

Catalytic Hydrogenation of Cyclohexene

8. Gas-Phase Reaction on Supported Nickel

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The gas-phase hydrogenation of cyclohexene was studied on seven nickel catalysts supported on silica. The initial turnover frequency was almost independent of the size of Ni particles between 1 and 5 nm. It declined with time during each run because of adsorbed benzene produced by a side reaction, the disproportionation of cyclohexene to benzene and cyclohexane. The latter were found to be products of the reaction in the absence of hydrogen. In the presence of hydrogen, benzene was formed but did not desorb as a reaction product at 273 K. The hydrogenation of cyclohexene was independent of particle size yet the disproportionation leading to benzene adsorption varied with particle size. © 1989 Academic Press, Inc.

INTRODUCTION

The sensitivity of a reaction to surface structure of metals can be determined by making supported metal catalysts with small metal particles ranging in size from 1 to 10 nm, and measuring the turnover rate on the metal. The idea is that as metal crystallites vary in size from 1 to 10 nm, the relative percentage of surface atoms with different coordination numbers also varies. If there is no variation in turnover rate, it is inferred that the reaction is structure insensitive. This method was employed in particular to show that the hydrogenation of cyclohexene is structure insensitive on platinum in the gas phase as reported by Segal *et al.* (1) and in the liquid phase as found by Madon *et al.* (2). The same conclusion was reached by Gonzo and Boudart (3) who studied the same reaction on palladium in both liquid and gas phases (3). Davis and Somorjai (4) observed turnover rates for cyclohexene hydrogenation on a single crystal of platinum, in excellent agreement with those reported on supported clusters of platinum (1). This con-

firms the structure insensitivity of the reaction.

The purpose of this effort was to study the gas-phase hydrogenation of cyclohexene on supported nickel catalysts with the idea of determining whether the reaction on nickel is structure insensitive as it was found to be on platinum and palladium. Difficulties were expected as reactions on nickel catalysts are often accompanied by deactivation. For example, poisoning of nickel by carbonaceous residues has been reported during hydrogenation of carbon monoxide (5) and during benzene hydrogenation (6). Of special significance is the finding by Imelik and Massardier (7) that hydrogenation of ethylene on nickel single crystals and supported nickel catalysts is structure insensitive while the breakdown of ethylene leading to deposition of carbonaceous residues is structure sensitive. A similar finding is reported here.

EXPERIMENTAL

Catalyst Preparation

Unless indicated otherwise, the support consisted of silica (HS-5 Cab-O-Sil) pre-washed with nitric acid and rinsed with de-ionized water. Seven samples were pre-

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pared by impregnation, homogeneous precipitation, and ion exchange. The impregnated sample was prepared according to Sinfelt *et al.* (8). The sample was calcined in air at 508 K for 23 h and reduced in flowing dihydrogen at 673 K for 4 h.

The method of homogeneous precipitation as described by van Dillen *et al.* (9) and Richardson and Dubus (10) utilizes slowly decomposing urea at 363 K as a controlled source of hydroxyl ions. When in the presence of nickel ions, the hydroxyls combine to precipitate nickel hydroxide. Precipitation and nucleation occur only on the silica and not in solution. A highly dispersed nickel hydrosilicate results.

The method of ion exchange as described for platinum by Benesi *et al.* (11) consists of fixing metal cations by exchange with ions on the surface of a support. The principle applies to any reducible metal on any support with ion exchange capacity according to the reaction $H^+A + NH_4^+ = NH_4^+A + H^+$, where A is the anionic support. With nickel, the method makes use of the exchange of $[Ni(NH_3)_6]^{2+}$ with silica.

A nickel stock solution was made by adding doubly distilled water to 29.9 g $Ni(NO_3) \cdot 6H_2O$ until the solution reached 0.1 liter. A 0.1 M hexamine nickel(II) solution was made by the addition of 10^{-2} liter nickel stock to 0.09 liter 1:1 $NH_4OH:H_2O$. The support slurry was made by the addition of 5 g silica to 0.1 liter 1:1 $NH_4OH:H_2O$ solution. The hexamine nickel(II) solution was added dropwise to the support slurry with constant stirring. The solution was mixed at 293 K for 1 h. It was then rinsed in a Buchner funnel with 1.5 liters doubly distilled water and dried in a convection oven at 383 K for 1.5 h. This sample is referred to as the unreduced precursor. Samples with varying weight loading were prepared by the ion exchange method by adding larger or smaller amounts of the stock $[Ni(NH_3)_6]^{2+}$ solution to the support slurry. The silica supports used in this case were Grade 950 silica gel from Davison, specific area $700 \text{ m}^2 \text{ g}^{-1}$,

specific pore volume $0.4 \text{ cm}^3 \text{ g}^{-1}$, and Cab-O-Sil (HS-5).

All catalysts were reduced at 673 K in flowing dihydrogen at a space velocity of 0.2 s^{-1} for 24 h. This temperature was chosen because it was found to give the highest extent of reduction without resulting in nickel crystal growth (10, 12–16).

Catalyst Characterization

The nickel content was determined by atomic absorption. Hydrogen chemisorption was used to determine the number of exposed nickel atoms. Each adsorbed hydrogen was assumed to represent one surface nickel atom as demonstrated by Pannel *et al.* (17). To find the degree of reduction of the nickel, freshly reduced samples were reacted with carbon monoxide at 318 K for 18 h according to Benson and Kwan (18). Carbon monoxide reacts only with zero-valent nickel giving volatile nickel carbonyl. A subsequent nickel atomic absorption analysis gave the amount of residual unreduced nickel, and the percentage dispersion of the reduced nickel (i.e., the percentage of metal exposed) could then be calculated. Results are shown in Table 1.

Apparatus and Procedures

Kinetic data were obtained in a new 3.54-liter batch Pyrex recirculation system (Fig. 1). A noncontaminating recirculation pump (Metal Bellows Corp.) supplied a gas flow

TABLE 1
Characterization of the Catalysts^a

Wt% Ni in sample	Wt% Ni after CO reaction	% Reduction	% Dispersion
1.09	0.64	41	100
1.90	0.76	60	82
2.78	1.64	41	97
2.19	0.29	87	70
2.25	0.32	86	58
21.6	0.85	96	36
4.98	0.86	83	18

^a Prepared by ion exchange except those containing 21.6 and 4.98 wt% Ni, which were obtained by homogeneous precipitation and impregnation, respectively.

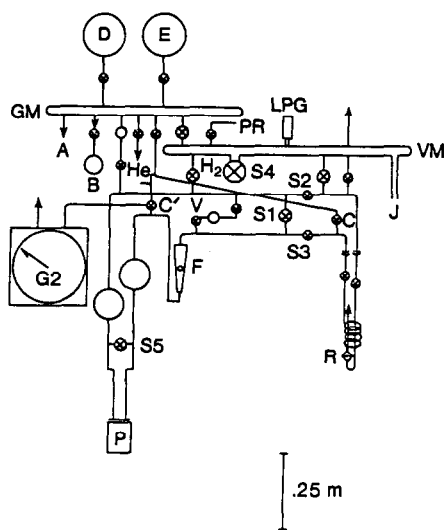


FIG. 1. Main apparatus for gas-phase hydrogenation. VM, Vacuum manifold; GM, gas manifold; A, 10/30 male joint; B, purified cyclohexene storage bulb; C, H₂ inlet to the reactor; C', H₂ inlet to recirculation loop; D, H₂ storage bulb; E, He storage bulb; F, flow meter; G1, Matheson pressure gauge; G2, Wallace and Tiernan pressure gauge; J, line to trap and rough pump; LPG, low-pressure gauge; R, reactor; S1-S5, stopcocks; V, sample valve.

rate of $33 \text{ cm}^3 \text{ s}^{-1}$ (19). The reactor was a Pyrex chamber with a 2.5-cm-diameter fritted disk supporting 3 to 20 mg of catalyst. The gases flowed down through a Pyrex preheating coil and through the fritted disk. For most of the experiments the reactor was immersed in a Dewar packed with ice and water. The temperature was measured with a thermocouple inserted into a well and centered over the catalyst sample. Gas samples were obtained with a Varian-Aerograph XA-210 six-way sample valve and were analyzed in a Varian-Aerograph A-90-P chromatograph with a Reoplex column at 349 K.

Chromatographic quality cyclohexene (Wylie Chemicals) was purified (2) through a column packed with the transitional alumina powder (Kaiser) pretreated with flowing helium at 673 K for 1 h. The bulb of unpurified cyclohexene was attached to the bottom of the column. A freeze-pump-

thaw technique was used to transfer the cyclohexene through the alumina to a clean storage bulb. The freeze-pump-thaw procedure was repeated to remove any helium dissolved in the stored cyclohexene. The dihydrogen (liquid Carbonic, 99.93% pure) was further purified through a Milton Roy palladium diffuser. The 99.995% pure helium (liquid Carbonic) was passed from the cylinder through a trap of 1 g freshly reduced nickel catalyst and a zeolite trap at 78 K.

Kinetic experiments were run on 1- to 10-mg catalyst samples rereduced at atmospheric pressure with excess dihydrogen. The catalyst sample was loaded into the reactor side of the recirculation loop. It was evacuated for 0.5 h prior to reduction. A furnace was put around the reactor, the temperature was raised to 673 K in 1 h, and reduction was carried out in dihydrogen at 673 K for 1 h.

As reduction proceeded, the bypass side of the loop was evacuated. At the end of reduction, the furnace was removed from the reactor, allowing the catalyst sample to cool in flowing dihydrogen. Meanwhile, the reactants were bled into the bypass manifold through the gas manifold. The gases were introduced in the following order: cyclohexene (1.4–2.6 kPa), dihydrogen (0–101 kPa), and helium to bring the system to atmospheric pressure. The reactants recirculated in the bypass loop for 0.5 h while the freshly reduced catalyst sample was cooling in flowing dihydrogen to the reaction temperature.

Just prior to reaction, the dihydrogen flow was stopped and the catalyst was evacuated for 30 s. To begin the reaction, the bypass loop was opened to the reactor, allowing the reactants to flow over the catalyst. Gas samples for analysis were taken at 50 s and then at 300-s intervals until the cyclohexene reached total conversion. At each sample time the temperature of the catalyst, the pressure in the reactor, and the heights of cyclohexene and cyclohexane peaks were recorded. A regression

curve was fitted to the conversion data and then differentiated to give the initial turnover frequency, N .

The batch recirculation apparatus used for the kinetic experiments was also used for qualitative temperature-programmed reduction (TPR) and desorption (TPD) experiments.

For both TPD and TPR experiments, a 0.4-g catalyst sample was loaded into the reactor and reduced overnight at 673 K. The catalyst was cooled in flowing dihydrogen while the reactants were added to the bypass loop and recirculated. The reactants were then recirculated over the catalyst. A reaction with 5 kPa cyclohexene, 20 kPa dihydrogen, and 76 kPa helium at 273 K was run to completion. Total conversion was reached in 300 s. Immediately after the reaction, the catalyst sample was flushed for 2 h with helium at 293 K to remove any physisorbed hydrocarbons from the surface.

For the temperature-programmed desorption experiments, helium was recirculated at atmospheric pressure in the reactor while the sample was heated from 292 to 623 K in 1 h. Gas samples were taken every 300 s. For the temperature-programmed reduction, dihydrogen at atmospheric pressure was recirculated over the catalyst at the end of the 2 h 293 K helium flush. The temperature was increased from 293 to 633 K in 6500 s. The gas was sampled every 500 s.

RESULTS

The absence of internal and external heat and mass transfer limitations can be demonstrated with the Koros–Nowak criterion as elaborated upon by Madon and Boudart (20). This requires an absence of change in turnover frequency of a reaction on supported metal catalysts with different metal loading. The values for the initial turnover frequency for four samples with loading from 1 to 22% Ni are shown in Table 2. As there is little difference in the value of the turnover rate on these catalysts at two dif-

TABLE 2

Wt% Ni	% Dispersion	Turnover Frequency N	
		$N(\text{s}^{-1})$	
		273 K	292 K
1.09	100	1.0	
2.78	97	1.2	
1.9	82	0.98	1.4
21.6	36	1.0	1.7

Note. H_2 pressure, 13 kPa. C_6H_{10} pressure, 3.1 kPa.

ferent temperatures, we may conclude that diffusional limitations are negligible (20).

Plots of cyclohexene concentration versus time revealed declining turnover rates. A plot of $\ln N$ vs \ln cyclohexene for constant dihydrogen pressure on a clean catalyst showed an apparent order in cyclohexene between 2 and 5 (Fig. 2). Initial rate experiments with a range of cyclohexene concentrations showed zero-order dependence upon cyclohexene. It was assumed that the catalyst was deactivating. Flushing the catalyst for 2 h with dihydrogen at room temperature allowed partial regeneration of the initial activity (Fig. 2). Subsequent experiments showed that the fraction of re-

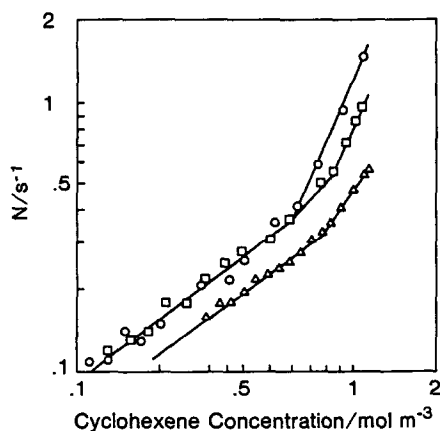


FIG. 2. Double logarithmic plot of turnover rate N vs cyclohexene concentration $[\text{C}_6\text{H}_{10}]$. \circ , Clean catalyst, 27 kPa H_2 ; \square , rerun catalyst, 27 kPa H_2 ; \triangle , rerun catalyst, 13 kPa H_2 ; $[\text{C}_6\text{H}_{10}]$ initially 1.29 mol m^{-3} ; 273 K; 21.6 wt% Ni catalyst.

covered activity was proportional to the hydrogen/cyclohexene ratio during the reaction on the clean catalyst.

When a reaction was run at 298 K on the 21.6% Ni catalyst in the absence of hydrogen, benzene and cyclohexane were the observed gas-phase products. The rate of cyclohexene disappearance was 1.5 times the rate of cyclohexane production. The pressure in the reactor remained constant with time. It was concluded that cyclohexene was disproportionating to benzene and cyclohexane:



When cyclohexene and dihydrogen were added to the reactor at the conclusion of the disproportionation reaction, the hydrogenation reaction did not proceed. The catalyst behaved as though it had been totally poisoned. Flushing this catalyst with room temperature dihydrogen for 2 h regenerated 60% of the initial active nickel area (Fig. 3). It appeared as though the disproportionation reaction had caused 40% of the active

nickel surface to be irreversibly deactivated.

Subsequent experiments on this catalyst showed no further suppression of the initial turnover rate. Catalyst activity was lost during the course of each reaction, yet the activity was totally regenerated with a room temperature dihydrogen flush. These catalysts are referred to as steady-state deactivated samples.

Another way to cause a catalyst to reach its deactivated state was to expose the sample to nonrecirculating reactants for 3000 s. During this exposure without mixing, hydrogenation did not occur and the sample was deactivated. Once the mixing was begun, the hydrogenation reaction proceeded with an initial activity corresponding to that of the deactivated state. Further hydrogenations and dihydrogen flushes failed to cause further irreversible deactivation.

The initial turnover frequency, N_0 , for the freshly reduced catalysts at 273 K and atmospheric pressure followed the kinetics $N_0 = k[\text{H}_2]$ with k values between 170 and 220 liters $\text{mol}^{-1} \text{s}^{-1}$ (Table 3). The initial turnover frequency, N_0 , for the deactivated catalysts at 273 K and 101 kPa followed the kinetics $N_0 = k'[\text{H}_2]^{1/2}$ with k' values from 6 to 8 liters $^{1/2} \text{mol}^{-1/2} \text{s}^{-1}$. The deactivated catalysts consistently showed zero order in cyclohexene. The order of reaction with respect to dihydrogen is clearly obtained for both clean and deactivated samples from the straight lines in Fig. 4.

The turnover frequency was found to be nearly invariant with nickel dispersion for particle sizes between 1 and 5 nm. The initial deactivated rate constant for the 21% nickel sample, which was reported by Coenen *et al.* (21) to be in the form of nickel antigorite with predominately Ni (111) planes exposed, was found to be 7.8 liters $^{1/2} \text{mol}^{-1/2} \text{s}^{-1}$ in close agreement with 6.6 liters $^{1/2} \text{mol}^{-1/2} \text{s}^{-1}$ observed on the randomly oriented 4.9% Ni sample.

During the TPD experiments, described in the procedure section, only a small amount of dihydrogen was desorbed and no

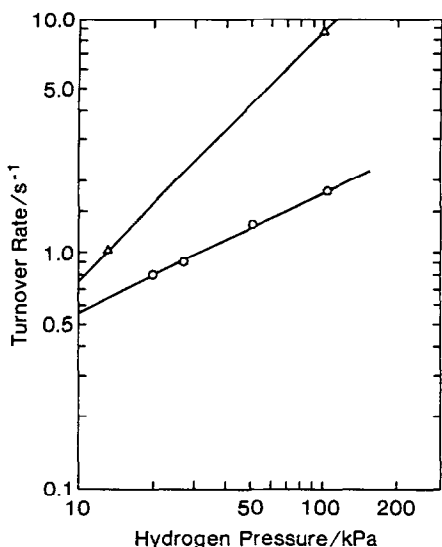


FIG. 3. $\text{Ln}(N)$ versus time. Δ , Clean catalyst; \circ , rerun catalyst after disproportionation reaction; dihydrogen pressure, 20.2 kPa; cyclohexene pressure, 2.3 kPa; 293 K; 21.6 wt% Ni catalyst.

TABLE 3
Rate Constants for Clean and Deactivated Catalysts at 273 K and Atmospheric Pressure

% Dispersion of Ni	Clean ($N = kH_2^2$) k (liters mol ⁻¹ s ⁻¹)	Deact ($N = k'H_2^2$) k' (liters ^{1/2} mol ^{-1/2} s ⁻¹)
100	221	8.8
97	220	6.3
82	182	8.7
70	230	3.0
36	171	7.8
18		6.6
36	310 ^a	17 ^a

^a Run at 292 K.

hydrocarbons appeared from the 4.9% nickel sample or the 21% nickel sample. This gas-phase dihydrogen may have corresponded to the dehydrogenation of adsorbed hydrocarbons.

During the TPR experiments, cyclohexane was formed in the gas phase. Maximum values for cyclohexane formation were observed at 293 and 428 K. For both the impregnated 4.9% Ni catalyst and the homo-

geneously precipitated 21% Ni catalyst, 60% of the cyclohexane produced during the TPR came at 293 K. The impregnated sample yielded an average of 8.51 molecules of cyclohexane/nm² nickel surface whereas the 21% Ni catalyst gave only 1.32 cyclohexane molecules/nm² nickel surface. These results are shown in Table 4. The 21% Ni catalyst sample, reported to be Ni(111), was less poisoned under these hydrogenation conditions. During kinetic experiments with 5 kPa cyclohexene, 20 kPa dihydrogen, and 76 kPa helium at 273 K, 50 to 60% of the activity was lost irreversibly and 10–30% was lost reversibly.

DISCUSSION

An explanation was needed for the deactivation observed during the hydrogenation of cyclohexene. The catalytic activity lost during the experiment could be regenerated either partially or totally, depending upon the initial experimental conditions. The fractional regeneration as a function of initial dihydrogen pressure suggests a form of reversible deactivation. Crystal growth was discarded as an explanation, for one would expect no regeneration. With crystal growth one would also expect the activity regeneration to be lowest for the experiments with the highest initial rates. The reverse was observed during the hydrogenation of cyclohexene experiments. The observation that the time required for deac-

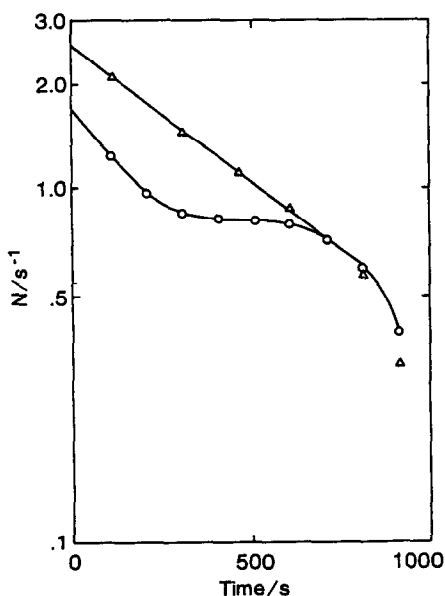


FIG. 4. $\ln(N)$ versus \ln dihydrogen pressure. 1.09 wt% Ni; 273 K; dispersion 1.0; cyclohexene concentration, 1.2 mol m⁻³; Δ , initial turnover rates; \circ , deactivated turnover rates at time zero.

TABLE 4
Cyclohexane from TPR

Wt% Ni	% Dispersion	Molecules C ₆ H ₁₂ /nm ² Ni surface		
		298 K	>400 K	Total
21.6	36	0.81	0.51	1.32
4.98	18	5.27	3.26	8.53

tivation decreases with increasing temperature suggests that an activated process is causing deactivation. The results also indicated two forms of deactivation, one rapid form causing the irreversible loss of activity, and another slower and reversible form.

From the observed disproportionation of cyclohexene to benzene and cyclohexane in the absence of dihydrogen, it was hypothesized that adsorbed benzene was the cause of deactivation. The TPR experiments lend strong support to the idea that surface benzene formation caused deactivation of nickel catalysts during cyclohexene hydrogenation. The experiments differentiate between strongly adsorbed benzene and weakly chemisorbed benzene.

The kinetic experiments also lend support to the above two forms of adsorbed benzene. The highly dispersed catalysts deactivated upon the initial reaction, then regained some activity with a room temperature dihydrogen flush. Subsequent duplicate reactions on one catalyst gave reproducible values of turnover frequency, yet only matched the initial turnover frequency of the clean catalyst when initially run with high hydrogen-to-cyclohexene ratios. This suggests an initial deactivation due to strongly bound benzene. The deactivation within a run could be due to weakly bound benzene which was easily reduced with a 293 K dihydrogen flush.

By comparison of the number of molecules of cyclohexane produced by the 293 K TPR with the reversible activity loss during the kinetic experiments, it is observed

that 60% of the surface benzene would correspond to the 20% of the surface area lost to reversible poisoning. Similarly, 40% of the TPR cyclohexane would correspond to the 40% irreversible activity loss during hydrogenation (Table 5). This again suggests two forms of benzene adsorption. The lightly adsorbed form reducible at 293 K would occupy less nickel surface area than the irreversibly adsorbed form. There were 1.6 times as many molecules adsorbed weakly as those adsorbed strongly, and yet catalytic area lost reversibly was one-half the area lost irreversibly.

Shopov *et al.* (22) found cyclohexane to dissociatively adsorb on nickel as benzene. Two forms of benzene were observed, one which could be hydrogenated and one which irreversibly adsorbed on the nickel surface. They found that dihydrogen pretreatment inhibited deactivation, just as we found deactivation to be inhibited by increasing dihydrogen pressure. The most deactivation occurred during Shopov's initial adsorption experiment, and the reversible component repeated itself during adsorption and desorption cycling. This is directly analogous to the reversible poisoning we

TABLE 5
Activity Lost during Hydrogenation

Wt% Ni	% Dispersion	% Total activity	
		lost reversibly	lost irreversibly
21.6	36	20	40
4.98	18	18	36

Note. 20 kPa H₂; 5 kPa C₆H₁₀; 273 K.

saw after the hydrogenation and dihydrogen flushing. Shopov also saw no change in the activation energy of benzene hydrogenation between the deactivated and the clean catalyst.

Tetenyi and Barberones (23) also found the nickel surface to be partially covered by benzene which could be removed only with a reduction to yield cyclohexane. We could remove our surface species only with a reduction in dihydrogen.

Van Meerten *et al.* (24) extensively studied the adsorption of benzene and cyclohexane on nickel surfaces. Nickel catalysts which were exposed to benzene during reaction with dihydrogen also chemisorbed benzene. Following the reaction with a dihydrogen flush at atmospheric pressure removed only 67% of the chemisorbed benzene. We could remove 60% of the adsorbed species with a similar flush during the TPR experiments. Van Meerten *et al.* also observed the disproportionation of cyclohexene to cyclohexane and benzene and found it to be favored at higher temperatures. We found an increase in deactivation rate at higher temperatures, which could be explained by an increase in benzene production rate and subsequent catalyst deactivation. Van Meerten *et al.* also found that increasing dihydrogen pressure increased the selectivity for cyclohexene hydrogenation over disproportionation.

Anderson and Kemball observed many results similar to ours when they studied cyclohexene and benzene hydrogenation on nickel films (6). The initial decrease in activity could not be explained by a dependence on gas pressure. The "surface poisoning" reached an "equilibrium deactivated state" after 0.5 h at 318 K. They could create the deactivation by pretreating the catalyst with benzene prior to hydrogenation. The rate and extent of deactivation increased with temperature analogous to our results. The surface was found to be 50% poisoned at 318 K; in this study it was 30–40% poisoned at 273 K. They also found that extent of poisoning to be dependent

upon the dihydrogen/hydrocarbon ratio. Deactivation was not observed on palladium. They concluded that the deactivation was due to the dissociative chemisorption of aromatic molecules, yet they did not try to identify the adsorbed species.

CONCLUSION

From the data in this study and the literature it can be concluded that the hydrogenation of cyclohexene at 273 K is accompanied by disproportionation to benzene. Benzene is adsorbed in two forms, one reducible at 293 K and the other reducible at above 400 K, with the former occupying less surface area per molecule than the latter. The number of adsorbed benzene molecules per surface nickel atom was six times higher for the impregnated sample than for the homogeneously precipitated catalyst. The initial deactivated turnover rate for cyclohexene hydrogenation compares favorably to the values obtained on platinum (1), palladium (3), and platinum black (25) (Table 6). These cyclohexene hydrogenation studies also show a zero-order dependence on cyclohexene (1, 3, 25).

The hydrogenation of cyclohexene on nickel was subsequently studied in the liquid phase by Boudart and Cheng (26). They found cyclohexene disproportionation to take place. Thus during cyclohexene hydrogenation, the catalyst was poisoned by benzene, which reached a steady-state surface coverage and was not hydrogenated under the conditions of the reaction. Small nickel particles were more resistant to poisoning than large ones. This suggests that disproportionation requires a larger ensem-

TABLE 6

Initial Turnover Frequency N (s^{-1}) for Gas-Phase Hydrogenation of Cyclohexene

Pt (Ref. (1))	Pd (Ref. (3))	Ni clean	Ni deact	Pt black (Ref. (25))
0.94	1.01	1.0	0.7	0.7–1.0

Note. 10 kPa H_2 ; 5 kPa C_6H_{10} ; 273 K.

ble of sites than cyclohexene hydrogenation.

The results of both studies of cyclohexene hydrogenation in the gas and liquid phases imply that the direct reaction, i.e., cyclohexene hydrogenation on supported nickel catalysts, is structure insensitive while the poisoning reaction, i.e., cyclohexene disproportionation, is structure sensitive. This phenomenon is similar to that also reported on nickel by Imelik and Massardier (7) for ethylene hydrogenation (structure insensitive) and ethylene breakdown to surface residues (structure sensitive). As the poisoning reaction proceeds, its rate slows down while the direct structure insensitive reaction continues, reaching a steady-state rate when the poisoning reaction finally stops (26).

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