ragaini, V., and Guella, F., *J. Catal.* **8,** 261 (1967).
10. Davis, S. M., and Somorjai, G. A., *J. Catal.* **65,** 78 (1980).
11. Crabtree, R. H., and Parnell, C. P., *Organometallics* **4,** 519 (1985).
12. Chaudret, B. N., Cole-Hamilton, D. J., and Wilkinson, G., *Acta Chem. Scand. Ser. A* **32,** 763 (1978).
13. Friend, C. M., Ph.D. thesis (LBL-13072). Univ. of California, Berkeley, 1981.
14. Tsai, M., Friend, C. M., and Muetterties, E. L., *J. Amer. Chem. Soc.* **104,** 2539 (1982).
15. Davis, S. M., and Somorjai, G. A., *in* "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (D. A. King and D. P. Woodruff, Eds.), Vol. 4, p. 217. Elsevier, Amsterdam, 1982.
16. Davis, S. M., Zaera, F., Gordon, B. E., and Somorjai, G. A., *J. Catal.* **92,** 240 (1985).
17. Zaera, F., Gellman, J., and Somorjai, G., *Acc. Chem. Res.* **19,** 24 (1986).
18. Neikam, W. C., and Vannice, M. A., *J. Catal.* **27,** 207 (1972).
19. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.
20. Boudart, M., and Cheng, W-C., *J. Catal.* **106,** 134 (1987).
21. Wieckowski, A., Rosasco, S. D., Salaita, G. N., Hubbard, A., Bent, B. E., Zaera, F., Godbey, D., and Somorjai, G. A., *J. Amer. Chem. Soc.* **107,** 5910 (1985).