JOURNAL OF CATALYSIS 75, 233–242 (1982)

Benzene Hydrogenation over Nickel Catalysts at Low and High Temperatures: Structure-Sensitivity and Copper Alloying Effects

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Received February 9, 1981

The rate of benzene hydrogenation has been measured over various silica-supported Ni, unsupported Ni, and Ni–Cu/SiO_2 catalysts from 300 to 600 K, and has been referred to unit area of metal. It is shown that benzene hydrogenation at low temperature is to be considered as a structure-sensitive reaction. As particle size increases from 2.5 to 6 nm, the activity increases. Reduction of catalysts at high temperature results in a marked decrease of activity. This behavior is very similar to that observed for ethane or propane hydrogenolysis. Copper addition slowly decreases the activity. The active site is an ensemble composed of 3 ∓ 2 adjacent nickel atoms. The influence of particle size and of copper alloying on the rates of benzene conversion into cyclohexane or methane at high temperatures is quite different from that observed at room temperature. Finally, a correlation between alloying effects and particle size-sensitivity for particles smaller than 6 nm is presented.

INTRODUCTION

Although benzene hydrogenation into cyclohexane has received much attention (*1*), no consensus of opinion exists in the literature about the structure-sensitivity of the reaction. The rate of reaction per unit metallic area over nickel catalysts is generally considered as being little influenced by surface structure (*2, 3*). There are, however, some papers dealing with benzene hydrogenation over nickel catalysts which report a more or less marked structure-sensitivity. On the one hand, Coenen *et al.* (*4*) found small nickel particles (size smaller than 1.2 nm) to be less active than large particles by a factor of 5. On the other hand, Selwood *et al.* (*5*) reported a drop in activity which greatly exceeds the fall of specific surface area when nickel catalysts are thermally sintered. This shows that the options on structure-sensitivity of benzene hydrogenation are far from being completely unequivocal.

It has been suggested that the structure-sensitivity of catalytic reactions could be related to alloying effects and that both phenomena could be ascribed to the number of metallic atoms involved in the active site (*6*). In this respect, of special interest is the influence of alloying nickel with copper on the rate of benzene hydrogenation. Some data are already available in the literature (*7, 8*). The activity of nickel toward benzene hydrogenation at low temperatures (below 373 K) decreases slowly as copper concentration increases (*7, 8*), while it increases at high temperatures (*8*). In both cases, however, the reaction was carried out on films (*7*) or powders (*8*) which are known to exhibit a strong surface enrichment in copper, thus making difficult a quantitative study of the alloying effect.

This situation has prompted us to reexamine the problem of benzene hydrogenation on nickel, and this paper presents new data on the structure-sensitivity of the reaction and on the influence of copper addition on the activity of well-defined catalysts.

EXPERIMENTAL

The morphological characteristics of the catalysts, which were partially described in previous papers (*9, 11*), are summarized in Table 1. Unsupported nickel powder samples were obtained by decomposition of

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TABLE 1

Sample Morphology of Nickel Catalysts

Number	Precursor	Ni loading (% wt)	Reducing temperature (°K)	Degree of reduction	D_s (nm)	S (m^2/g Ni)
1	$Ni(OH)_2$	62	520		80[a]	12
2	$Ni(OH)_2$	62	570	1.01	67[a]	10
3	$Ni(OH)_2$	62	670		96[a]	7
4	$Ni(OH)_2$	62	770		167[a]	4
5	$Ni(OH)_2/SiO_2$ (hexamine)	4.5	800	0.95	2.5	
6	$Ni(OH)_2/SiO_2$ (hexamine)	4.5	920	1	3.2	
7	$Ni(OH)_2/SiO_2$ (hexamine)	11	970	1	5.7	
8	$Ni(OH)_2/SiO_2$ (hexamine)	23	920	0.98	6.3	
9	$Ni(OH)_2/SiO_2$ (hexamine)	23	1000	1	7.5	
10	$Ni(OH)_2/SiO_2$ (hexamine)	23	1200	1	14	
11	Ni^{2+}/SiO_2 (ex nitrate)	6	770	1	12	

[a] As deduced from the BET surface area assuming spheres.

nickel hydroxide (prepared by the ammonia method) in flowing helium for 1 hr, followed by reduction for 2 hr in flowing hydrogen (gas flow, at a rate of 4 liters/hr), at temperatures listed in the table. Surface areas were calculated from nitrogen adsorption data at liquid nitrogen temperature. The Ni/SiO_2 catalysts were prepared by reduction for 15 hr of precursors obtained by reacting the support (SiO_2, Aerosil Degussa, 200 m^2/g) with a solution of nickel nitrate hexamine (samples 5 to 10) or with a solution of nickel nitrate (sample 11). Reduction temperatures and metallic loadings were varied to cover a wide range of particle sizes. Prior to reduction, samples 5 and 11 were treated *in vacuo* for 1 hr at the reduction temperature. Magnetic measurements showed that reduction of the samples was almost complete and also allowed us to calculate the surface average diameters, D_s, listed in Table 1 (*9, 11*). The volumes of adsorbed hydrogen at saturation were found to be in agreement with the BET surface area of sample 2, and with diameters of the other samples calculated from magnetic data. The $Ni-Cu/SiO_2$ catalysts were prepared by reduction at 920 K in flowing hydrogen of precursors obtained by adding silica to solutions of nickel and copper nitrate hexamine (*12*). Adsorption and magnetic studies have shown that a homogeneous alloy was formed and that the surface composition of the metallic particles (diameter, 6 nm) was very similar to the bulk composition (*12*), in contrast with the surface enrichment in copper generally observed on Ni–Cu films and unsupported powders.

Kinetic experiments were carried out in a flow system with a fixed-bed reactor at atmospheric pressure. The microreactor consisted of a quartz tube with a porous disk and samples were held by quartz wool. The total flow at room temperature was 120 ml/min. Hydrogen and helium (used as a diluent) had an initial purity better than 99.99%, and were further purified by a Deoxo catalyst followed by a zeolite trap. Partial pressures of benzene were varied by bubbling a flow of helium in liquid benzene. Pure thiophene-free benzene from Merck was further purified by adding metallic sodium and by a clean Pt/SiO_2 catalyst to remove minute amounts of sulfur compounds (no important difference of behavior however, was detected between initial and purified benzene). Gas analyses were performed by gas chromatography with a flame-ionization detector. Conversion was always less than 2% except for aging experiments. The rates reported here refer to the rate of conversion of the parent hydrocarbon (benzene).

RESULTS

Benzene Hydrogenation at Low Temperatures

The variations of catalytic activity with time were first examined. As can be seen in Fig. 1, the phenomenon of catalyst aging is observed for samples prepared below 520 and 770 K for unsupported and supported catalysts, respectively. The observed decrease of activity with time obeys a simple logarithmic law which allows extrapolation to initial time. The variations of the initial activity per unit area with metallic particle diameters are shown in Fig. 2. Experimental points have been arranged more or less arbitrarily into two groups (curve A and B in Fig. 2) corresponding to data obtained with samples reduced at temperatures higher and lower than 770 K, respectively. Results obtained by Coenen *et al.* (*13*) and by Nikolajenko *et al.* (*2*) can be compared to ours in Fig. 3. Figure 4 shows the activities of samples 5–10 toward various reactions, namely, benzene hydrogenation, and hydrogenolysis of ethane and propane (*14*, *15*). From these data, it can be seen that the various activities vary more or less in a parallel way, particularly for particle diameters larger than 6 nm. Below this critical diameter, the activities decrease with nickel particle size and the corresponding slopes vary according to the reaction considered. Variations of the rate of benzene hydrogenation at low temperature with the copper concentration x are shown in Fig. 5, from which it can be deduced that the variations of the activity A_x with x can be approximately represented by

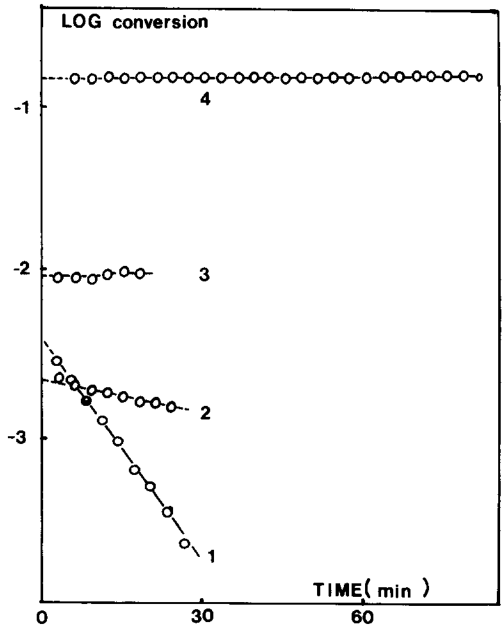

FIG. 1. Catalyst aging: Log conversion as a function of time for samples 1, 11, 3, and 8 (curves 1–4, respectively).

$$A_x = A_0(1 - x)^N$$

with $N = 3 \mp 2$.

Apparent activation energies, E_a, and partial reaction orders with respect to hydrogen and benzene partial pressure, n_H and n_B, of the samples were also measured. The results thus obtained can be compared in Table 2. To a first approximation, they can be considered as constant, showing that the mechanism does not change with particle size and alloying.

Reaction of Benzene with Hydrogen at High Temperatures

The reaction was also studied over a wide range of temperature. A typical Arrhenius plot showing the influence of temperature on conversion is represented in Fig. 6. As

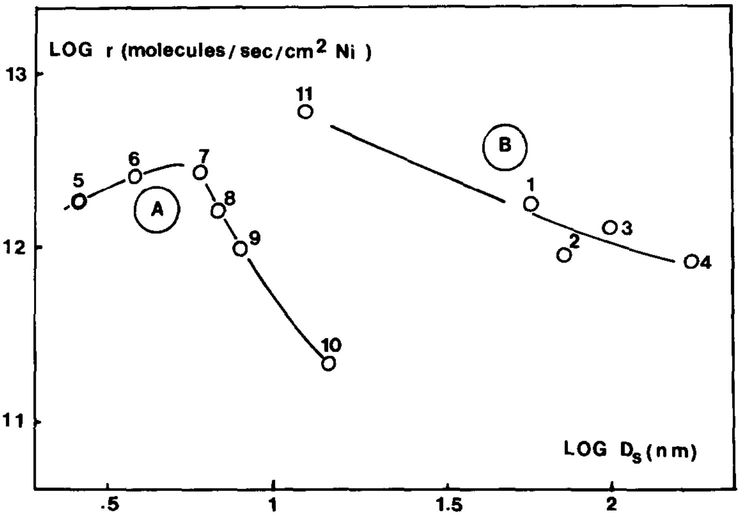

FIG. 2. Log rate hydrogenation of benzene into cyclohexane at T = 303 K, P_H = 600 Torr, P_B = 4 Torr as a function of the average particle size D_s. Curves A and B correspond to samples reduced at temperatures higher and lower than 770 K, respectively.

previously observed (*16–18*), the curve goes through a maximum at 420 K and in the high temperature region the apparent activation energy is −20 kcal/mole; the orders with respect to partial pressures are n_H = 3 and n_B = 0.4, in accord with the data of van Meerten and Coenen (*16*). Beside cyclohexane, formation of methane is also observed at high temperatures, corresponding probably to benzene hydrogenolysis according to:

$$C_6H_6 + 9H_2 \rightarrow 6CH_4$$

The apparent kinetic parameters of this reaction are E_a = 28 kcal/mole, n_H = 0.3, and n_B = −0.4 at 520 K. Small amounts of

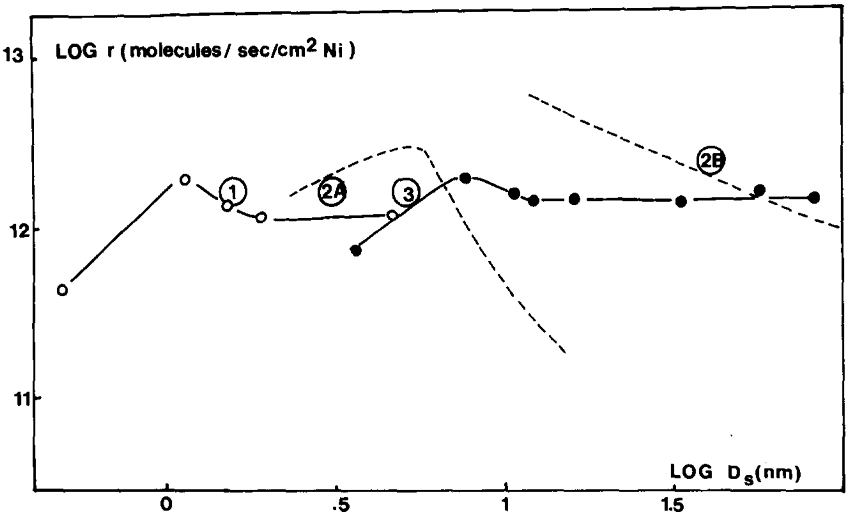

FIG. 3. Structure-sensitivity of benzene hydrogenation: comparison of our data (curves 2A and 2B) with those of Coenen *et al.* (*4*) and Nikolajenko *et al.* (*2*), curves 1 and 3, respectively.

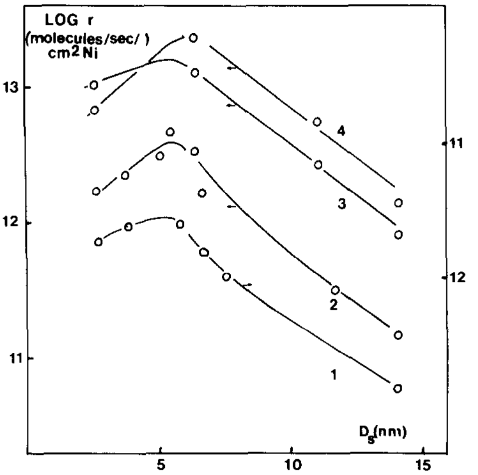

FIG. 4. Log rate as a function of the average nickel particle size: Curve 1: Benzene hydrogenation at T = 303 K, P_H = 600 Torr, P_B = 4 Torr. Curve 2, 3, and 4: hydrogenolysis of ethane, hydrogenolysis of propane into methane + ethane, and hydrogenolysis of propane into 3 molecules of methane, respectively, at T = 507 K, P_H = 160 Torr, and $P_{\text{hydrocarbon}}$ = 25 Torr.

cyclohexene are also detected, as illustrated in Fig. 6, particularly on sample 10. The apparent kinetic parameters of cyclohexene formation on sample 10 at 500 K are $E_a = -19$ kcal/mole, $n_H = 1.7$, and $n_B = 1.1$.

TABLE 2

Apparent Kinetic Parameters of Benzene Hydrogenation[a]

Samples	Number	Cu content	E_a (kcal/mole)	n_H	n_B
Unsupported Ni	1		13	0.45	—
	2		11.4	0.54	0.06
	3		12	—	—
Ni/SiO$_2$	5		10.4	0.55	0.14
	8		11.6	0.51	0.12
	10		11.7	0.57	0.05
	11		13	0.45	—
Ni-Cu/SiO$_2$	12	14	12.7	—	—
	13	36	12.1	0.48	0.08
Average values			11.9	0.5	0.09

[a] Measured at room temperature, P_H = 300 Torr, P_B = 40 Torr.

In Fig. 6 is also shown the thermodynamic equilibrium curve of reaction of benzene hydrogenation into cyclohexane, calculated on the basis of data given in Ref. (*16*). It shows that the approach to the thermodynamic equilibrium conversion does not seem to limit the reaction rate, as already concluded by van Meerten and Coenen (*16*). This has been experimentally verified by varying the gas flow. The percentage of benzene converted into cyclohexane is proportional to the contact time, showing that thermodynamic equilibrium is not attained.

The variations with particle size of the rate of benzene conversion into cyclohex-

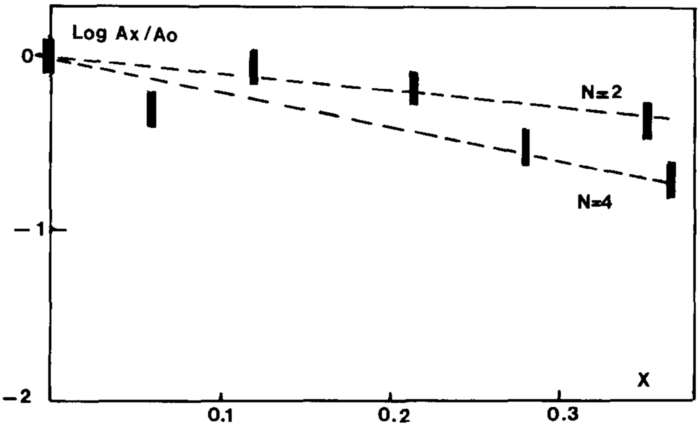

FIG. 5. Log activity in benzene hydrogenation measured at T = 303 K, P_B = 30 Torr, P_H = 730 Torr, as a function of x, the copper concentration of the alloy. The dashed curves are calculated assuming that the rate varies as $(1 - x)^N$.

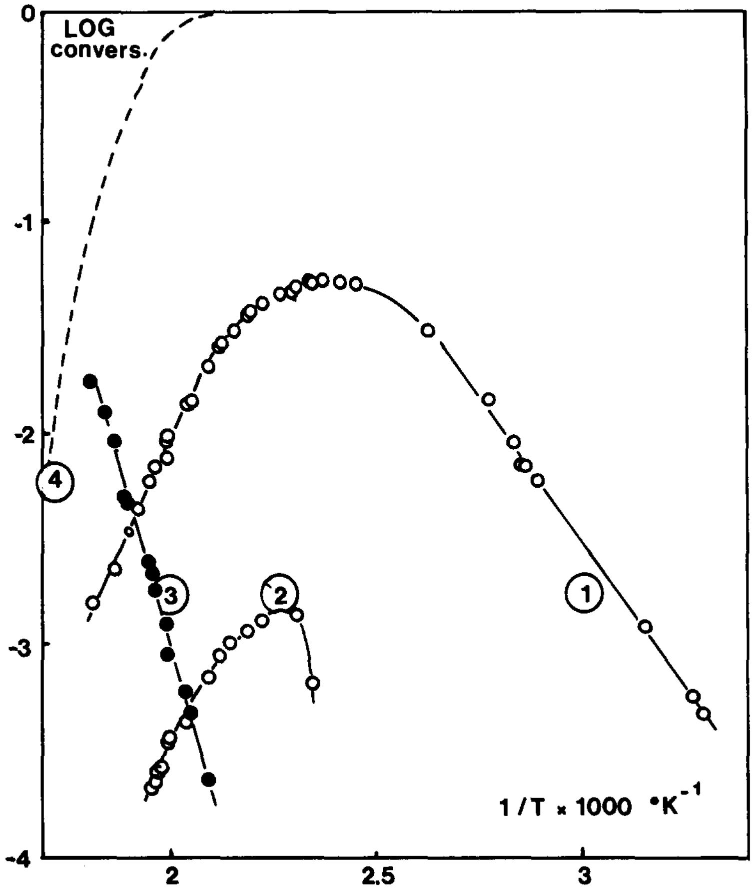

FIG. 6. Log conversion as a function of the reciprocal temperature measured at P_H = 300 Torr, P_B = 40 Torr for sample 10. Curve 1, benzene hydrogenation into cyclohexene. Curve 2, benzene hydrogenation into cyclohexene. Curve 3, benzene hydrogenolysis into methane. Curve 4, thermodynamic equilibrium benzene–hydrogen–cyclohexane.

ane and methane at high temperatures are shown in Fig. 7. The curve corresponding to the former reaction is very different from that observed for benzene hydrogenation at low temperatures (Fig. 2). As particle size increases from 2.5 to 6 nm the high temperature rate decreases slowly (curve 1, Fig. 7). Beyond 6 nm, the activity remains constant. The rate of benzene hydrogenolysis into methane (curve 2, Fig. 7) first increases as particle size increases, then remains more or less constant. It can be noticed that the structure-sensitivity of benzene hydrogenolysis is different from that of ethane and propane hydrogenolysis and is very similar to that of CO hydrogenation (*19*).

The effects of alloying nickel with copper are shown in Fig. 8. As already reported by Van Barneveld and Ponec (*8*), copper addition depresses the rate of benzene hydrogenolysis, and increases the rate of benzene hydrogenation at high temperatures (*8*). It can be noticed that alloying produces opposite effects on benzene hydrogenation at low and high temperatures.

DISCUSSION

Structure-Sensitivity

Results reported in Fig. 2 show unambiguously that benzene hydrogenation into cyclohexane at low temperatures is a struc-

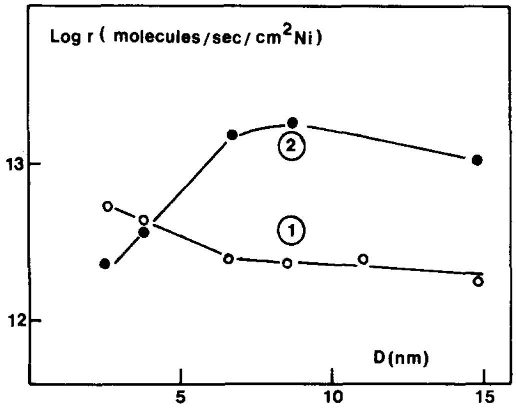

FIG. 7. Log rate conversion of benzene into cyclohexane (curve 1) and methane (curve 2) measured at $T = 572$ K, $P_H = 600$ Torr, $P_B = 40$ Torr as a function of nickel particle size D_s.

ture-sensitive reaction. If we compare our results with those of Coenen *et al.* (*4*) and of Nikolajenko *et al.* (*2*), the same general trend is noticed (Fig. 3). As particle size increases the activity first increases, reaches a maximum, then remains constant or decreases. The diameter corresponding to the maximum is 6 nm in our case. The value is between those observed by Nikolajenko *et al.* (7 nm) and Coenen *et al.* (1.2 nm). It is hard to decide whether these discrepancies are significant—differences in particle size distributions, degrees of reduction, or in experimental conditions may be invoked to account for observed differences—or are to be attributed to artifacts resulting from the different techniques and assumptions used to estimate nickel particle sizes. These points probably require further investigations.

Our results show also that activity does not depend unequivocally on particle size but rather on conditions prevailing as particles are prepared, particularly for large particle sizes. When samples are prepared at moderate temperatures, say below 750 K, variation of the activity with diameter is not very pronounced (curve B in Fig. 2). This observation is in agreement with data in papers reporting on nickel catalysts prepared below 750 K (*2, 3, 4, 20, 21*). In contrast, when large diameters are obtained by reduction at high temperatures, there is a sharp decrease in activity as diameters increase (curve A in Fig. 2). This finding confirms earlier results obtained by Selwood *et al.* (*5*) and reconciles the apparently conflicting results of the literature.

What is the origin of the low activity toward benzene hydrogenation at room temperature and ethane or propane hydrogenolysis exhibited by Ni/SiO_2 reduced at high temperatures? This point has been already partly discussed in previous work (*11*). Let us recall that the hypothesis of the formation of bulk Ni–Si alloys with a concentration of silicon larger than 1% is to be ruled out and that the gas accessibility is not dramatically affected. In another paper (*22*), we have suggested that Ni/SiO_2 reduced at high temperatures could be in a state similar to that observed on Pt/TiO_2 reduced at ca. 800 K (the so-called SMSI state), since O_2 treatments followed by a low-temperature reduction are capable of restoring the activity of the Ni/SiO_2 catalyst. It can be noticed that the reduction of Ni/SiO_2 at

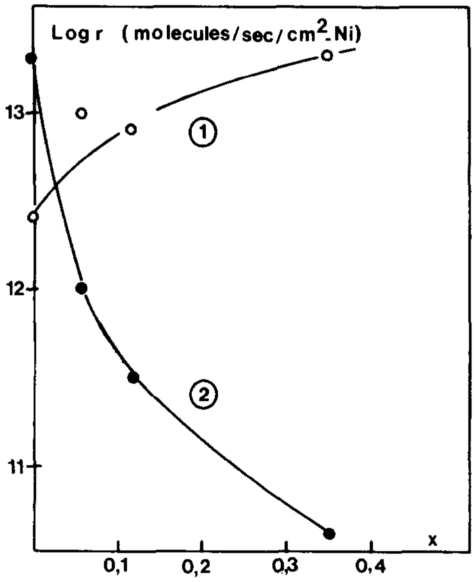

FIG. 8. Log rate conversion of benzene into cyclohexane (curve 1) and methane (curve 2) measured at $T = 572$ K, $P_H = 600$ Torr, $P_B = 40$ Torr as a function of the copper concentration x of the alloy.

high temperatures does not seem to have any influence on benzene hydrogenolysis into methane, and benzene hydrogenation at high temperatures (Fig. 7). This means that the occurrence of the SMSI (strong metal-support interaction) state affects some catalytic reactions but does not influence others. Further work is desirable to elucidate this intriguing behavior.

Results reported in this study show clearly that the structure-sensitivity of a given reaction may depend on conditions prevailing as the rate is measured. When measured at high temperatures, benzene hydrogenation into cyclohexane appears to be a reaction which is less structure-sensitive than at low temperatures. The small structure-sensitivity of benzene hydrogenation at high temperatures reported here agrees well with the conclusions of Dalmai-Imelik and Massardier (*23*) who have reported no significant differences of activity toward benzene hydrogenation on (111), (100), and (110) planes of nickel, when the reaction is performed at 443 K under P_H = 50 Torr, i.e., in high-temperature conditions (*16*).

Alloying Effects

The variations of the rate of benzene hydrogenation at low temperature on Ni–Cu with x, the copper concentration, can be represented by a law of the type $(1 - x)^N$ with $N = 3 \mp 2$. It can be recalled that $(1 - x)^N$ is the probability of finding an ensemble of N adjacent Ni atoms assuming the random distribution of metallic atoms (*24*). This means that the active site of benzene hydrogenation at low temperature is an ensemble of $N = 3 \mp 2$ adjacent nickel atoms. The number of nickel atoms of the active site may be compared to that deduced from volumetric measurements by Candy *et al.* (*25*). The consumption of hydrogen in contact with a nickel surface precovered with benzene shows that the number of nickel atoms bonded to one molecule of benzene which is hydrogenated is n = 1.6 (average value of five determinations). We think, however, that this value is underestimated, since these authors have assumed that saturation in hydrogen coverage is obtained at room temperature under 10 Torr. We know, now, that this is to be considered as a first approximation, and that in these conditions, θ_H lies between 0.6 and 0.8 (*10*), 0.7 being a plausible average value. If one corrects the n value obtained by Candy *et al.*, one obtains $n = 1.6/0.7 = 2.3$. We can consider that this value is in agreement with N as deduced from Ni–Cu experiments.

When the reaction is performed at high temperatures, the effect of copper addition on benzene hydrogenation is reversed (Fig. 8). Our data confirm those of Van Barneveld and Ponec (*8*). Let us recall that these authors have attributed this positive alloy effect to some inhibition of side-reactions, like coke formation and hydrogenolysis, which would result in an increase of the activity toward benzene hydrogenation. Our results confirm that copper addition decreases sharply the rate of benzene hydrogenolysis into methane, in accordance with this hypothesis (*8*).

Finally, it is interesting to notice that the hypothesis of Van Barneveld and Ponec (*8*) accounts for the results of Fig. 7. When nickel particle sizes increase from 2.5 to 15 nm, the activity toward benzene hydrogenation at high temperatures first decreases then remains constant, when the activity toward benzene hydrogenolysis, one of the side-reactions invoked by these authors, first increases then remains constant.

Reaction between Alloying Effect and Structure-Sensitivity

Let us define the particle size-sensitivity α and the alloying-sensitivity β as,

$$\alpha = \frac{dA}{dD}, \qquad \beta = \frac{dA}{dx}$$

where A is the activity per unit area, D the particle diameter, and x the copper concentration. In Table 3 are displayed the signs of α and β for the reactions studied here and

TABLE 3

Alloying Effects and Particle Size Sensitivity

Reactions	Alloying effects[a]	Particle size sensitivity[a]	
	$\alpha = \frac{dA}{dx}$	$D < 6$ nm $\beta = \frac{dA}{dD}$	$D > 6$ nm $\beta = \frac{dA}{dD}$
$C_6H_6 + 3H_2 = C_6H_{12}$ low temperature	−	+	−
$C_6H_6 + 3H_2 = C_6H_{12}$ high temperature	+	−	0
$C_6H_6 + 9H_2 = 6CH_4$	−	+	0
$CO + 3H_2 = CH_4 + H_2O$	−	+	0

[a] +, 0, and − mean that α or β are positive, nearly equal to zero, or negative, respectively.

for methanation (19) on samples 5–11. There is no correlation between alloying and particle size effects for particles larger than 6 nm. Below this critical size, however, a clear parallelism is observed: copper addition leads qualitatively to the same effect as decreasing particle size. This correlation results probably from the fact that the active site involves a certain number of adjacent metallic atoms varying from one reaction to another (15, 19, 24), accounting for the observed decrease of activity and change of selectivity with copper addition. As particle size decreases, the number of available metallic surface atoms per particle decreases, then the activity is expected to vanish below some critical diameter. However satisfying from the qualitative viewpoint this explanation may be, it cannot be overlooked that it raises some difficulties from the quantitative viewpoint since critical diameters thus calculated are very small (ca. 0.5 nm for a reaction involving 12 adjacent nickel atoms). Moreover, it is not easy to understand why the particle size effects of benzene hydrogenation at low temperatures and of ethane hydrogenolysis which require ca. 3 and 12 or more adjacent nickel atoms, respectively, are of the same order of magnitude. As a matter of fact, it will be shown in another paper (26) that the size sensitivity, α, of a reaction which requires an ensemble of N adjacent metallic atoms is a complex function of N, D, diameter of particles, and also of θ, the degree of coverage with adsorbed species. This function is capable of accounting for the observed particle size sensitivities in a more quantitative way.

CONCLUSION

From this work it can be therefore concluded that: (i) benzene hydrogenation at room temperature exhibits a structure-sensitivity similar to that of ethane or propane hydrogenolysis, particularly for particle sizes larger than 6 nm; (ii) the influence of particle size and of copper alloying on the rate of benzene reaction with hydrogen at low temperature is quite different from that observed when the reaction is performed at high temperatures; (iii) a correlation does exist between alloying effects and particle size sensitivity for particles smaller than 6 nm.

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