

Free Surface Determination of Used Ni/SiO₂ Hydrogenation Catalysts by CO Adsorption and H₂/D₂ Reaction

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The free surface area of a Ni/SiO₂ catalyst, which has been used in hydrogenation of 2-ethylhexenal for 1 h up to 5 days, has been determined by CO adsorption and H₂-D₂ reaction. CO was adsorbed at 25°C by a step adsorption technique. The area was also correlated to the H₂-D₂ exchange reaction rate. The CO adsorption and the H₂-D₂ reaction gave comparable results, indicating an almost linear dependence of exchange reaction and free surface area. The ratio of free surface area to initial surface area was determined to be ~0.1 at 51°C, ~0.2 at 87°C, and ~0.4 at 112°C after 1 h on stream. Almost all the decrease in surface area occurs when the catalyst is first exposed to the reactants. After this first decrease there is little further decrease in surface area while the conversion continues to decrease. © 1994 Academic Press, Inc.

INTRODUCTION

During hydrogenation reaction the catalyst becomes covered by reactants and more or less irreversibly adsorbed carbonaceous compounds. The accumulation of these compounds occurs rapidly the first few hours. After this initial period there is a slow accumulation that continues for the whole lifespan of the catalyst. This accumulation occurs both on the active metal and on the support.

The mechanism for deactivation is not well understood but there is usually an initial adsorption on the metal followed by dehydrogenation and a spillover of the carbonaceous compounds to the support. At low temperature, below 150°C, there is very little breaking of the C-C bonds, while at high temperature both dehydrogenation and C-C cleavage increase (1).

The activity and selectivity of hydrogenation reactions are closely related to the carbonaceous layer on the metal surface (2). These carbonaceous compounds have both a geometrical effect by decreasing the available surface area for reaction and an electronic effect by an electron exchange between the surface and the carbonaceous residue.

The available metal surface area changes with reaction conditions and decreases with time on stream. By estimating the free surface area we get important information about the deactivation of a working catalyst. The purpose of this work is to find a reliable method to determine the free surface area of a used hydrogenation catalyst.

Hydrogen adsorption has been used by several authors (3, 4). This method works well on catalysts with a stable carbonaceous layer that does not react with hydrogen. Duprez *et al.* (3) used a hydrogen pulse method and hydrogen titration to determine free surface area on a used reforming catalyst. Lieske *et al.* (4) measured the free surface area with hydrogen adsorption after adsorption of different hydrocarbons on Pt/Al₂O₃. They found that hydrocarbons adsorbed above 450°C did not react with hydrogen at low temperature and the hydrogen adsorption at room temperature gave accurate measurements of the free surface area.

Rivera-Latas *et al.* (5) investigated the free surface of a Pt/Al₂O₃ catalyst after hydrogenolysis of hexane. They used four different methods: titration of preadsorbed oxygen by hydrogen, hydrogenation rate of ethylene, infrared spectroscopy of chemisorbed carbon monoxide, and chemisorption of carbon monoxide. All four methods showed that about 50% of the Pt surface remained free on the used catalyst. Jackson *et al.* (6) have used carbon monoxide adsorption to determine the free surface area of a Ni/Al₂O₃ catalyst that had been exposed to different hydrocarbons. They found that the free surface was reduced to 25–50% of the free surface on the fresh catalyst. Carbon monoxide does not react with the hydrocarbon residue on the catalyst. At low temperature it displaces hydrogen and reversibly adsorbed hydrocarbons on the metal surface. The disadvantages with carbon monoxide are that it can form carbonyls with several metals and that the stoichiometry of the adsorption is ambiguous. Bartholomew and co-workers (7–9) have shown that the stoichiometry varies with temperature, pressure, preparation method, dispersion, and support material. However, they found that the carbonyl formation is usually a slow process at room temperature.

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It is also possible to estimate the free metal surface area with the H_2 - D_2 exchange reaction. The rate of HD production is to some extent proportional to the free metal surface area (10, 11). Pradier *et al.* (10) found a linear dependence between reaction rate and surface area for Pt poisoned with sulfur on a (100) surface but a more complex dependence on a (111) surface. Ross and Stonehart (11) found a second-order dependence on free surface area on platinum and rhodium poisoned with carbon monoxide.

Consecutive hydrogenation of 2-ethylhexenal to 2-ethylhexanal and 2-ethylhexanol has been selected as a model reaction. This reaction has been extensively studied at our laboratory. Niklasson and Smedler (12) studied the kinetics and Eek and co-workers (2) studied the deactivation and found that the selectivity was sensitive to coke formation on the catalyst.

EXPERIMENTAL

Catalyst

In this study silica (Girdler T1571), 5 mm pellets, ground to 0.5–1.0 mm particles, was used as support. The silica was impregnated with 2 M $Ni(NO_3)_2$ solution. The catalyst was dried (90°C, 24 h), calcined in air (300°C, 10 h), and reduced in a hydrogen–nitrogen atmosphere (20% hydrogen, 350°C, 17 h). The final catalyst contained 24 wt% Ni, the metal dispersion was 6.3%, and the BET surface area was 143 m²/g.

CO Adsorption, Hydrogenation

The main reactions were the consecutive reaction 2-ethylhexenal (A) → 2-ethylhexanal (B) → 2-ethylhexanol (C) but also some dimerization of the aldehydes, and the formation of heptane by decarbonylization was seen. In this work only the turnover number for the reactions of 2-ethylhexenal and 2-ethylhexanal were considered. All experiments were performed at atmospheric pressure and at a reaction temperature of 120°C. The hydrogen pressure was 1250 Pa (1.23% H_2) and $P_A = 600$ –900 Pa (0.6–0.9%), $P_B = 150$ Pa (0.15%). The total flow rate was 240 ml/min and the reaction was run between 1 h and 5 days in a 4-mm-inner-diameter stainless-steel tubular reactor. Before each experiment series the catalyst, 0.2 g, was reduced *in situ* (10 ml/min, 50% hydrogen, 50% nitrogen, 380°C, 16 h).

CO Adsorption

CO was adsorbed by a step change in concentration of CO in N_2 . The flow of A and B was stopped and the catalyst was exposed to 3 ml/min H_2 and 237 ml/min N_2 for 30 min at 120°C to desorb the reactive species from the catalyst surface. The catalyst was then cooled to 25°C

in the same flow. N_2 containing 94 ppm CO was flowed over the catalyst at a rate of 200 ml/min and the outlet concentration was measured with a CO IR detector. The flow was switched to pure nitrogen and the procedure was repeated on the already CO covered surface. The different amount of CO detected between these two step responses was the amount of CO adsorbed.

The reactor was heated to 120°C again and the hydrogenation of A and B was resumed. The procedure was repeated until the end of the experiment series when the catalyst was either regenerated or replaced.

H_2 - D_2 Reaction

The same reaction was used but the reaction conditions were somewhat different. All experiments were performed at atmospheric pressure and at reaction temperatures of 51, 87, or 112°C. The total flow rate was 159 ml/min, 0.3% 2-ethylhexenal, 1.82% D_2 , 5.59% H_2 , and 92.3% N_2 . The same catalyst as for the CO-adsorption experiments was used but in some runs the catalyst was crushed to a fine powder. The catalyst, 0.01 g, was reduced *in situ* (20% H_2 , 350°C, 16 h) before each experiment.

Two stainless steel plug flow reactors (inner diameter 4 mm) were used. One of the reactors was loaded with ca 0.01 g catalyst. A very small amount of catalyst was necessary to be sure that the equilibrium concentrations of H_2 , D_2 , and HD were not reached on the fresh catalyst. The second reactor was located in series after the first one but with possibility to bypass it. It was loaded with 0.5 g Pd, enough catalyst to be sure that the equilibrium concentrations were reached. Both reactors were placed in an oven. D_2 and HD concentrations were measured continuously with a quadropole mass spectrometer (Baltzer QMG 311). It was not possible to measure the concentration of H_2 with this equipment.

The reactants and products, 2-ethylhexenal, 2-ethylhexanal, and 2-ethylhexanol were analyzed both in the inlet and in the outlet flow from the reactors by a gas chromatograph with a capillary column (DB-5, 30 m) and a FID-detector.

H_2 - D_2 Reaction, Calculations

The kinetics of the H_2 - D_2 reaction on this catalyst has been determined previously by Niklasson and Andersson (13) giving

$$r_{HD} = k \frac{(p_{HD} + 2p_{H_2})(p_{HD} + 2p_{D_2})/P_T - 2p_{HD}}{(1 + \sqrt{KP_T})^2}, \quad [1]$$

where

$$P_T = p_{H_2} + p_{D_2} + p_{HD},$$

k is the rate constant, and K the adsorption equilibrium constant.

Assuming spherical particles, plug flow and neglecting the isotopic effects, we can express the HD pressure in the reactor outlet,

$$p_{\text{HD}} = 2 \frac{p_{\text{D}_2}^0 p_{\text{H}_2}^0}{p_{\text{D}_2}^0 + p_{\text{H}_2}^0} \cdot (1 - e^{-k_v \eta(V/q)}) = p_{\text{HD}}^{\text{equil}} \cdot (1 - e^{-k_v \eta(V/q)}), \quad [2]$$

where $p_{\text{HD}}^{\text{equil}}$ is the equilibrium pressure, k_v is the rate constant, and V/q is the residence time, and the effectiveness factor from

$$\eta = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \quad [3]$$

with

$$\phi = \frac{d_p}{2} \sqrt{\frac{k_v}{D_{\text{eff}}}}$$

and

$$k_v = \frac{k_p R T}{(1 + \sqrt{K P_T})^2}$$

By measuring the HD production or the D_2 consumption we can estimate the number of sites available for the H_2 - D_2 reaction assuming:

- the H_2 - D_2 exchange reaction rate is proportional to the number of sites;
- the deactivation does not change the site activity

To adjust for hydrogen and deuterium that react in the mass spectrometer we can modify Eq. [2] in the following way:

$$p_{\text{HD}} = p_{\text{HD}}^{\text{equil}} (1 - e^{-k_v \eta(V/q) - k_{\text{MS}} \tau_{\text{MS}}}). \quad [4]$$

Here

$$p_{\text{HD}} = p_{\text{HD}}^{\text{equil}} (1 - e^{-k_{\text{MS}} \tau_{\text{MS}}})$$

corresponds to the amount of HD produced in the MS.

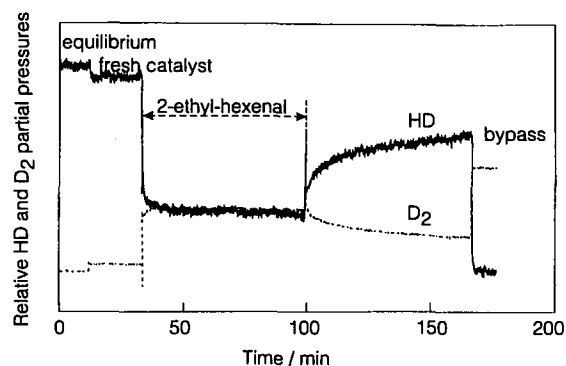


FIG. 1. D_2 consumption and HD production on a Ni/SiO_2 catalyst.

RESULTS AND DISCUSSION

H_2 - D_2 Exchange

Figure 1 shows a typical result. First the reactants are flowing through both reactors to measure the equilibrium concentrations. Then the palladium-containing reactor is bypassed to measure the HD production on the fresh catalyst which is high but less than the equilibrium. When 2-ethylhexenal is added, the HD production decreases due to a decrease in free surface area and a consumption of hydrogen in the hydrogenation. The exchange of deuterium with hydrogen in the 2-ethylhexenal molecule was too small to be observed in the MS. The product 2-ethylhexenal contained deuterium from the hydrogenation but very little from exchange of deuterium with hydrogen in the molecule. The rate of deuterium exchange into the 2-ethylhexenal was well below 1/10 of the rate of hydrogenation. The presence of hydrocarbons decreases the D_2 signal by about 5% and the HD signal by approximately 15% in the MS.

After the 2-ethylhexenal has been turned off the HD production increases. First there is a rapid increase due to desorption of the reacting species still on the surface making more surface available for the H_2 - D_2 reaction and because the consumption of hydrogen and deuterium in the hydrogenation reaction has stopped. There is also a slow increase due to hydrogenation of the carbonaceous residue and regeneration of the deactivated surface. Figure 1 also shows that there is some HD produced when the reactor was bypassed. This amount is attributed to reaction occurring in the MS.

The calculation of the rate constant, k_v , is visualized in Fig. 2. The right part of the figure is identical to Fig. 1. The left part of the figure shows the D_2 and HD pressure as a function of rate constant calculated from Eq. [2]. From this figure we can calculate the rate constant needed for a certain conversion. We can see that the reaction occurring in the MS and the reaction on the fresh catalyst correspond to a certain rate constant.

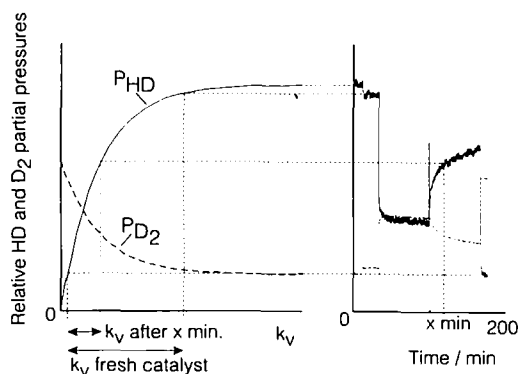


FIG. 2. Calculation of the rate constant for HD formation.

Figure 3 shows the same experiment but recalculated, using Eq. [4], to show how the rate constant changes at different temperatures. The rate constant is normalized to be unity for the fresh catalyst and can be an estimate of the available surface area with the assumption that the rate constant is proportional to the available surface area. The areas calculated from HD production and the D_2 consumption give the same results.

The turnover frequency for the hydrogenation is of the order of 0.1 s^{-1} at 110°C and 0.05 s^{-1} at 50°C , which gives 1–2 min to hydrogenate the reactants adsorbed on the

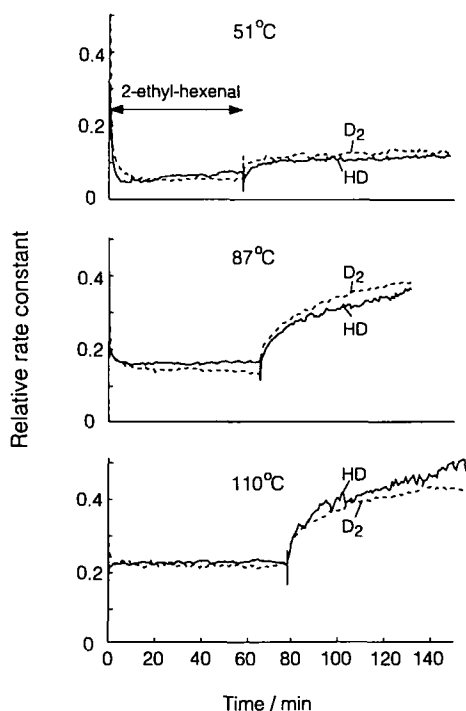


FIG. 3. Relative rate constants at different temperatures for the powdered catalyst.

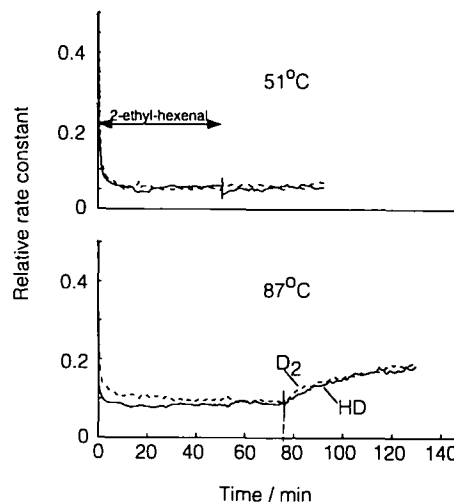


FIG. 4. Relative rate constants with large particle catalyst.

surface. This is clearly seen in Fig. 3 where most of the increase in surface area occurs within 2–5 min. The slow increase in surface area after the first few minutes is attributed to a catalyst regeneration by hydrogenation of the carbonaceous layer.

The available surface area increases with increasing temperature. At 51°C only 10% of the total catalyst surface area is available for H_2 – D_2 reaction and the regeneration of the catalyst in hydrogen is very slow. At higher temperatures both the available surface area and the rate of regeneration increases.

The influence of mass transfer was tested with particles in the range 0.5–1 mm. The effectiveness factor for the H_2 – D_2 reaction on the fresh catalyst was estimated to be 0.3–0.4 and for the deactivated catalyst to be 0.65–0.9. The influence of the external mass transfer was insignificant even for Sherwood number $Sh = 4$. The hydrogenation reaction was more than a magnitude slower than the H_2 – D_2 reaction and consequently not affected by mass transfer limitations. The estimated free surface area on this catalyst was about half the area of the powder catalyst even after correction for the mass transfer. The calculated effectiveness factor for the deactivated catalyst could be too high if the effective diffusivity decreases due to deactivation. This difference is not large enough to explain the large difference in available surface area. It seems that the available surface area on the larger particles is significantly lower than that on the powdered catalyst. See Fig. 4.

CO Adsorption

Figure 5 shows two consecutive CO adsorptions on the same catalyst. In the first adsorption a large amount is adsorbed. After 7 min in inert gas the catalyst is exposed

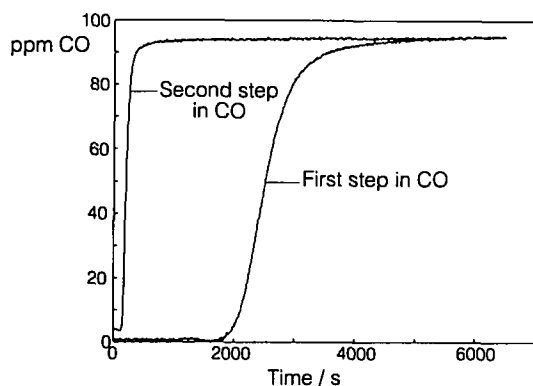


FIG. 5. Step adsorption of CO on a Ni/SiO₂ catalyst.

to a second step change in CO. A very small amount of CO is desorbed into the inert gas and adsorbed in the second step. The amount of irreversible adsorbed CO was calculated from the difference between these curves.

The reversibility of the CO adsorption was tested at 250 and 120°C. The experiments in Table 1 show adsorption of CO at 25°C, experiment 1 on a fresh catalyst, experiment 2 after desorption of CO at 250°C, and experiment 3 after desorption of CO at 120°C. At 250°C the CO desorbs completely in hydrogen, but at 120°C only 80% desorbs after 2 h. The surface areas of the used catalysts are given in Table 2. To avoid contamination by CO on the free surface area on the fresh catalyst in experiments 13–15, the surface area was not measured but taken as the average of the previously measured area on catalysts from the same batch. The surface area for this used catalyst was the same as for the catalysts that was exposed to CO initially. Also in experiments 2–5 and 7–10 repeated CO adsorptions give the same surface area, which indicates that no CO is accumulated on the surface. We therefore conclude that in the presence of the unsaturated aldehyde and hydrogen almost all CO desorbs at 120°C.

The measured surface area depends on the treatment of the catalyst after the reactants were turned off, as can be seen from the H₂-D₂ reaction. We have measured the CO adsorption after 30 min in hydrogen at 120°C. In experiment 16 the catalyst was treated in hydrogen at 200°C

TABLE 1
Test of the Reversibility of CO Adsorption

Experiment no.	Catalyst	Surface area (mol × 10 ⁻⁶)
1	Fresh	31.8
2	CO desorbed at 250°C	33.0
3	CO desorbed at 120°C	25.1

TABLE 2

Amount of CO Adsorbed on Fresh Catalyst and after Reaction with 2-Ethyl-Hexenal and Hydrogen

Experiment no.	Hours of reaction	Conversion of A (%)	Surface area (mol × 10 ⁻⁶)	Surface area (% of clean catalyst)
1 ^a	0	—	16.0	100
2	18	93.7	6.9	42.9
3	32	93.2	7.3	45.7
4	46.5	90.6	6.8	42.3
5	115.5	90.9	5.9	36.5
6 ^a	0	—	17.5	100
7	18.5	87.2	5.5	31.7
8	35.5	85.3	4.9	27.9
9	55	86.9	5.6	32.1
10	65.5	85.2	5.7	32.6
11 ^a	0	—	14.9	100
12	16	83.9	6.2	41.7
13 ^a	1	99	4.26	37.6
14 ^a	1	92.2	6.16	51.1
15 ^a	3	89.7	4.49	37.3
16	6.5	87.4	9.5	64.8 ^b
17	9	83	5.5	37.5
18	33	79.6	5.5	37.5

^a The catalyst was regenerated or replaced before these experiments.

^b The catalyst was treated with hydrogen at 200°C before CO adsorption.

before the CO adsorption, which gave a much higher surface area.

Almost all decrease in surface area occurs when the catalyst is first exposed to the reactants. After this initial rapid decrease there is little further decrease in surface area while the conversion continues to decrease. There is a difference between repeated experiments which is shown both in surface area and conversion.

The CO adsorption and the H₂-D₂ reaction rate gave the same result within experimental error. Our assumptions of a linear dependence between the H₂-D₂ reaction, CO adsorption, and surface area seem to be valid. The adsorption of 2-ethylhexenal probably deactivates adjacent sites. Each molecule can cover up to four nickel atoms. With random adsorption of 2-ethylhexenal, a second-order dependence on free surface area for hydrogen dissociation will only be noted at high coverage of 2-ethylhexenal.

CONCLUSIONS

The surface area of a used catalyst that is not covered by irreversibly accumulated "coke" can be measured by the H₂-D₂ exchange reaction or by CO adsorption. The H₂-D₂ reaction shows an increase in available surface area with increasing temperature, from 5% at 50°C to 40% at 110°C. Both the CO adsorption and the H₂-D₂ reaction

gives about 40% free surface after reaction at 110°C. The available surface area increases with reaction temperature and can partly be regenerated in hydrogen.

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