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The Effect of Pore Diffusion in Enantioselective Hydrogenation with Supported Nickel Catalysts

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Nickel dispersed on wide-pore silica has been used as catalyst in a study of the reaction kinetics of the hydrogenation of methyl-acetoacetate (MAA). The hydrogenation in the gas phase with a H_2/MAA ratio of $\sim 10^3$ is found to be limited by the catalytic reaction proper if the rate is kept low, but tends to become limited by pore diffusion of MAA when higher temperatures, higher Ni surface areas, or lower space velocities are used. In the liquid (MAA + methanol) phase the rate is limited by pore diffusion of dissolved hydrogen. Consequently the rate depends on the catalyst pellet size, as does also the enantioselectivity for samples modified with aqueous *R,R*-tartaric acid.

INTRODUCTION

Nickel and other transition metal catalysts, when "modified" with an asymmetric molecule such as *R,R*-(+)-tartaric acid, become "enantioselective," i.e., they acquire the ability of hydrogenating molecules with a prochiral center in such a way that one enantiomer prevails in the product (*1–7*). It has been suggested (*8, 9*) that modification with tartaric acid is a corrosive chemisorption, whereby Ni atoms leave the crystal and form complexes with asymmetric tartrate ligands. Some of these complexes remain on the surface and are assumed to be the sites of enantioselective hydrogenation.

A convenient test reaction is the hydrogenation of methyl-acetoacetate (MAA) to methyl-hydroxybutyrate. It can be carried out in the liquid or gas phase. The knowledge of the kinetics of this reaction is, however, still unsatisfactory and published data show poor agreement (*9–12*). Upon considering that all reported data were obtained with high surface area catalysts, i.e., most of the nickel surfaces being present in pores, we have been wondering whether mass transport was controlling the observed rates r_{obs} in part of previous work, in particular for liquid-phase hydrogenation. It is known that for diffusion-controlled processes the measured activation energy and the reaction orders significantly differ from the corresponding parameters of the "intrinsic" reaction r_i. Only if the chemical processes on the catalyst surface are much slower than all transport phenomena will the effectiveness factor $\eta = r_{\text{obs}}/r_i$ be unity and the kinetic parameters be characteristic of the rate-limiting step.

The present work, therefore, has as objectives: (i) to determine the kinetic parameters under conditions where $\eta = 1$; (ii) to establish under which conditions the reaction is pore diffusion controlled ($\eta \ll 1$).

We believe that knowledge of the kinetic regime is essential for understanding observed differences in enantioselectivities measured under different conditions. If catalyst modification is also a pore diffusion limited process, the outer zones of each catalyst particle are likely to be better modified than the kernel. The measured enantioselectivity will then be large for $\eta \ll 1$, as in this case only the outer zones are utilized. Crushing the pellet, for example, would then cause an increase in r_{obs}, but a decrease in enantioselectivity, as the kernel of the original pellet also contributes to the reaction. This idea outlines a simple,

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though not unambiguous, experiment to verify whether the hydrogenation of MAA in the liquid phase is pore diffusion controlled.

EXPERIMENTAL

In order to minimize errors due to chemical impurities we decided to use a standardized Ni/SiO_2 catalyst which was reduced at 400°C in H_2 for 18 hr. This high reduction temperature is not practible for unsupported powders, where sintering would reduce the surface area.

To create conditions where $\eta \simeq 1$, we used a very wide pore (40–80 nm) SiO_2 support, a very low Ni load (~0.5% wt), a small quantity of catalyst (0.4–0.6 g), and carried out the hydrogenation in the gas phase in a plug-flow reactor at a high space velocity of, typically, 8400 hr^{-1}. The reactor and the catalyst preparation were described elsewhere (*9*). The partial pressures of H_2 and MAA were 760 and 0.44 Torr, respectively. Under these conditions the enantioselectivity was small so that the kinetic parameters for modified and unmodified catalyst samples are equal within the error of the experiment.

The opposite case of $\eta \ll 1$ was experimentally approached by hydrogenating in liquid MAA. A stirred atmospheric batch reactor was used, filled with 10 ml 50/50 (v/v) MAA/methanol. The same silica support was used in these experiments, but the nickel load was 10 times higher (5%) and the catalyst quantity was in most runs roughly twice the quantity mentioned for the gas-phase experiments. The rates and selectivities were compared before and after disintegration of the catalyst pellet due to the mechanical action of the stirrer.

RESULTS AND DISCUSSION

Gas-phase conversion of MAA increased linearly with the inverse flow rate as shown in Fig. 1. The Arrhenius plot of the rates determined from such curves is shown in Fig. 2 and the log rate versus log partial pressure curves in Fig. 3. From these plots

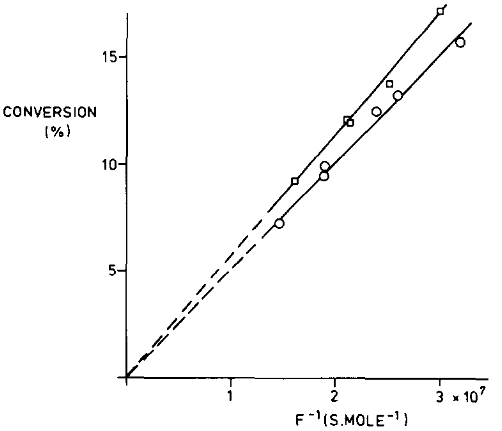

FIG. 1. MAA conversion vs (feed rate)$^{-1}$ for modified (○) and unmodified (□) Ni/SiO_2 catalysts.

an activation energy of 61 ± 5 kJ/mole and an order in MAA of 0.40 ± 0.05 was determined. The order in hydrogen was found to be 0.20 ± 0.03. These values do not differ significantly from our previous results (*9*). As side-products of the gas-phase hydrogenation small amounts of acetone and methanol were detected.

For the liquid-phase reaction the data in Table 1 show that a decrease in pellet size causes an increase in hydrogenation rate by a factor of nine and a substantial decrease in selectivity. This is in agreement with the expected pore diffusion controlled kinetics of the liquid-phase hydrogenation. As under these conditions the concentration of

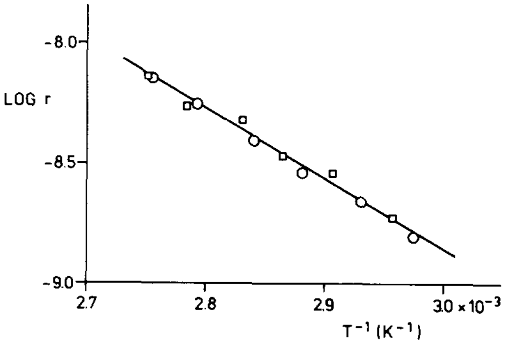

FIG. 2. Arrhenius plot of gas-phase MAA hydrogenation on modified (ES ≤ 15%) (○) and unmodified (□) Ni/SiO_2 catalysts. Rate (*r*) in mole per cm^3 catalyst per second.

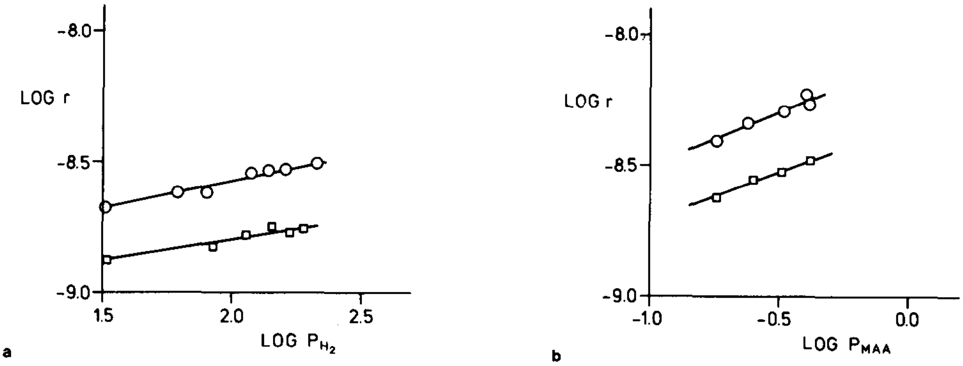

FIG. 3. Reaction order plots for gas-phase hydrogenation at 90°C. (a) Log rate vs log p_{H_2} at p_{MAA} = 0.44 Torr, adjusted with helium to total pressure of 760 Torr; (b) log rate vs log p_{MAA} at p_{H_2} = 760 Torr.

hydrogen in the liquid is much smaller (*13, 14*) than that of MAA it has to be hydrogen the diffusion of which controls the rate. This conclusion is in line with an estimate of the Thiele modulus for hydrogen which we calculate to be roughly two orders of magnitude larger in liquid MAA than in the gas phase. Pore diffusion control by hydrogen was also found by Coenen (*15*) to be rate limiting for the liquid-phase hydrogenation of fatty acids with silica-supported nickel catalysts.

For the gas-phase reaction it is interesting to consider the Thiele modulus ϕ. As under the conditions described the ratio H_2/MAA was in the order of 10^3, it is justified to include the hydrogen pressure in the reaction-rate constant and write

$$\phi = R_p \left(\frac{k' C_{MAA}{}^{n}}{D_{eff} C_{MAA}}\right)^{1/2} \qquad (1)$$

where R_p is the radius of the spherical pellet and D_{eff} is the effective diffusion coefficient of MAA. The number of parameters to be estimated is reduced by considering the product

$$\eta\phi^2 = R_p{}^2 \frac{r_{obs}}{D_{eff} C_{MAA}}. \qquad (2)$$

TABLE 1

Activity and Enantioselectivity of Modified Ni/SiO$_2$ Catalysts in Liquid-Phase Hydrogenation of MAA

Sample	Stirring	Pellet diameter after hydrogenation (mm)	Hydrogenation rate (mole/cm^3, s)	Enantioselectivity (%)
1	–	2.7	8.3×10^{-9}	58
2	+	10^{-1}–10^{-2}	7.7×10^{-8}	44

A mathematical discussion of this product, for which we refer to standard textbooks of chemical engineering (e.g., Ref. (*16*)), shows that the reaction rate is "intrinsic" ($\eta = 1$) for $\eta\ \phi^2 \leq 6$, if $n = 0$; it is "essentially intrinsic" ($\eta \geq 0.94$) for $\eta\phi^2 \leq 1$, if $n = 1$. In estimating D_{eff} we assumed that for the low MAA pressure of our experiments the mean free path of MAA is larger than the pore diameter, which justifies considering the diffusion as of the Knudsen type. For 82°C, for example, a value of 0.01 cm^2 s^{-1} has been assumed for D_{eff}. With this number and $R_p = 1.35$ mm, $\eta\ \phi^2$ was calculated from the observed rates which were in the range of $(3.0–8.4) \times 10^{-9}$ (mole cm^{-3} s^{-1}) for temperatures below 90°C. It follows that for the temperature range between 71 and 87°C $\eta\ \phi^2$ is in the range of 0.2–0.7. For temperatures above 90°C, however, values above 1.0 are calculated. Even when admitting a considerable error in the estimated diffusion coefficient we feel that it is justified to conclude that below 90°C the gas-phase hydrogenation of MAA measured under the conditions specified above is "essentially intrinsic." It also appears, however, that higher rates (due to higher temperatures, higher metal loadings, or lower space velocities) lead to conditions where pore diffusion of MAA is interfering with the reaction rate, even in the gas phase. The same is to be expected for catalyst samples with narrower pores.

It is interesting to face these conclusions with results reported in the literature. Kinetic parameters have been reported by Ozaki *et al.* (*10, 11*) and by Yasumori *et al.* (*12*). The former group studied the hydrogenation in the liquid phase. If the active sites are identical in their and our catalytic experiments we would predict that their rates were pore diffusion controlled, i.e., with an activation energy near $\frac{1}{2}(E_{\text{true}} + E_{\text{D}})$. With $E_{\text{true}} = 61$ kJ/mole this amounts to 35 kJ/mole. The value reported is 44 kJ/mole, i.e., nearer this estimate than our E_{true}. Also the low order in MAA of 0.2 is consistent with this model.

Yasumori *et al.* (*12*) worked in the gas phase. In the limit of MAA pore diffusion control one would expect $E = 35$ kJ/mole and $n = \frac{1}{2}(n_{\text{true}} + 1) = 0.7$ for n_{MAA}. The reported values are 45 kJ/mole and 0.8. That both groups find activation energies above the value calculated from our data for the limit of complete control by pore diffusion, indicates that their conditions were somewhere between the limits of the "intrinsic" and pore diffusion controlled regimes. Another possibility, of course, is that the modified unsupported catalysts of these groups differed chemically from our samples.

In summarizing we conclude that hydrogenation of MAA as usually carried out tends to be diffusion controlled, but experimental conditions can be adapted such that the intrinsic reaction is measured. The set of conditions as chosen in this work unfortunately implies low enantioselectivity. Future work will have to establish conditions where high enantioselectivity can be achieved under non-diffusion-limited conditions, in order to decide whether true activation energies are different for enantioselective and nonselective sites on nickel catalysts.

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