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Apparent Particle Size Sensitivity in Hydrocarbon Reactions

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The particle size sensitivity of catalytic reactions has been studied with Ni catalysts and hexane, neohexane, and methylcyclopentane in hydrogen mixtures. It is established that besides intrinsic differences in the behavior of the small and large particles (formation of the multiple bonds) there are also poison-induced differences. The latter can even reverse the order of intrinsic activities.

INTRODUCTION

The problem of the sensitivity of catalytic reactions to catalyst particle size is not new. It was first tackled in relation to surface heterogeneity and its potential importance for catalytic activity (see Ref. (*1*) for reviews). Later, it was recognized that two classes of catalytic reactions exist in general, namely structure-sensitive and structure-insensitive ones (*2–4*), and many reactions have been tested in the course of time for structure sensitivity.

A convenient way to test the structure sensitivity of catalytic reactions is to vary the particle size of the catalysts. It can be expected that the relative importance of various sites (edges, corners, and sites of unusual coordination such as the so-called B_5 sites) varies with the particle size (*3, 4*). A few examples from the literature (*5–8*) demonstrate the type of information obtained. However, a generalizing theory is still missing. Catalytic activity in related reactions has been found to vary sympathetically, antipathically, or to go through a maximum, when the metal particle size increases. Some authors predict that the effects should not be very pronounced in any case (*4*).

Another complicating factor appeared to be the fact that the structure sensitivity or particle size sensitivity can be caused not only by the reaction studied but also by its side reactions (*9, 10*). Therefore, to make progress in explaining the structure sensitivity of reactions, one needs to gain information on the structure (particle size) sensitivity of the individual steps of the total reactions and of their side reactions.

Recently, a study has been performed on the relation between the hydrogenolytic activity of various metals (Ni, Co, Ru, Rh, Ir, Pd, Pt) and the propensity of these metals to form multiple bonds between the metal surface and the hydrocarbon molecules, or their fragments. It appeared (*11*) that a high activity in hydrogenolysis requires an easy formation of multiple bonds, the latter being obviously a very essential particular step in the overall reaction. With three of the metals, viz., Ni, Ir, and Pt, a study has been performed on the influence of the particle size on the propensity to form multiple bonds. It has been established (*12*) that the smallest particles show the lowest activity in the formation of multiple bonds and the lowest hydrogenolytic activity at low pressures of hydrocarbons and under mild reaction conditions. However, such a conclusion is at variance with the earlier data and statements in the literature (*13, 14*) that the smallest particles are just those most active in hydrogenolysis. In order to contribute to the clarification of the problem, this short study has been performed.

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EXPERIMENTAL

Apparatus and procedure. The apparatus used and the procedure of data evaluation were the same as in our earlier papers (e.g., Ref. (*15*)). A typical experimental run, supplying results such as those shown in the figures, was as follows. A weighed amount (10–50 mg) of the catalyst (prereduced *ex situ*, in advance) was brought into the reactor, either as such or diluted with an inert silica (to achieve a continuous layer on the sintered-glass filter in the reactor). Thereafter, the catalyst was reduced *in situ* at 663 K for 14 h in a flow of hydrogen (10 ml/min). After cooling to a desired start-temperature, the hydrogen flow was led via a saturator, filled with a liquid hydrocarbon. The ratios used (established by the thermostated temperature of the saturator) were: hexane/H_2 = 1/16; methylcyclopentane (MCP)/H_2 = 1/17; 2,2-dimethylbutane (neohexane)/H_2 = 1/18. After about 30 min a steady state was achieved, the activity and selectivity at that temperature were determined, and then the temperature was increased by 10–20 K. Again, for a 30 to 40 minute period the system was allowed to reach the value which is plotted in the graphs. At higher temperatures the decay of the activity of the catalyst activity was more pronounced than at the lowest temperatures.

Catalyst preparation. Catalysts used were from a series of Ni catalysts prepared (by homogeneous precipitation by urea of Ni nitrate on Degussa Aerosil as support) and fully characterized in another laboratory by chemical analysis, chemisorption measurements, and TPD profiles (*16*). Our short study had a limited aim, which was to establish whether the ratio of the hydrogenolytic activities of the small and large particles does depend on the reaction conditions and mainly on carbon(aceous) layer deposition. For this purpose we simply selected two catalysts, one with the smallest and one with the largest particles. Assuming that the Ni particles form spheres, the average diameters for the particles were about 1 and 6 nm, respectively.

RESULTS

When the catalytic activity is measured by the method applied here, the total specific rate vs temperature curves have the form shown in Figs. 1–3. The specific rate is expressed here as number of molecules reacting on 1 m^2 of Ni per second.

The dependence of the rate on the temperature is Arrhenius-like in the region of lowest temperatures and in this region (as we know from other experiments) the changes with temperatures are reversible. However, at higher temperatures the curves are no longer Arrhenius-like and in

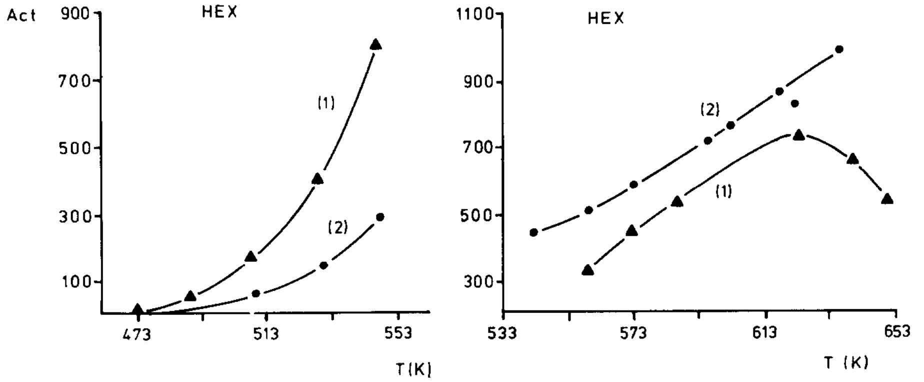

FIG. 1. The specific rate (in 10^{15} molecules/s · m^2 Ni) of the reaction of *n*-hexane (HEX) as a function of the temperature. Low- and high-temperature regions are shown for a "large" and a "small" Ni particle catalyst. (1) $\bar{d}$ = 6 nm and (2) $\bar{d}$ = 1 nm.

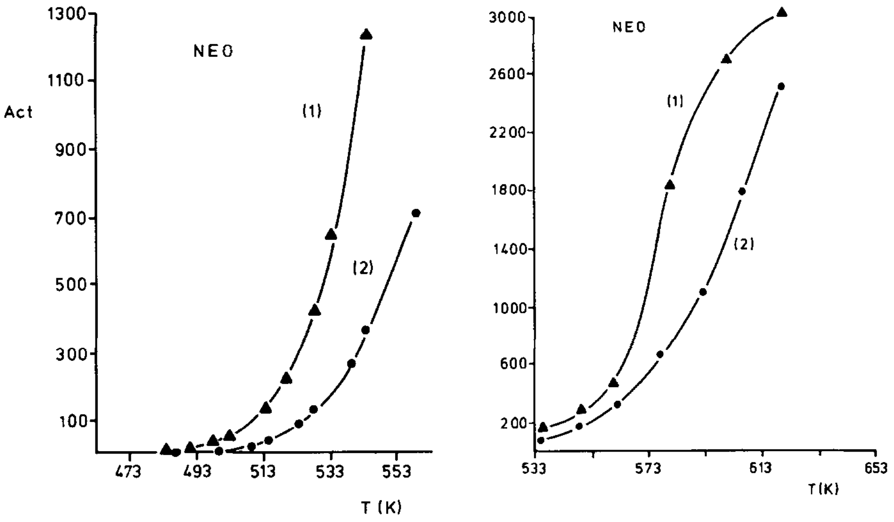

FIG. 2. The specific rate (in 10^{15} molecules/s · m^2 Ni) of the reaction of neohexane (NEO) as a function of the temperature. Low- and high-temperature regions are shown for a "large" and a "small" Ni particle catalyst. (1) $\bar{d}$ = 6 nm and (2) $\bar{d}$ = 1 nm.

some cases (Fig. 1, 6-nm particles) the decrease of the activity by self-poisoning (by the reaction mixture itself) with increasing temperature is more pronounced than the increase (due to the increasing temperature) of the rate of the reaction on the remaining working surface.

Tables 1–3 collect the corresponding data on the selectivities. The differences in the selectivities are not very pronounced, which is a favored aspect for the conclusions which will be made below.

The main reaction with hexane is hydrogenolytic cracking, occurring at all temperatures with a selectivity $S > 90\%$. The main reaction with 2,2-dimethylbutane (neohexane) is again hydrogenolytic cracking ($S > 90\%$). The prevailing mode of adsorption of neohexane upon the reaction is the $\alpha\beta$-diadsorbed species ($\alpha\beta$-binding the carbon C_3 and C_4). By the $\alpha\gamma'$ mode we understand the iso (3C-complexes) group round the C_2-carbon with the C_3-carbon involved; with $\alpha\gamma$, the C_1-carbon and one of the other CH_3

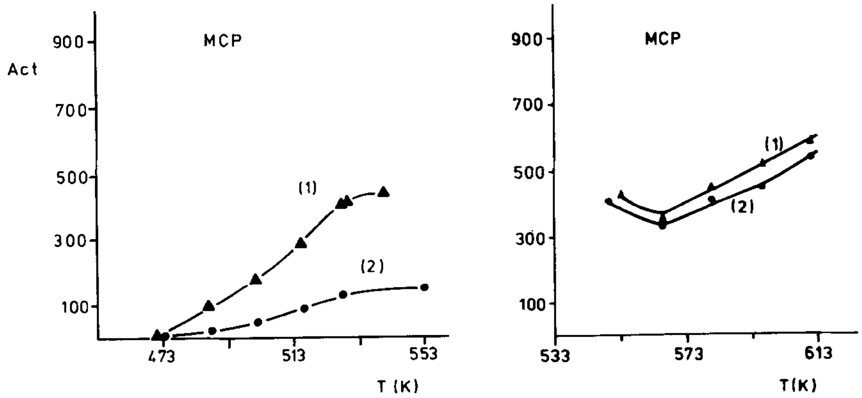

FIG. 3. The specific rate (in 10^{15} molecules/s · m^2 Ni) of the reaction of methylcyclopentane (MCP) as a function of the temperature. Low- and high-temperature regions are shown for a "large" and a "small" Ni particle catalyst. (1) $\bar{d}$ = 6 nm and (2) $\bar{d}$ = 1 nm.

TABLE 1

Reactions of *n*-Hexane on Ni/SiO$_2$ Catalysts

Catalyst	$\bar{d}$ (nm)	T (K)	Conv.	S_{cr} (%)	S_{iso} (%)	S_{cycl} (%)
Ni(2)	1	488	0.6	93	7	0
		530	6.9	96	3	1
		573	4.6	94	4	2
		622	6.5	94	3	3
Ni(1)	6	490	1.0	97	3	0
		529	7.7	98	2	1
		572	1.3	99	1	0
		624	2.1	98	1	1

Note. T, measurement temperature; Conv., conversion; S_{cr}, selectivity for hydrogenolysis; S_{iso}, selectivity for isomerization; S_{cycl}, selectivity for dehydrocyclization.

TABLE 3

Reactions of MCP on Ni/SiO$_2$ Catalysts

Catalyst	$\bar{d}$ (nm)	T (K)	Conv. (%)	S_{cr} (%)	2MP	3MP	Hex	$\frac{\text{Hex}}{\text{2MP}}$	$\frac{\text{2MP}}{\text{3MP}}$	$\frac{\text{Hex}}{\text{3MP}}$
Ni(2)	1	488	0.8	20	52.4	39.2	8.3	0.16	1.34	0.21
		528	4.4	34	58.0	32.6	9.3	0.16	1.78	0.28
		581	4.1	57	67.5	25.2	7.3	0.11	2.67	0.29
Ni(1)	6	487	1.9	30	46.0	44.3	9.6	0.21	1.04	0.21
		529	8.0	64	56.4	33.4	10.2	0.18	1.69	0.30
		582	3.6	81	66.9	25.7	7.4	0.11	2.61	0.29

Note. S_{cr}, selectivity for hydrogenolysis to C_1–C_5; 2MP, percentage of 2-methylpentane of the total ring-opening products; 3MP, percentage of 3-methylpentane of the total ring-opening products; Hex, percentage of *n*-hexane of the total ring-opening products; for other symbols see Table 1.

groups are involved. The main reaction with MCP is again hydrogenolysis. With MCP two types of hydrogenolysis can be distinguished: (a) the ring-opening to 2-methylpentane (2MP), 3-methylpentane (3MP), and *n*-hexane (Hex), and (b) the deeper hydrogenolysis to the C_1–C_5 products. As far as the influence (not a very strong one) of the particle size on the selectivities is concerned, the following is observed. With hexane (Table 1) a small shift is seen from destructive to the nondestructive reactions when going from large to small particles. With MCP (Table 3) a shift can be observed from deeper destructive hydrogenolysis to hydrogenolysis leading to ring-opening products when comparing the large metal particle catalyst with the small metal particle catalyst. Unlike Pt but like Ir (or Rh), diminishing of the particle size does not lead to a substantial increase in the ring-opening into hexane ("nonselective" splitting).

TABLE 2

Reactions of Neohexane on Ni/SiO$_2$ Catalysts

Catalyst	$\bar{d}$ (nm)	T (K)	Conv. (%)	$\alpha\beta_{cr}$ (%)	$\alpha\gamma_{cr}$ (%)	$\alpha\gamma'_{cr}$ (%)	p + b
Ni(2)	1	499	0.6	87.1	5.3	4.8	2.7
		528	7.4	80.1	5.1	9.8	5.0
		578	5.0	69.1	2.8	15.1	13.0
		620	18.8	64.4	0.7	8.8	26.1
Ni(1)	6	498	0.5	83.1	8.0	6.8	2.1
		528	6.9	75.9	4.5	12.8	6.8
		578	1.9	68.7	3.9	12.8	14.7
		621	6.9	79.3	2.0	10.3	8.4

Note. p + b = percentage of propanes and butanes formed (multiple reactions); for other symbols see Table 1 and the text.

When looking into Figs. 1–3 we notice that the ratio of the activities observed with small and large particles depends (a) on the reaction (i.e., hydrocarbon used), and (b) on the temperature region in which the rate is determined. Under mild conditions, where no extended deposition of carbonaceous layers takes place, the small particles are *less* active in hydrogenolysis then the large ones. However, when the catalysts are compared at higher temperatures, under the conditions of a more severe self-poisoning, the difference between the activities of particles of various sizes becomes less pronounced and with hexane the activity of large particles even drops below the level of that of small particles.

DISCUSSION

Data collected on Ni in this paper and the earlier data on Pt (*10, 12*) clearly show that the structure sensitivity of hydrocarbon reactions is partially due to the reactions themselves and partially due to the side reaction of self-poisoning by carbon(aceous) layers. This conclusion is based on the following considerations.

Smaller particles of metals are less active in the formation of the metal–hydrocarbon multiple bonds (*12*) while they are less self-poisoned by carbonaceous layers (*10, 12*) than the large particles. Since the formation of multiple bonds is (if influenced at all) most likely suppressed by the carbonaceous layer, the formation of multiple bonds should be less restricted by self-poisoning on small particles. Nevertheless, these particles are less active in the multiple-bond formation, which leads to the conclusion that the lower activity of small particles in forming the multiple bonds is an intrinsic property of them and this difference is not induced by self-poisoning. However, the total specific activity observed as a function of the particle size offers a different picture: depending on the temperature range or the molecule used, the small particles show either a lower or a higher total specific activity. This points to the role of self-poisoning, which is known to be less extensive on small particles of all metals studied by us up to now, namely Pt (*10, 12*), Ni ((*12*) and this paper), and Ir (*12, 15*). Accepting that the two factors, the intrinsic property and the size-dependent self-poisoning, operate simultaneously, one can understand why the activities can vary antipathically, sympathetically, or as a curve with a maximum when the size of particles is varied. At low temperatures and low hydrocarbon pressures or, more generally, under conditions where self-poisoning is limited, the role of the intrinsic properties (surface structure, multiple-bond formation) prevails. Under conditions of more severe poisoning, the carbon(aceous) layer can dramatically change the activity and selectivity of the hydrocarbon reactions. The ultimate form of the activity curves thus depends on how severe the self-poisoning is in the given temperature range. Our data also imply that self-poisoning is more pronounced with molecules which can produce the graphitizing polyaromatic structures most easily. From our data, hexane and MCP are clearly more active in that respect than neohexane.

Data of this paper confirm the trend observed earlier with Pt (*10, 12*), Ir (*12, 15*), and Ni (*12*), namely that small particles are less self-poisoned than the larger ones. Furthermore, by a comparison of this paper with other references (*10, 12, 15*) one learns that Pt is always more affected by self-poisoning than Ni or Ir. For this reason it is not easy to create with large particles of Pt a situation such that the activity would be mainly determined by the properties of the clean Pt surface.

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