

Catalytic Hydrogenation of Cyclohexene

7. Liquid Phase Reaction on Supported Nickel

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Cyclohexene (*C*) hydrogenation in the liquid phase on nickel catalysts with 29 to 66% metal exposed proceeds at turnover rates that vary little with particle size. In the absence of dihydrogen, benzene (*B*) is produced by disproportionation of *C*. This reaction is inhibited by dihydrogen. Yet it also occurs during hydrogenation of *C*. The catalyst becomes poisoned by *B* which is not hydrogenated when *C* is. Deactivation stops after a fraction of hydrogenation sites is poisoned. Small nickel particles are more resistant to poisoning than large ones. These results can be understood if disproportionation requires a larger ensemble than hydrogenation. Thus hydrogenation of *C* on nickel is structure insensitive but is accompanied by disproportionation of *C* which is structure sensitive, and therefore stops while hydrogenation of *C* proceeds at a steady rate. © 1987 Academic Press, Inc.

INTRODUCTION

Hydrogenation of cyclohexene has been studied on platinum, palladium, and nickel (1-6). Values of the turnover rate of this reaction on platinum, palladium, and nickel at 298 K and a dihydrogen pressure of 10.1 kPa are presented in Table 1. Under these conditions, the turnover rate v_t of cyclohexene hydrogenation *in the gas phase* on a series of supported platinum catalysts with 14 to 100% metal exposed agrees extremely well with v_t on clean powders of platinum (6) and on a stepped Pt(223) single-crystal surface (7). The reaction may be regarded as structure insensitive. This reaction was also found to be insensitive to surface modifiers. Thus, Leclercq and Boudart (4) measured the rate of cyclohexene hydrogenation in the gas phase on clean and sulfur-poisoned platinum catalysts and showed that the rate of reaction per unpoisoned surface platinum atom, as determined by dihydrogen chemisorption, was the same for the clean and sulfur-poisoned catalysts.

The turnover rate of cyclohexene hydrogenation *in the liquid phase* on platinum (2), *in the gas phase and liquid phase* on palladium (3), and *in the gas phase* on nickel (5) was also found to be independent of the metal particle size. Moreover, values of the turnover rate on platinum, palladium, and nickel were all comparable. The weak dependence of the turnover rate on the nature of the metal is further evidence that cyclohexene hydrogenation is structure insensitive.

McConica and Boudart (5) observed that during the hydrogenation of cyclohexene *in the gas phase*, nickel catalysts deactivated with time. Deactivation was not observed on platinum or palladium. The deactivation was attributed to the strong chemisorption of benzene, formed by the disproportionation of cyclohexene,



The objectives of this investigation were to determine if disproportionation on nickel would also occur in the liquid phase and how this reaction and the hydrogenation of cyclohexene would be affected by the particle size of supported nickel.

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TABLE 1

Turnover Rates of Cyclohexene Hydrogenation on Group VIII Metals

Catalyst	Metal exposed (%)	Turnover rate (s ⁻¹) at 298 K and P _{H₂} = 10.1 kPa ^a	
		Gas phase	Liquid phase ^b
Supported Pt	14-100	2.72-2.94 (1)	0.55-0.66 (2)
Pt(223)		2.8 (7)	
Supported Pd	11-76	2.38-3.98 (3)	1.35-1.72 (3)
Supported Ni	36-100	1.53-2.44 (5)	0.32-0.66 This work

^a The rate was zero order with respect to cyclohexene in all cases.

^b Solvent: cyclohexane.

EXPERIMENTAL METHODS

Catalyst Preparation

The nickel catalysts used in this study were prepared by incipient wetness impregnation, controlled pH precipitation, and ion exchange. Silica (Cabosil HS-5, Cabot Corp.) was the support for all the samples. The impregnation sample was prepared by Iglesia (8) according to the procedures of Sinfelt *et al.* (9). This sample was reduced at 723 K in flowing dihydrogen at a space velocity of 0.2 s⁻¹ for 15 h. The method of controlled pH precipitation has been described in detail by van Dillen *et al.* (10) and Richardson and Dubus (11). This method uses the slow decomposition of urea at 363 K as a controlled source of hydroxyl ions to precipitate nickel in the forms of nickel hydroxide and nickel hydrosilicate at a controlled rate so as to give a very uniform particle size distribution of nickel. The sample, prepared by precipitation, was reduced at 673 K in flowing dihydrogen at a space velocity of 0.2 s⁻¹ for 3.5, 10, and 15 h. The method of ion exchange has been described by McConica (12). It was originally applied by Benesi *et al.* (13) to pre-

pare supported platinum catalysts. In this method, nickel hexamine was exchanged with the cations of the support at room temperature for 1 h. At the end of this period, the mixture was filtered and washed with distilled water and dried at 383 K. This sample was reduced at 648 K in flowing dihydrogen at a space velocity of 0.2 s⁻¹ for 15 h.

Catalyst Characterization

The particle size of nickel was measured according to the method of Bartholomew and Pannell (14). The number of surface nickel atoms was determined by dihydrogen chemisorption at room temperature. Monolayer coverage was taken as the value of uptake of dihydrogen obtained by extrapolating the linear part of the adsorption isotherm to zero pressure. The stoichiometry for H:Ni of 1:1 was assumed. The degree of reduction was determined by measuring the uptake of dioxygen at 673 K and assuming that all the zero valent nickel atoms were converted to NiO. The results of these experiments are shown in Table 2. Values of the particle size were calculated by assuming spherical geometry and an equal distribution of the three low index planes of nickel (14).

The particle size of nickel was also determined by magnetic susceptibility measurements. The design and operation of the Faraday balance has been described previously (15, 16). Ferrous ammonium sulfate Fe(SO₄)₂(NH₄)₂·6H₂O and ferrous sulfate FeSO₄·7H₂O were used for calibration. The ranges of particle size, as determined by the low- and high-field approximations to the Langevin equation (17), are also shown in Table 1. Magnetic susceptibility measurements provide a volume average while chemisorption provides a surface average particle size. Thus, the particle size measured by these two techniques differs. However, the trend is the same, namely, the particle size is greatest for the sample prepared by impregnation and smallest for the sample prepared by ion exchange.

TABLE 2
Characterization of Nickel Catalysts

Preparation method	Ni loading (wt%)	Ni reduced (%)	Particle size (nm)		
			% Metal exposed	Dihydrogen chemisorption	Magnetic susceptibility
Impregnation	3.5	100	29	3.4	4.0–7.0
Precipitation	8.7	65	33	2.9	3.5
Ion exchange	25.7	21	66	1.5	<1.7

In addition, these samples were examined by ferromagnetic resonance spectroscopy (FMR) and extended X-ray absorption fine structure (EXAFS).

The FMR experiments were performed on a Varian E-3 EPR spectrometer with a 9.5-GHz microwave bridge and a TE₁₀₂ cavity. Line position was calibrated with α, α' -diphenyl- β picryl hydrazyl (DPPH) powder. A specially designed cell which has an EPR tube as one arm was used for sample treatment. Reduced and passivated samples were re-reduced at 623 K for 2 h in flowing dihydrogen and evacuated at the same temperature for 1 h. After this treatment, the samples were transferred to the EPR tube, and a spectra was taken.

Figure 1a, b, and c show the room temperature FMR spectra of the catalyst samples with 29, 33, and 66% metal exposed. In addition to having a metallic nickel peak at $g = 2.20$, the spectra of the sample with 66% metal exposed (Fig. 1c) contains several smaller peaks, most notably the one at $g = 4.06$. These additional peaks are due to the presence of unreduced Ni²⁺ species (18). The same peaks are also observed in the spectra of the unreduced precursor of this catalyst (Fig. 1d). It is evident from this that the sample with 66% metal exposed is poorly reduced. The spectra of the sample with 33% metal exposed (Fig. 1b) exhibits a shoulder at $g = 4.06$ which indicates that this sample is also not fully reduced. However, the spectra of the sample with 29% metal exposed shows only the peak

due to metallic nickel and nickel appears to be fully reduced. The broadening of the FMR line of the sample with 29% metal

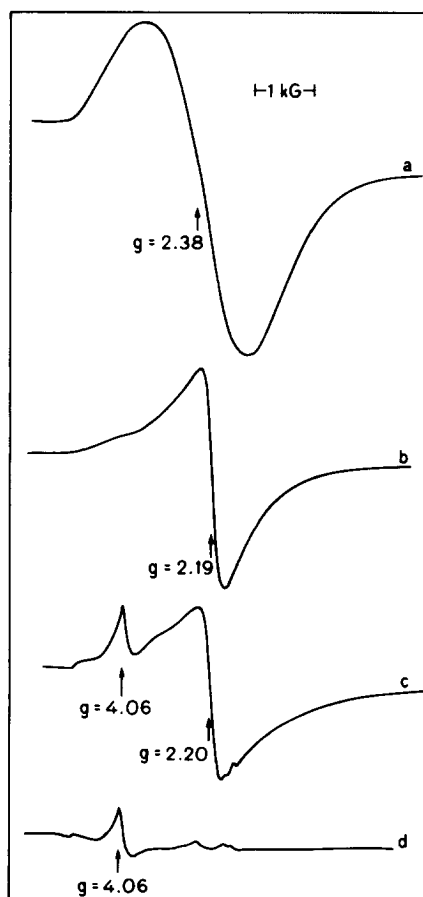


FIG. 1. Room temperature ferromagnetic resonance spectra of samples with varying percentage of metal exposed: (a) 29%, (b) 33%, (c) 66%, and (d) 66% prior to reduction.

exposed is probably due to magnetic anisotropy of the nickel particles.

The EXAFS data were collected at the Stanford Synchrotron Radiation Laboratory. The samples were pressed into self-supporting wafers and treated in a controlled-atmosphere cell previously described by Gallezot *et al.* (19). Reduced and passivated samples were re-reduced at 623 K for 2 h in flowing dihydrogen. The samples were kept at room temperature and under a dihydrogen atmosphere during the collection of the spectra. Analysis of EXAFS data has been described by Sánchez (20). In the treatment of EXAFS data, the EXAFS function $\chi(k)$ was multiplied by k^2 so that the weaker oscillations at high k could be more readily observed. The function $k^2\chi(k)$ was then Fourier transformed over a region $k = 40$ to 150 nm^{-1} to yield the radial structure function (21).

The function $k^2\chi(k)$ and the radial structure function for each of the three catalysts are shown in Fig. 2. Also shown in Fig. 2 are the data of a 22% Ni/SiO₂ sample prepared by Iglesia (8). The 22% Ni/SiO₂ sample has an average nickel particle size of 13.2 nm and a degree of reduction of 94% as measured by chemisorption of dihydrogen and reaction with dioxygen. The particle size of this sample is much larger than those of all our catalyst samples. Therefore, the 22% Ni/SiO₂ sample is a good reference material for metallic nickel. A comparison of Fig. 2a and b shows that the sample with 29% metal exposed has the same radial structure function as that of the 22% Ni/SiO₂ sample. As there appear to be no nickel–oxygen neighbors, we may conclude that the nickel in this sample is completely reduced. The average nickel–nickel coordination number can be roughly calculated (to within 20% accuracy) by comparing the height of the nearest neighbor peak of the radial structure function of this sample to that of the reference. Since the nickel in the reference sample has a coordination number of 12 (fcc crystal), the nickel in the sample with 29% metal exposed has a

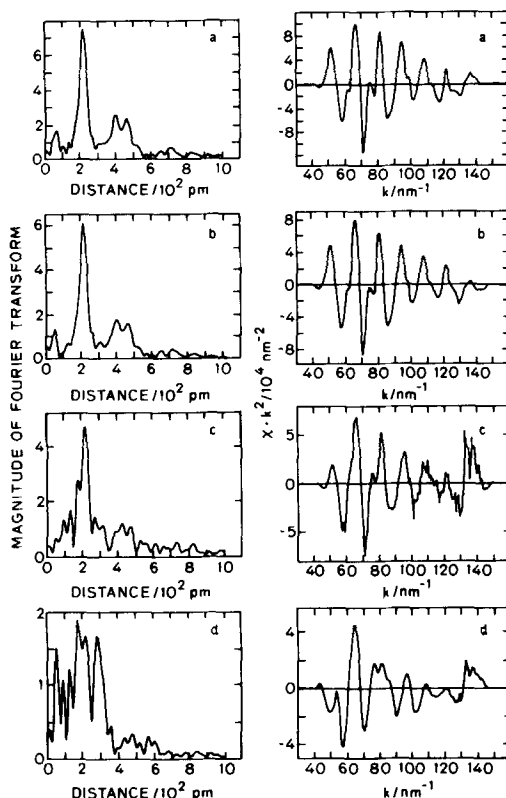


FIG. 2. Radial structure function and EXAFS of samples with (a) an average nickel particle size of 13.2 nm, (b) 29% metal exposed, (c) 33% metal exposed, and (d) 66% metal exposed.

coordination of 10.4. Figure 2c and d show that the samples with 33 and 66% metal exposed are not completely reduced. The nickel–nickel peak at 218 pm, characteristic of metallic nickel, is present in the radial structure function of both samples, but a nickel–oxygen peak near 175 pm and a nickel–nickel peak near 270 pm, characteristic of the unreduced phases, are also present. The peaks at $R < 135$ pm are artifacts due to imperfect background subtraction.

In summary, we have prepared three samples with 29, 33, and 66% metal exposed, which corresponds to particle sizes equal to 1.5, 2.9, and 3.4 nm, respectively. The nickel in the first sample is completely reduced, while it is only partially reduced in the last two samples.

Apparatus and Procedure

A schematic diagram of the liquid phase hydrogenation apparatus is shown in Fig. 3. Dihydrogen used for reaction as well as reduction of samples is purified over a Deoxo catalyst and a molecular sieve trap at 77 K. Purified dihydrogen is then stored in a compressible stainless-steel bellow (Metal Bellows Corp.). Pressure is continuously measured by a pressure transducer (Validyne AP10, and CK12 indicator). As dihydrogen is consumed during the reaction, the system pressure decreases. To maintain the pressure constant, a relay circuit has been set up so that when the pressure falls below the set point, a signal is sent to the stepping motor which drives a shaft that compresses the bellow. The volume change of the dihydrogen reservoir, measured by the position change of the bellow, is a direct measure of the extent of reaction. The position of the bellow is recorded on a chart recorder. The rate of reaction is taken as the slope of this curve. The rocking slurry reactor is connected to the main rig via a flexible stainless-steel coil and a Teflon bow. The latter is needed to dissipate the vibrations. A Tygon line insulates the Teflon bow, and dinitrogen is made to flow through the annular region between the Tygon and the Teflon lines to minimize air diffusion into the system. A 20-cm-long, 2-mm-diameter capillary tube separates the bellow from the connections to the reactor; this prevents the back diffu-

sion of solvent vapors into the bellow during the reaction. The design of the rocking slurry reactor has been described by Madon *et al.* (2). Temperature control is provided by a constant temperature bath/circulator (Laude K-2/R), which circulates a heat transfer fluid through the jacket of the reactor. Rocking of the reactor is provided by a $\frac{1}{8}$ hp, variable speed motor with speeds up to 400 rpm (Zero Max 400).

Cyclohexene (99.9%) and cyclopentene (99.9%), obtained from Wylie Chemicals, were further purified by passage through an acidic alumina bed (Merck) in the manner described by Madon *et al.* (2). Cyclohexane (Baker Analyzed Reagent) was degassed by a 15-min He purge. The solvent and the reactants were introduced to the reactor by gas tight syringes (Hamilton 1002LLT and 1050LT). Typically 20 cm³ of solvent and 0.3 cm³ of reactant were used in each run.

The hydrogenation reactor was so designed that *in situ* catalyst reduction at high temperature was not possible. Instead, 2 g batches of catalysts were first reduced at a high temperature and passivated at room temperature for 1 h in a flowing stream of 1% O₂ in He at a space velocity of 0.2 s⁻¹. Then preweighed amounts of catalysts were re-reduced at 623 K for 2 h and sealed inside breakable Pyrex ampules.

At the start of each experiment, the reactor, containing a catalyst ampule, was pumped down to 6×10^{-4} Pa. The entire system was purged with dihydrogen twice and then filled with 101 kPa of dihydrogen.

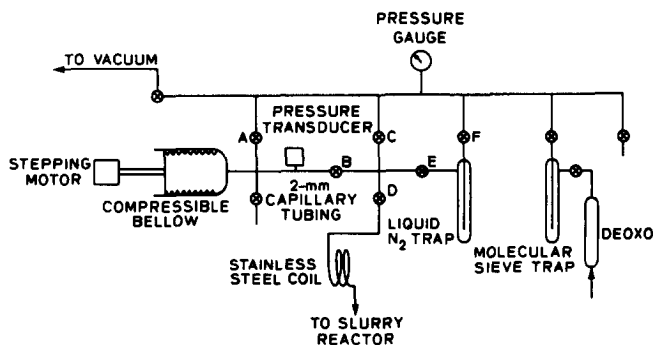


FIG. 3. Liquid phase hydrogenation apparatus.

Stopcock *D* was closed while the solvent was injected into the reactor. The rest of the system was now filled with more dihydrogen, to a pressure of 101 kPa plus the solvent vapor pressure at the reactor temperature. The reactor was shaken for 5 min to break the ampule and to equilibrate the solvent temperature to that of the heat transfer fluid (time required <300 s). Stopcocks *B* and *C* were closed and *D* opened to allow the entire system to equilibrate to one pressure. It was necessary to have stopcocks *B* and *C* closed so that solvent vapors could not reach the bellow. The pressure could be adjusted to the desired setting by either evacuating or supplying more dihydrogen. When the desired pressure was reached, stopcocks *A* and *E* were closed. Cyclohexene was introduced, and almost simultaneously, the relay circuit was turned on, stopcock *B* was opened, and the rocker was started. At the completion of each run the rocker was turned off, stopcock *B* was closed, and the bellow was expanded back to its original position and replenished with dihydrogen.

RESULTS AND DISCUSSION

A Koros–Nowak test (22, 23) was performed to ensure that the measured rates were not influenced by slow heat or mass transfer. The Koros–Nowak Criterion requires that the values of the turnover rate of a reaction on catalysts with the same metal particle size but different metal loading be the same, for the measured rate to reflect only the chemical process. It is necessary to keep the metal particle size the same since size may affect the turnover rate. Fortunately it was possible to prepare precipitation catalysts that fulfill this requirement. As described by Richardson and Dubus (11), at a given reduction temperature, increasing the reduction time for the precipitation catalyst only increases the amount of reduced nickel but leaves the particle size distribution unchanged. Samples of the precipitation catalyst were reduced for 3.5, 10, and 15 h at 673 K in

flowing dihydrogen at a space velocity of 0.2 s^{-1} . The nickel surface area was measured by chemisorption of dihydrogen at room temperature. The degree of reduction was determined by reaction with dioxygen at 673 K. The results are shown in Table 3. The turnover rates on these catalysts at 109 kPa dihydrogen, 299 K, and with cyclohexane as solvent are also shown in Table 3. As there is little difference in the value of the turnover rate on these catalysts, which have different amounts of surface nickel but similar percent metal exposed, we may conclude that diffusional interference is negligible.

Values of the turnover rate reported in Table 3 are those of the initial runs. Subsequent runs on the same catalysts produced lower values of the rate.

In order to understand this deactivation, an experiment was performed in which the same amount (0.3 cm^3) of cyclohexene was successively injected into the reactor containing the catalyst and 20 cm^3 of cyclohexane—each injection being made after the previous one had completely reacted. Since the solvent, cyclohexane, was also the product of hydrogenation, repeated injections did not change the composition of the solvent. Values of the rate of hydrogenation, measured as the initial slope of the dihydrogen uptake vs time curve of each run, are shown in Fig. 4. The

TABLE 3
Koros–Nowak Criterion^a

Metal exposed (%)	Ni reduced (%)	Amount surface Ni in catalyst ($\mu\text{mol g}^{-1}$)	Turnover rate (s^{-1})
36	40	546	1.27
33	65	780	1.14
36	69	910	1.26

^a All experiments at 299 K and a dihydrogen pressure of 109 kPa. The three samples were obtained by reducing the catalyst with 8.7 wt% Ni at 673 K for 3.5, 10, and 15 h in flowing hydrogen.

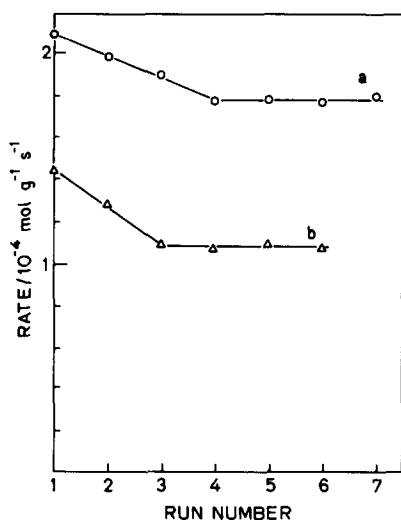


FIG. 4. Rate of hydrogenation of cyclohexene in cyclohexane on a nickel catalyst with 33% metal exposed as a function of the run number, at 299 K and pressure of dihydrogen (a) 106 kPa and (b) 55 kPa. The maximum amount of deactivation is 15 and 26% for (a) and (b), respectively.

activity of the catalyst decreases during the first few runs but stabilizes at about the third to the fourth run. The rate of deactivation is faster at the lower dihydrogen pressure. Also, the ratio of the rate at which no further deactivation occurred to the initial rate is lower at the lower dihydrogen pressure.

This observation is very similar to the one made by McConica and Boudart (5). During cyclohexene hydrogenation on nickel in the gas phase, the rate decreased with time, but a rate which was 60% of the initial value could be obtained reproducibly each time after a room temperature dihydrogen flush. McConica and Boudart (5) showed that cyclohexene disproportionation to form benzene and cyclohexane does occur during cyclohexene hydrogenation and that benzene hydrogenation under these conditions is four orders of magnitude slower than cyclohexene hydrogenation. Therefore, one possible explanation for the deactivation is that benzene, formed by disproportionation, competes with cyclohexene for the surface

nickel sites, but since benzene is only very slowly hydrogenated under these conditions, it acts as a poison for the catalyst. Disproportionation is inhibited by dihydrogen (24, 25); this explains the slower rate of deactivation and higher steady state activity of the catalyst used at the higher dihydrogen pressure. In the absence of dihydrogen, benzene production could be detected by UV spectroscopy. At room temperature, benzene was produced at a site time yield of 0.04 s^{-1} , or about 2 orders of magnitude slower than the turnover rate of cyclohexene hydrogenation at 299 K and a dihydrogen pressure of 101 kPa.

That benzene is the culprit in the deactivation of nickel during cyclohexene hydrogenation receives further support by the lack of deactivation during cyclopentene hydrogenation (Fig. 5). The rate of the latter reaction on the same nickel catalyst decreased less than 5% over a period of eight runs. In this case there was no side reaction, as the disproportionation of cyclopentene to cyclopentadiene and cyclopentane is thermodynamically unfavorable under the conditions of the experiment, as shown by Taylor (26).

One way to explain our results is to postulate that disproportionation is struc-

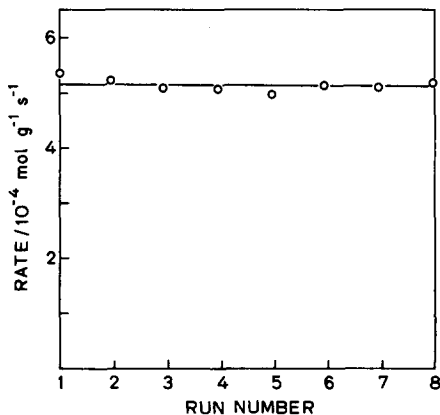


FIG. 5. Rate of cyclopentene hydrogenation on a nickel catalyst with 33% metal exposed as a function of run number. Dihydrogen pressure = 85 kPa, $T = 283 \text{ K}$, and the solvent is cyclopentane. Less than 5% deactivation was observed over a period of eight runs.

ture sensitive for intermolecular hydrogen transfer, because it requires large surface ensembles. So after enough multiple sites have been eliminated, the nickel catalyst is no longer able to catalyze disproportionation. However, cyclohexene hydrogenation is expected to be structure insensitive on nickel as it was found to be on platinum and palladium and could therefore proceed on the unpoisoned simple sites consisting of small ensembles or possibly of individual metal atoms. So, at steady state we have a fixed number of metal sites poisoned by benzene, so that hydrogenation occurs on the simple metal sites, while disproportionation is stopped. To test the hypothesis that disproportionation is structure sensitive, we studied the effect of Ni particle size on the rate and extent of deactivation during cyclohexene hydrogenation. Four nickel catalysts with 29 to 66% metal exposed were studied (Table 4). At any given pressure, the extent of deactivation decreases markedly as the percent metal exposed increases. Disproportionation and catalyst deactivation occur more readily on larger particles of nickel. Indeed, the catalyst with the greatest percent metal exposed showed very little deactivation for dihydrogen pressures above 55 kPa. The second trend, one that we have already seen, is that the lower the dihydrogen pressure, the greater the deactivation. These data indicate that disproportionation is indeed structure sensitive.

TABLE 4

Particle-Size Effect: Maximum Percentage of Deactivation at 299 K

P_{H_2} (kPa)	Metal exposed (%)	29	33	36 ^a	66
24		60	—	50	32
55		45	25	20	<5
106		—	15	10	<5

^a Sample with 40% Ni reduced (see Table 3).

TABLE 5

Particle-Size Effect: Cyclohexene Hydrogenation Turnover Rate at 299 K and a Dihydrogen Pressure of 101 kPa

Metal exposed (%)	Turnover rate (s ⁻¹)
29	0.98
36 ^a	1.08
66	2.15

^a Samples with 40% Ni reduced (see Table 3).

On the other hand, Table 5 shows that the turnover rate for cyclohexene hydrogenation on fresh catalysts varied by only a factor of 2 over the same range of percent metal exposed. So cyclohexene hydrogenation on Ni can be considered structure insensitive. In the absence of deactivation, the reaction orders were zero with respect to cyclohexene and one-half with respect to dihydrogen.

Thus the kinetics of cyclohexene hydrogenation on nickel is similar to that on palladium (3). On palladium, it was postulated that adsorbed hydrogen was in equilibrium with the dihydrogen in the liquid phase and the rate limiting step was the addition of adsorbed hydrogen to the half-hydrogenated, mono-adsorbed cyclohexyl radical ($C_6H_{11}^*$) to form cyclohexane.

When the reaction was carried in cyclohexane, the activation energy was found to be 22.8 kJ mol⁻¹. Values of the turnover rate, extrapolated to 298 K and 10.1 kPa dihydrogen, varied between 0.32 and 0.66 s⁻¹. These values may be compared with the ones in Table 1. Hydrogenation of cyclohexene possesses all three properties of a structure-insensitive reaction: its turnover rate is insensitive to the structure of the catalyst, modifications to the surface of the catalyst (e.g., by poisoning), and the nature of the metal (27). Note also from Table 1 that on nickel, palladium, and pla-

tinum, turnover rates in the gas and liquid phases are the same in order of magnitude although they appear consistently somewhat smaller in the liquid phase than the gas phase. It was suggested earlier (3) that this situation may be due to a smaller concentration of available free sites because of the higher concentration of cyclohexene in the liquid phase as compared to that in the gas phase.

CONCLUSION: STRUCTURE INSENSITIVE
REACTIONS WITH SIMULTANEOUS
STRUCTURE SENSITIVE DEACTIVATION

That nickel catalyzes the disproportionation of cyclohexene to benzene and cyclohexane has been known for a long time. In fact, nickel is an effective hydrogen transfer catalyst and its behavior with respect to cyclohexene is also found in the case of ethylene.

Thus results analogous to those discussed in this paper have been found by Beeck (28) for ethylene hydrogenation on nickel-evaporated films. During ethylene hydrogenation on these films, there was a buildup of a carbonaceous deposit which reduced the activity of the catalyst. However, a steady state was reached after 40% of the catalyst had been poisoned. Similarly, Hirota and Teratani (29) showed that disproportionation of ethylene to acetylene and ethane on a nickel powder stopped after 45% of the surface had been covered with acetylene.

But the most direct proof that surface disproportionation of ethylene on nickel is structure sensitive while the hydrogenation of ethylene on nickel does not seem to be comes from the work of Dalmai-Imelik and Massardier (30). They showed that the hydrogenation of ethylene at 298 K proceeds at turnover rates that differed by about a factor of 2 on Ni(111) and (110) while it did not take place at all on the (100) face because of catastrophic rapid carbon buildup on that face. Consequently, if hydrogenation of ethylene were carried out on small particles of supported nickel in the size

range where changes in relative amounts of surface structures are expected, a turnover rate based on the *total* number of nickel atoms exposed would depend on particle size, as if the reaction were structure sensitive. But if the turnover rate had been based on the number of carbon-free nickel atoms after structure sensitive disproportionation of ethylene has taken place, the hydrogenation of ethylene would appear structure insensitive as it was found to be on platinum (31).

This is essentially what was found in the present work for the hydrogenation of cyclohexene (structure insensitive) and the disproportionation of cyclohexene (structure sensitive) on supported nickel. In the above discussion we have ascribed the structure sensitivity for disproportionation of cyclohexene to the need for large ensembles required for that reaction. An alternative plausible explanation would be to ascribe it simply to certain surface structures as found, for instance, on the (100) face of nickel. Further work is necessary to decide between these alternatives. In the meantime, it appears clear that the disproportionation of cyclohexene is structure sensitive while the hydrogenation of cyclohexene is not. Another example is the oxidation of carbon monoxide on palladium (structure insensitive) accompanied on sufficiently small particles by structure sensitive disproportionation of CO to CO₂ and surface carbon (32). It will be interesting to watch for other examples in the future.

APPENDIX

Table 6 summarizes the effect of solvents on the turnover rate of cyclohexene hydrogenation. The solvents used in this study were: UV Grade acetonitrile, dioxane, and PSA Grade ethyl acetate (Burdick and Jackson Laboratories, Inc.) and Spectrograde *n*-heptane (Matheson-Coleman-Bell). The solvents were degassed with flowing helium for 0.25 h before being used. When the reaction was carried out in non-polar solvents, values of the turnover rate

TABLE 6
Solvent Effect for Catalyst with
3.5 wt% Ni

Solvent	Turnover rate (s^{-1}) at 299 K, $P_{H_2} = 101$ kPa
Cyclohexane	2.15
<i>n</i> -Heptane	1.81
iso-Octane	1.50
Ethyl acetate	0.18
Dioxane	0.09
Acetonitrile	0.07

on nickel were comparable to those on platinum (3) and palladium (4). Polar or oxygen-containing solvents had an inhibiting effect on nickel. Values of the turnover rates in these solvents are one order of magnitude lower than those in hydrocarbon solvents. This inhibition was not observed on platinum and palladium. Polar and oxygen-containing solvents appear to adsorb more strongly on nickel than platinum and palladium. This could be a subject for future investigation.

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