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Influence of Potassium Salt Addition on the Catalytic Properties of Silica-Supported Nickel

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The influence of potassium nitrate addition to Ni/SiO_2 catalysts on the kinetic parameters of various reactions (ethane and propane hydrogenolysis, D_2–CH_4 exchange, benzene and CO hydrogenations) has been investigated. The changes in the catalytic pattern and in kinetic parameters are similar to those reported for other host metals such as Fe and Ru. On potassium addition, the true activation energies (deduced from the Temkin relation) of hydrogenolysis, exchange and CO hydrogenation over Ni increase; the Ni–H bond strength decreases, while the nickel–carbon monoxide bond is reinforced. Potassium cannot be considered as a poison, blocking selectively specific sites of the metallic surface, but rather as an electronic modifier, giving rise to an electron enrichment of the metallic phase, strengthening or weakening the Ni–adsorbate bonds. This hypothesis is also in agreement with the higher selectivity of Ni–K/SiO_2 catalysts for ethylenics in the CO + H_2 reaction and cyclohexene in benzene hydrogenation.

INTRODUCTION

The addition of small amounts of alkali has long been known to modify the activity and the selectivity of heterogeneous catalysts, or to improve their lifetime (*1–3*). In spite of its economic importance, however, little is known about the mechanism of the influence of alkali addition, and on the subsequent changes of the kinetic parameters of catalytic reactions.

Alkali doping is generally interpreted in terms of electronic effects (*4, 5*): the additive is considered as a base, transferring electrons to the metallic phase, thus increasing the bond strength of electron-acceptor molecules such as CO, N_2 and decreasing that of electron-donor elements such as hydrogen. If this interpretation is correct, it can be inferred that the kinetic parameters of the reactions which take place on the metallic phase should be modified. Conversely, if no change in kinetic parameters is observed, the modification of the catalytic pattern is better interpreted in terms of variations in the number of unperturbed active sites.

In the literature the data concerning the influence of alkali doping on kinetic parameters are sparse. Cimino *et al.* (*6*) reported an increase in the order in hydrogen and a decrease in the apparent activation energy of hydrogenolysis over potassium–iron powders, without speculating on the possible link between this observation and the change in electronic properties of the metal phase.

This situation has led us to reexamine this problem, and in this paper we report on the influence of potassium addition on the apparent and true kinetic parameters of hydrocarbon hydrogenolysis, D_2–hydrocarbon exchange and the hydrogenations of benzene and CO over Ni to examine whether the changes in selectivity and kinetic parameters can be rationalized by the simple principle of electron transfer. It was shown previously that KNO_3 addition to a $Ni(OH)_2/SiO_2$ precursor followed by hydrogen reduction results in a modified catalyst which has the following features.

(i) The catalytic pattern is changed in a way similar to that observed on other metals (*7*).

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(ii) The electron density of the metallic phase as deduced from XPS and infrared spectroscopy of adsorbed carbon monoxide is increased (*8*).

(iii) Potassium is mainly present as K$^+$ on the solid: one part of the potassium is fixed on the silica support and another on the Ni surface where it forms patches or islands, a certain fraction of the Ni surface remaining free (*8*) while the remainder covered with potassium is inaccessible for adsorption of large molecules.

In a forthcoming paper of this series, we will address the question of the long-range action of potassium (*9*).

METHODS

The preparation of the catalysts has already been described elsewhere (*7*, *8*). The Ni(OH)$_2$/SiO$_2$ precursor (24.8% Ni by weight) was prepared by reacting silica (Degussa, 200 m^2/g) with a nickel nitrate hexammine solution. The K-containing solids were prepared by suspension of the precursor in KNO$_3$ solutions. The solids contain ca. 2.5 wt% K (two batches were used, containing 2.35 and 2.7 wt%. No difference was detected between these two catalysts). In the present paper the catalysts are designated by Ni–K but this does not imply necessarily the presence of "metallic" potassium. Solids were reduced *in situ* under a hydrogen flow (5 liters h^{-1}) by linearly raising the temperature from 298 to 923 K at 2 or 20 K min^{-1}. The reduction was continued overnight and then the solids were cooled under H$_2$ to the temperature of the reaction. For these conditions the samples were shown to be completely reduced. The average surface diameters of Ni particles in samples reduced at a low heating rate (2 K min^{-1}) calculated from magnetism and electron microscopy were around 4.0 and 5.7 nm for Ni/SiO$_2$ and Ni–K/SiO$_2$ catalysts, respectively, and the surface stoichiometries for hydrogen chemisorption were H/Ni$_S$ = 1.1 and 0.8, respectively. Slightly larger diameters were obtained after reduction at 20 K min^{-1} (4.5 and 6.4 nm for Ni and Ni–K catalysts, respectively). Kinetic experiments were carried out in flow systems with fixed-bed reactors at atmospheric pressure. Helium was used as a diluent. Reactant and product gases were automatically analyzed by gas chromatography and by mass spectrometry for exchange reactions. Conversion was always kept low to prevent diffusion and thermal effects. The intrinsic activities were calculated on the basis of the surface area of nickel estimated from magnetic measurements (*10*).

RESULTS

Ethane Hydrogenolysis

As reported elsewhere (*7*), potassium addition results in a decrease of the specific rate of ethane hydrogenolysis (expressed per Ni unit area as deduced from magnetic method) of one or two orders of magnitude (Table 1).

At P_{H_2} = 340 Torr (1 Torr = 133.3 N m^{-2}) the order in ethane measured at 546 K over Ni–K/SiO$_2$ catalysts reduced at 923 K (20 K min^{-1}) is 1.0 below P_{eth} = 10 Torr and 1.5 above it. Similar results are obtained for other experimental conditions (533 and 613 K, 150 and 340 Torr of hydrogen) and for Ni–K/SiO$_2$ reduced with a heating rate of 2 K min^{-1}. This behavior is very similar to that observed with Ni/SiO$_2$ catalysts (*11*). The order 1.5 above 10 Torr has already been explained by some bimolecular pro-

TABLE 1

Ethane Hydrogenolysis: Influence of the Potassium on Rate and Apparent Kinetic Parameters

Solid	Heating rate during the reduction (K min^{-1})	$r \times 10^{-10}$[a] (molecules s^{-1} (cm^2 Ni)$^{-1}$)	E_a[b] (kJ mol^{-1})	n_{H_2}[c]	$n_{C_2H_6}$[d]
Ni/SiO$_2$	20	104	170	−1.9	+1
	2	50	167	−1.8	+1
Ni–K/SiO$_2$	20	2.3	109	−1.2	+1
	2	3.8	125	−1.5	+1

[a] r at 533 K, 338 Torr H$_2$, 6 Torr C$_2$H$_6$.
[b] E_a: 338 Torr H$_2$, T between 503 and 573 K, 6 Torr C$_2$H$_6$.
[c] n_{H_2}: 546 K, P_{H_2} between 230 and 380 Torr, 6 Torr C$_2$H$_6$.
[d] $n_{C_2H_6}$: 546 K, $P_{C_2H_6}$ between 2 and 10 Torr, 338 Torr H$_2$.

cess occurring between gaseous ethane and adsorbed hydrocarbon species (*11*).

The partial order with respect to H_2 (n_{H_2}) over Ni–K catalysts is less negative than over pure Ni solids, and the apparent activation energy E_a is smaller (Table 1). This shows clearly that potassium addition to Ni catalysts results in the same trend as that observed by Cimino *et al.* (*6*) on iron-based catalysts.

E_a and n_{H_2} are ethane-pressure independent in the studied range (2–30 Torr), but in what follows the study has been restricted to the region in which the order with respect to ethane is equal to unity, the hydrocarbon pressure being maintained constant at 6 Torr. The kinetic study has been performed over a rather large range of temperature and pressure (500–620 K, $P_{H_2} = 148$–338 Torr) for both reduction processes (20 or 2 K min^{-1}). As already observed for Ni/SiO_2, the order with respect to hydrogen increases when the hydrogen pressure decreases and when the temperature increases. There are parallel variations of the apparent activation energy with the temperature and the hydrogen pressure for both catalysts.

The variations of n_{H_2} and E_a probably reflect the variations of hydrogen coverage with T and P. As pointed out by Temkin (*12*), differences under experimental conditions can give rise to differences in activation energies, viz. "the apparent activation energy, E_a, of a reaction which takes place in an adsorbed layer differs generally speaking from the true activation energy E_0 on account of the change in surface concentration with a change of temperature" (or pressure). Temkin has demonstrated that the apparent and true activation energies are related by the equation

$$E_a = E_0 - \Sigma n_i Q_i,$$

where n_i is the order in the reactant i, and Q_i the isosteric heat of adsorption of the reactant i under the conditions of the reaction.

Another demonstration of this equation, and applications to ethane hydrogenolysis and CO hydrogenation, can be found elsewhere (*11, 13*).

For the case of ethane hydrogenolysis, the surface can be considered as covered mainly with hydrogen, and the rate equation can be written (*11*)

$$r = k \exp(-E_0/RT) P_{eth} f(\theta_H),$$

where P_{eth} is the ethane pressure and θ_H the hydrogen coverage.

The Temkin equation then becomes

$$E_a = E_0 - n_{H_2} Q_H.$$

As a first approximation Q_H is more or less constant in the reaction conditions, so that one should observe a straight line by plotting E_a against n_{H_2}. This is indeed observed in Fig. 1, from which one can deduce E_0 by extrapolation to $n_{H_2} = 0$ and Q_H from the slope. The true activation energy increases from 58 ± 4 to 75 ± 4 kJ mol^{-1} upon potassium addition while the isosteric heat of hydrogen adsorption decreases from 62 ± 4 to 37 ± 4 kJ mol^{-1} under the conditions of the reaction. E_0 and Q_H are independent of the procedure used for the reduction.

For the Ni/SiO_2 solid without potassium the rate decreases by around a factor 2 (Table 1) with the heating rate of the reduction going from 20 to 2 K min^{-1}. This is probably

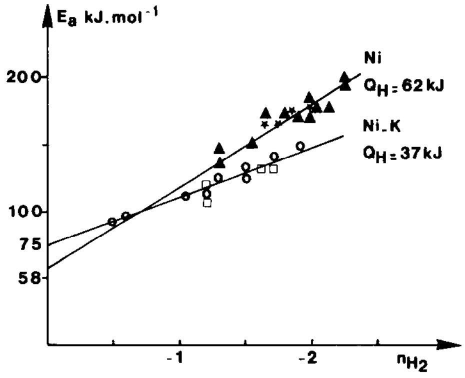

FIG. 1. Apparent activation energy (E_a) vs partial order with respect to H_2 (n_{H_2}) for ethane hydrogenolysis. Range 500–615 K, 145–338 Torr H_2, 6 Torr C_2H_6. Ni: (★) 20 K min^{-1}, (▲) 2 K min^{-1}. Ni–K: (□) 20 K min^{-1}, (○) 2 K min^{-1}.

related to the decrease in the Ni particle diameter, the hydrogenolysis being a size-sensitive reaction (*11, 14*). A low heating rate favors low particle sizes and narrow distribution widths.

Propane Hydrogenolysis

In propane hydrogenolysis two possible reactions are to be considered:

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6 \qquad (1)$$

$$C_3H_8 + 2H_2 \rightarrow 3\ CH_4 \qquad (2)$$

The specific rates of propane consumption (per unit area of metallic surface calculated from magnetic methods) are referred to as r_n for reaction (n). The specific activities and the selectivities $S = r_1/r_2$ are reported in Table 2. For a same reaction temperature (502 K) rates are considerably lowered in presence of potassium and the selectivity to ethane is clearly enhanced. This increase in selectivity holds even at 546 K, where the conversion over Ni–K is comparable to that observed at 502 K over Ni/SiO$_2$.

As for the ethane hydrogenolysis the order with respect to propane over Ni/SiO$_2$ and Ni–K/SiO$_2$ is equal to unity for both reactions (1) and (2) below 10 Torr. It is also independent of the hydrogen pressure and of the temperature (502 K, 250 Torr H$_2$; 546 K, 250 Torr H$_2$; 546 K, 418 Torr H$_2$). The apparent activation energies E_a are smaller and the orders with respect to H$_2$ are less negative in the presence of potassium (Table 2). As these kinetic parameters vary with the temperature and the H$_2$ pressure, the kinetic study has been performed over the ranges 473–573 K, 200–450 Torr H$_2$ for $P_{\text{propane}} = 6.5$ Torr. A linear relationship between E_a and n_{H_2} is observed for Ni–K/SiO$_2$ catalysts.

The slopes of the E_a vs n_{H_2} curves for reactions (1) and (2) over Ni–K/SiO$_2$ catalysts are equal to $Q_H = 37$ kJ mol^{-1} (Fig. 2) in good agreement with the value deduced from ethane hydrogenolysis experiments (Fig. 1).

The true activation energies E_{0_1} and E_{0_2} calculated from extrapolation to $n_{H_2} = 0$ are 71 ± 4 and 58 ± 4 kJ mol^{-1} for reactions (1) and (2), respectively, over Ni–K/SiO$_2$ catalysts. These values are to be compared with

TABLE 2

Propane Hydrogenolysis: Influence of Potassium on Rate, Selectivity, and Kinetic Parameters for Reactions (1) and (2)

Reaction conditions	Solid	Reaction temperature (K)	$r \times 10^{-10}$ [molecules s^{-1} (cm^2 Ni)$^{-1}$]	Selectivity r_1/r_2	n_{H_2}	E_a (kJ mol^{-1})
I	Ni	502	(1) 40		(1) −2	(1) 183
			(2) 18	2.2	(2) −3.2	(2) 217
	Ni–K	502	(1) 0.55		(1) −1	(1) 109
			(2) 0.13	4.2	(2) −2.1	(2) 150
II	Ni	480	(1) 30			
			(2) 15	2.0		
	Ni–K	546	(1) 30			
			(2) 7	4.3		

Note. Reduction at 923 K. Heating rate 20 K min^{-1}. Conditions I. r: 250 Torr H$_2$, 6.5 Torr C$_3$H$_8$, 100 ml min^{-1}, 502 K, 70 mg Ni/SiO$_2$ (0% K), 80 mg Ni–K/SiO$_2$ (2.7% K). n_{H_2}: 502 K, 6.5 Torr C$_3$H$_8$, H$_2$ between 200 and 300 Torr. E_a: 250 Torr H$_2$, 6.5 Torr C$_3$H$_8$, temperature between 473 and 518 K. Conditions II. r: 418 Torr H$_2$, 6.5 Torr C$_3$H$_8$, 100 ml min^{-1}, 20 mg of both solids.

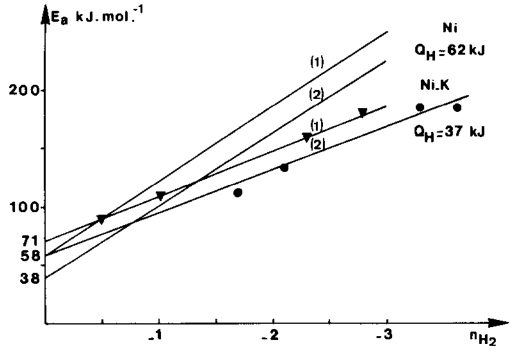

FIG. 2. Apparent activation energies (E_a) vs partial order with respect to H_2 (n_{H_2}) for propane hydrogenolysis for reactions (1) and (2). Temperature range 473–573 K, 200–450 Torr of H_2, 6 Torr C_2H_6, reduction procedure 20 K min^{-1}.

those previously reported for Ni/SiO_2 (*15*), namely 58 and 38 kJ mol^{-1}, respectively. Thus addition of potassium results in an increase in the true activation energy of both reactions.

Benzene Hydrogenation

The rates of benzene hydrogenation into cyclohexane measured at 303 K (720 Torr H_2, 40 Torr C_6H_6, total flow rate 50 or 120 ml min^{-1}) are 106×10^{10} and 35×10^{10} molecules s^{-1} (cm^2 Ni)$^{-1}$ for the Ni and the Ni–K solids, respectively. The rate of benzene hydrogenation into cyclohexane is decreased by the presence of potassium, but to a much lower extent than the rates of hydrogenolysis. The heating rate used during the reduction pretreatment does not influence the activities of the solids. The order with respect to H_2 (0.5 for hydrogen pressures ranging from 500 to 720 Torr) as well as the apparent activation energy measured between 303 and 363 K (around 44 kJ mol^{-1}) are the same for Ni and Ni–K catalysts. With increasing reaction temperatures, the formation of cyclohexane goes through a maximum and then decreases for both types of catalyst (Fig. 3). This decrease does not correspond to the thermodynamic equilibrium benzene–hydrogen–cyclohexane (*16*). In the presence of potassium the maximum occurs at a higher temperature and the decrease is less marked. This makes the Ni–K sample more active than the Ni sample at temperatures higher than 473 K. Similarly the methane formation which corresponds to the benzene hydrogenolysis develops at higher temperatures for Ni–K/SiO_2 than for Ni/SiO_2, the apparent activation energy being for both cases around 105 kJ mol^{-1}. Such maxima in benzene conversion into cyclohexane have not been clearly explained as yet. Concerning the low temperature range (right half of Fig. 3) the parallel Arrhenius plots tend to indicate that some of the active sites of the Ni–K sample are not accessible to the reactants, in particular to large molecules, in agreement with previous conclusions from quantities of adsorbed CO (8). In effect the nickel has been shown to be more accessible to hydrogen adsorption than to CO adsorption, chemisorbed hydrogen being capable of migrating between the Ni surface and the K-containing phase.

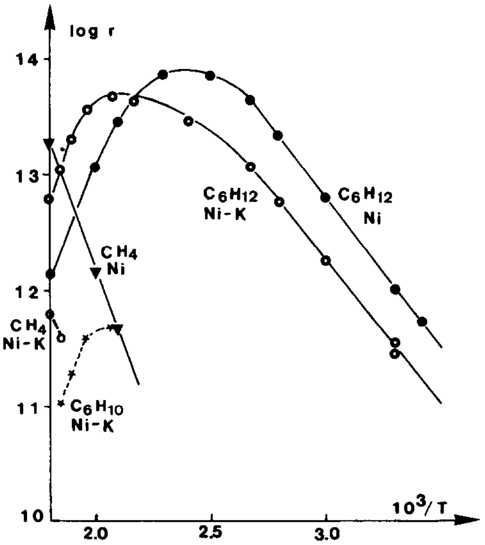

FIG. 3. Log rate (r) as a function of the reciprocal temperature for benzene hydrogenation. Conditions: reduction 923 K, 20 K min^{-1}, 720 Torr H_2, 40 Torr C_6H_6, total flow rate 50 ml min^{-1}, r in molecules s^{-1} (cm^2 Ni)$^{-1}$. Benzene hydrogenation into cyclohexane: Ni (●), Ni–K (○). Benzene hydrogenolysis into methane: Ni (▼), Ni–K (◘). Benzene hydrogenation into cyclohexene: Ni–K (★).

Concerning the high-temperature range, although poisoning or diffusion effects have been ruled out in Ref. (*17*), the formation of reversibly adsorbed hydrocarbon deposits coming from benzene cracking which would decrease rapidly the density of active sites cannot be excluded. In this hypothesis, the Ni–K sample for which the hydrogenolysis is unfavored could become more active for cyclohexane formation than the pure-nickel sample at high temperatures, as experimentally observed. Changes in surface coverage by the reactants could also account for the experimental observations. Van Meerten and Coenen (*18*) have described the reaction by a mechanism based on the assumption that all hydrogen additions have the same rate constant. Recently, an isotopic transient study carried out in our laboratory (*19*) has revealed that the maximum of cyclohexane formation coincides with the disappearance of a benzene reservoir coating the catalyst surface and ensuring the saturation of a very small amount of active sites (less than 1% of the metallic surface). The potassium effect could then be to change the adsorptive properties of the nickel (concerning benzene, for instance) without changing the proper mechanism of the reaction. This could result in the observed shift of the Arrhenius plot toward higher temperatures. Further work is needed to reinforce this idea.

Let us note also that small amounts of cyclohexene are detected in the range 473–543 K on the $Ni-K/SiO_2$ solid. Teichner *et al.* (*20*) have already observed that some benzene is transformed into cyclohexene in the presence of metals enriched in electrons, in agreement with our own observations.

Methane Exchange with Deuterium

The exchange of methane with deuterium has been shown in Ref. (*21*) to proceed on nickel catalysts via two distinct mechanisms, depending on the surface coverage with deuterium.

(i) An associative mechanism leading to single-atom exchange, i.e., the formation of CH_3D molecules. A reacting site formed from around four Ni atoms free from deuterium and a preadsorbed deuterium atom is assumed for this case.

(ii) A dissociative mechanism leading to many-atom exchange (mainly CD_4) implying a site of around seven adjacent nickel atoms, free from deuterium. A surface carbide species, Ni_3C, is postulated as an intermediate of the perdeuteration process.

A kinetic treatment similar to the one

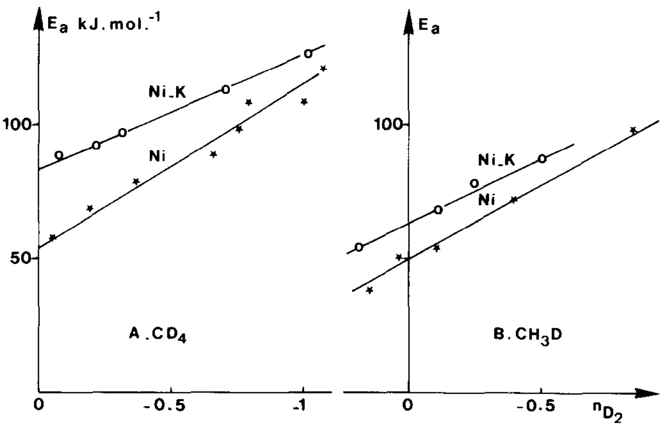

FIG. 4. Apparent activation energy (E_a in kJ mol^{-1}) as a function of partial order with respect to deuterium pressure for single and total exchange of methane with deuterium. Temperature range 473–673 K, 10 to 300 Torr D_2, 5 Torr CH_4 (n_{CH_4} = 1).

used for ethane and propane hydrogenolysis has been applied to the raw exchange data, and this allows us to determine the true activation energy E_0 and the isosteric heat of deuterium adsorption Q_D. In Figs. 4A and B, various values of the apparent activation energy E_a measured for different temperature and pressure conditions (473–673 K, P_{CH_4} = 5 Torr, P_{D_2} = 10 up to 300 Torr) are plotted against the corresponding partial orders with respect to deuterium pressure, n_{D_2}. Let us assume, as was previously done in Ref. (*21*), that the changes in activation energy E_a for both single and total exchange reactions are accounted for by the general Temkin equation $E_a = E_0 - n_{D_2}Q_D$. For the case of the total exchange reaction, it is observed that the true activation energy, E_0, increases from 54 ± 8 to 84 ± 8 kJ mol^{-1} upon potassium addition while the isosteric heat of deuterium adsorption, Q_D, decreases from 62 ± 8 to 42 ± 8 kJ mol^{-1}. The kinetic parameters of the single exchange reaction vary in a similar way although to a lesser extent, namely E_0 from 50 ± 8 to 63 ± 8 kJ mol^{-1} and Q_D from 58 ± 8 to 46 ± 8 kJ mol^{-1} (Fig. 4). If we consider now the changes in catalytic activities measured for similar temperature and pressure conditions upon alkali doping, the experimental ratios r_{Ni}/r_{Ni-K} stand in the range 40–100 for both single and total exchange reactions (for instance, at 553 K, P_{CH_4} = 5 Torr and P_{D_2} = 54 Torr, r_{Ni}/r_{Ni-K} = 52 for CH_3D formation and 44 for CD_4 formation). For the Ni/SiO_2 solid, rate of methane disappearance is 17.4×10^{12} molecules s^{-1} (cm^2 Ni)$^{-1}$, rate of CH_3D formation 6.3×10^{12} molecules s^{-1} (cm^2 Ni)$^{-1}$, and rate of CD_4 formation 7.5×10^{12} molecules s^{-1} (cm^2 Ni)$^{-1}$.

Carbon Monoxide Hydrogenation

As previously reported (*7*), potassium addition to a Ni/SiO_2 catalyst leads to a drastic decrease in activity; this drop depends on the temperature of reaction. The activity towards CH_4 formation per metallic unit area (as deduced from magnetic measurements) is divided by ca. 150 at 523 K and by ca. 50 at 573 K. The selectivity toward C_{2+} hydrocarbon formation is clearly enhanced for a given reaction temperature when adding potassium (Fig. 5). Moreover, unsaturated products (which were not detected under our conditions on pure Ni catalysts) are also observed. These results are in good keeping with the observed changes in Fischer–Tropsch synthesis products when adding alkali promoters to iron catalysts (*2, 22, 23*).

Saturated products. Kinetic parameters (apparent activation energy E_a, orders with respect to reactants n_{H_2}, n_{CO}) were measured for C_1 and C_2 products and compared with results obtained on pure Ni catalysts (*13, 24*). Figure 6 shows the variations of E_a with the temperature of reaction T. E_a is clearly higher when adding potassium. The orders with respect to CO are more negative for K-promoted samples, this effect being much larger for C_2 production (Fig. 7). On the contrary the orders in hydrogen appear less altered by K addition (Fig. 8). For temperatures below 573 K n_{H_2} orders (for C_1 and C_2 productions) are near 1, as observed on Ni catalysts; above 573 K n_{H_2} decreases but data on the pure Ni catalyst are missing in this range (a decrease of the order with respect to H_2 is reported in CO

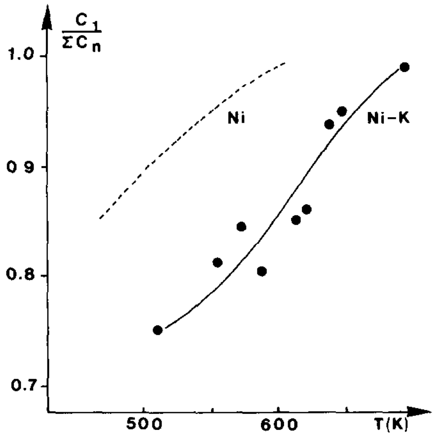

FIG. 5. Selectivity toward CH_4 formation in CO + H_2 reaction (H_2/CO = 4). Full line, Ni–K catalysts; dashed line, Ni catalysts.

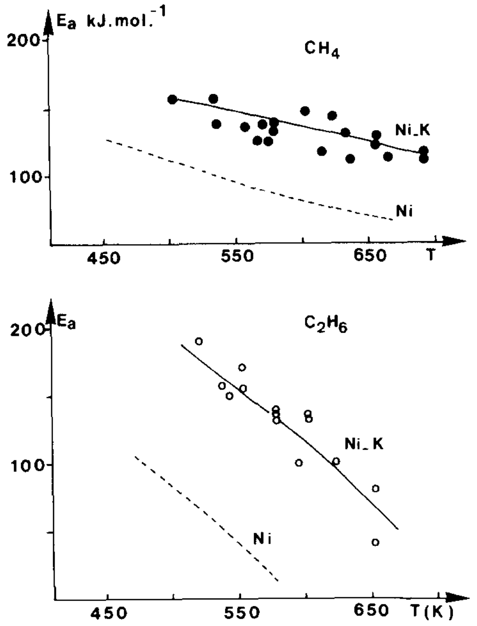

FIG. 6. Apparent activation energies E_a for CO methanation as a function of temperature. Full line, Ni-K catalysts; dashed line, Ni catalysts.

methanation at high temperature (*25*) on Ni catalysts).

From these results it can be observed that, although some changes do exist in the values of the kinetic parameters between Ni and Ni-K catalysts, the nature of the variations of these parameters with the temperature of reaction, T, are similar on both solids; when T increases, E_a decreases, n_{CO} for CH_4 formation increases and tends to zero, n_{CO} for C_2H_6 formation increases and becomes positive at high temperature, n_{H_2} is near 1 in the same range of temperature. This observation suggests some similarities between the mechanisms on both solids: on K-promoted catalysts the surface is also probably mainly covered with unreactive CO adspecies. This allows us to use the Temkin relation $E_a = E_0 - n_{CO}Q_{CO}$ to try to determine the true activation energy E_0 for C_1 and C_2 formation. Figure 9 shows plots of E_a against n_{CO} from the data of Figs. 6 and 7, using only results ob-

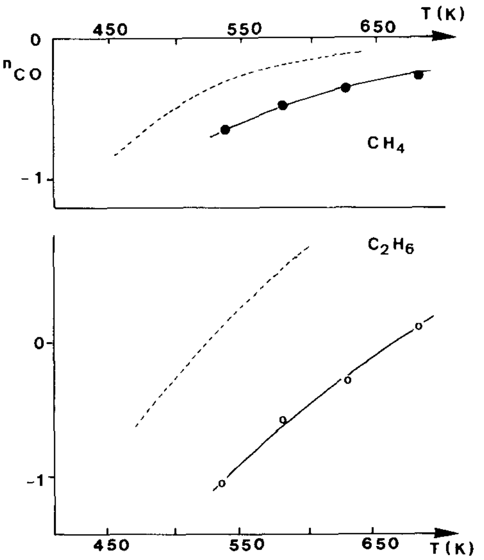

FIG. 7. Order with respect to CO in CO methanation as a function of temperature (P_{H_2} = 500 Torr; 10 ≤ P_{CO} ≤ 250 Torr). Full line, Ni-K catalysts; dashed line, Ni catalysts.

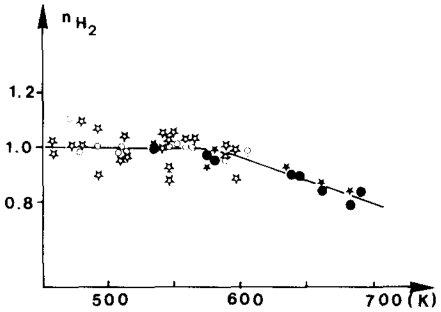

FIG. 8. Order with respect to H_2 in CO methanation as a function of temperature (P_{CO} = 125 Torr; 150 ≤ P_{H_2} ≤ 630 Torr). CH_4 formation: (●) Ni-K, (☆) Ni catalysts. C_2H_6 formation; (★) Ni-K, (○) Ni catalysts.

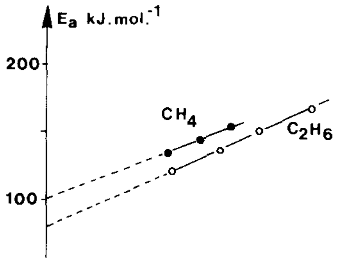

FIG. 9. Apparent activation energy for CO methanation vs order with respect to CO for Ni-K catalysts. (●) CH_4 formation, (○) C_2H_6 formation.

tained at temperatures below 573 K, where $n_{H_2} = 1$. Due to the relative lack of reproducibility of the experimental points the uncertainty for E_0 is higher than for Ni catalysts. E_0 is 100 ± 12 kJ mol^{-1} for CH_4 formation (71 ± 8 kJ mol^{-1} for unpromoted catalysts) and 80 ± 12 kJ mol^{-1} for C_2H_6 formation (71 ± 8 kJ mol^{-1} for unpromoted Ni).

The isosteric heat of adsorption of CO, Q_{CO}, as deduced from the slopes is 84 ± 8 kJ mol^{-1}; on pure Ni catalysts the corresponding value is 58 ± 8 kJ mol^{-1} (*13*). This increase of Q_{CO} when adding potassium to Ni catalysts agrees with calorimetric measurements of CO adsorption on Fe and Fe–K catalysts (*26*).

Unsaturated compounds. Ni–K catalysts lead to olefinic products which are not detected over Ni solids. Their formation decreases rapidly when increasing the reaction temperature T and the contact time of reactants (Fig. 10). Kinetic parameters for olefinic production are different from those for corresponding saturated compounds (Table 3). Apparent activation energies are smaller and decrease more rapidly when increasing T in comparison with corresponding paraffinic hydrocarbons. Orders in CO increase when increasing T or decreasing CO pressure and are higher than for saturated products. Orders in H_2 are near zero. The important differences of kinetic parameters between saturated and olefinic compounds suggest that the rate-determining steps are different. As olefinic intermediates probably precede the formation of paraffinic products, the rate determining step of olefinic production is very probably connected with the desorption step of the unsaturated intermediates. Further studies are under way in order to clear up this point. Let us underline that the specificity of Ni–K catalysts toward olefinic compounds in the CO + H_2 reaction parallels the selectivity for cyclohexene observed at high temperature on Ni–K catalysts during C_6H_6 hydrogenation.

TABLE 3

Kinetic Parameters for Olefinic Production in CO + H_2 Reaction[a]

Product	C_2H_4		C_3H_6	
Temperature (K)	533	573	533	573
E_a (kJ mol^{-1})	104 (146)	38 (134)	159 (209)	63 (167)
n_{CO}	0.3 (−1)	1 (−0.4)	0.2	1
n_{H_2}	0.1 (1)	−0.1 (0.7)	0	0

[a] Values in parentheses correspond to the saturated compound.

DISCUSSION

Table 4 summarizes our main observations concerning the rates, the true activation energies of ethane and propane hydrogenolysis, CH_4/D_2 exchange and CO hydrogenation and the isosteric heats of CO and hydrogen (or D_2) adsorptions under the conditions of the studied reactions.

Comparison with the Literature

It has been shown that potassium addition to iron catalysts leads to a sharp decrease in the rate of ethane hydrogenolysis, an increase in the order in hydrogen which becomes less negative and a decrease in the apparent activation energy (*6*) Rostrup-Nielsen (*27*) has shown that addition of alkali to Ni catalysts leads to a significant drop in activity for steam reforming and ethane hydrogenolysis. Our own observations are in good keeping with these results.

For the case of the CO hydrogenation the decrease in activity and the increase in selectivity we have obtained upon potassium addition are in good agreement with previous works concerning potassium-promoted supported high surface area Ni catalysts (*2, 3, 28, 29*). The same tendencies are observed on Ru catalysts (*30, 31*) and on Ni single crystals promoted by metallic potassium (*32*). On Fe catalysts potassium addition also increases the selectivity toward high hydrocarbons and ethylenics (*2, 3, 22, 23*). However, in this case if rates are generally depressed by potassium addition, an enhancement has been observed by Dry *et al.* (*22*). This increase seems to be the

TABLE 4

Influence of K Addition on Rates, True Activation Energies, and Heats of Adsorption

	Ethane hydrogenolysis[a]		Propane hydrogenolysis[b]			CH_4/D_2 exchange[c]			CO hydrogenation[d]		
	Ni	Ni–K		Ni	Ni–K		Ni	Ni–K		Ni	Ni–K
Relative rates	1	0.002	r_1	1	0.014	CH_3D	1	0.019	CH_4	1	0.007
			r_2	1	0.007	CD_4	1	0.023	C_2H_6	1	0.03
E_0 (kJ mol^{-1})	58	75	E_{0_1}	58	71	CH_3D	50	63	CH_4	71	100
			E_{0_2}	38	58	CD_4	54	84	C_2H_6	54	80
Q_H or Q_D (kJ mol^{-1})	62	37		62	37	CH_3D	58	46			
						CD_4	62	42			
Q_{CO} (kJ mol^{-1})										58	84

[a] ethane $C_2H_6 \rightarrow CH_4$ (533 K, 338 Torr H_2, 6 Torr C_2H_6).

[b] Propane r_1: $C_3H_8 \rightarrow CH_4 + C_2H_6$ (502 K, 250 Torr H_2, 6 Torr C_3H_8) r_2: $C_3H_8 \rightarrow CH_4$.

[c] Exchange: formation of CH_3D and CD_4 (553 K, 5 Torr CH_4, 54 Torr D_2).

[d] CO hydrogenation: formation of CH_4 and C_2H_6 (523 K, 500 Torr H_2, 125 Torr CO).

only difference between Fe and other metals. The method of catalyst preparation (*29, 30*), the potassium content (*2, 3*) or the morphological changes of iron-based catalysts during the CO hydrogenation might be major factors explaining this special feature.

Concerning changes in activation energy for methanation upon K addition, an increase has been observed on Ru catalysts (*30*), a potassium salt being added to high-area catalysts, and on Fe catalysts prepared from K–Fe carbonyls (*23*) in agreement with our observations on Ni. Goodman *et al.*, however, do not observe any variation for the case of Ni(100) promoted by metallic K (*32*), indicating that addition of "metallic" (metal added to metal films or polycrystalline metals) and "chemical" (addition of a salt to high-area catalysts) potassium can give rise to some different effects.

We have shown that the heat of adsorption of hydrogen over Ni is depressed by K addition. This observation accords well with data reported for iron-based Fischer–Tropsch catalysts (*22, 23*). It should be noted that the reverse is observed when metallic potassium is added to Fe single crystals (*34–36*). The increase of the heat of adsorption of CO which is observed in this work is in good agreement with the increase of the binding energy of molecular CO found by alkali addition on Fe (*22, 26, 33, 34, 37*) or Ni solids (*35*) as well on single crystals rather than on actual catalysts.

It can be concluded that the introduction of a potassium salt to precursors of high-area catalysts gives rise to catalytic effects which are, to a first approximation, independent of the nature of the host metal and similar but not identical (in particular for the heat of hydrogen adsorption) to those obtained when metallic potassium is adsorbed on single crystals.

Geometric or Electronic Nature of the Modifications Due to Potassium

Let us first recall that potassium addition results in a blocking of a part of the metallic phase, decreasing the quantity of adsorbed CO (*8*) to a larger extent than the quantity of adsorbed H_2. It can be considered first that the electronic properties of the free Ni atoms are not altered by the presence of potassium.

A possible explanation of the potassium effect could be to consider it as a poison, merely blocking the Ni atoms without modifying the electronic properties of the neighbors (*31, 38*). If the Ni surface is a priori considered as homogeneous it is very hard to account for the increase in selectivity to C_{2+} hydrocarbons which is observed in the CO hydrogenation reaction and toward the demethylation reaction in propane hydrogenolysis. A distribution of potassium atoms or its clustering into potassium patches over the Ni surface would produce either a decrease of selectivity, analogous to that observed in the case of copper addition (*39*), or no change in selectivity at all, as for H_2S poisoning (*21*). Moreover, it is difficult to explain the XPS and infrared data (*8*). Hence this hypothesis can be ruled out.

The Ni surface could also be considered as composed of heterogeneous sites corresponding to different activation energies. On pure nickel the most active sites, sites I, associated with the lowest activation energy, would be responsible for the greatest part of the activity. K addition could selectively poison these active sites, leaving free the less active ones with higher activation energies, sites II (*40*). A parallel rate decrease and activation energy increase would result from this hypothesis which would account for most of our observations: K would act as a selective poison (*30*).

Several considerations can be provided against such a model.

(i) According to it, cyclohexene from the benzene hydrogenation and ethylenics from the CO hydrogenation would be formed on the less active sites II since they are observed on Ni–K catalysts. These by-products should also be formed on pure Ni since the less active sites II exist for this catalyst, but this is not observed. It could be argued that on pure Ni, unsaturated hydrocarbons can be formed as a first step, then hydrogenated on the active sites I. This hypothesis is not valid since pure Ni catalysts are less active toward the hydrogenation of benzene into cyclohexane (Fig. 3) at temperatures above 473 K where cyclohexene and ethylenics are observed on K-promoted samples.

(ii) The Arrhenius-type plots of log r vs $1/T$ for CO hydrogenation over Ni and Ni–K catalysts cross at around 723 K. This means that, at temperatures above 723 K, sites II become more active than sites I. Hence Ni and Ni–K catalysts should have comparable catalytic behavior. In particular, at very high temperatures, ethylenics should be detected on pure Ni catalysts, but this is not observed. It is therefore concluded that potassium cannot be considered as a poison merely blocking more or less selectively the free Ni atoms. It is assumed that potassium changes the electronic properties of free Ni atoms in agreement with the conclusion drawn from a previous work on the physicochemical properties of Ni–K catalysts (*8*).

Relation between the Changes in Electronic and Catalytic Properties of Nickel

On the basis of the frequency shift of the CO vibration and of XPS data, it has been concluded that Ni to which K has been added is enriched in electrons (*8*). This view agrees with the observed changes of the energetic and catalytic properties of Ni due to potassium addition, especially in the case of CO hydrogenation.

For the exchange reactions and the hydrogenolysis, the possible changes in the Ni–H bonding have to be considered. If one examines the controversial data in the literature concerning the partial charge of adsorbed hydrogen it is very hard to predict whether an increase of the electron density of Ni leads to the weakening or to the strengthening of the Ni–H bond. The observed decrease in the isosteric heat of hydrogen (or deuterium) agrees with the data of Dry *et al.* on iron-based catalysts (*22*). This involves the weakening of the bond strength between H and Ni upon potassium addition. This weakening is consistent with the enhancement of the true activation energies as the rate-determining steps involve a more or less pronounced dehydrogenation of the hydrocarbon molecules. This model allows us to explain why the activation energy increase is smaller for the single-atom exchange where one H is to be removed while the many-atom exchange implies the removal of four H. Besides this, possible Ni–C bond changes should be also considered since the formation of surface carbide is assumed for most of the reactions. However, we have no data regarding the extent to which the possible changes in Ni–C or C–C bonds would reinforce or be at variance with our conclusions drawn from the Ni–H bonding changes.

For the CO hydrogenation, the observed increase in the isosteric heat of CO adsorption agrees with the enrichment of nickel in electrons, since the charge transfer from Ni to the CO($2\pi^*$) level is enhanced and the metal–CO bond is strengthened (*41*). The bond strength between Ni and the reaction intermediate of the methanation reaction is thus probably reinforced, the surface carbon C_s coming from CO dissociation (*13*) (or the partially hydrogenated monocarbon fragments) being an electro-acceptor molecule. If then it is assumed that the rate-determining step is the hydrogenation of the surface carbon, the corresponding activation energy should be larger, in agreement with our observations. At this stage it can be remarked that if the rate-determining step of CO hydrogenation were the CO dissociation, then potassium should increase the methanation rate and decrease the activation energy, the C–O bond being weakened and so the dissociation of CO enhanced, at variance with our observations.

The hypothesis of the Ni enrichment in electrons of free Ni atoms on potassium addition is also capable of explaining the better selectivity of Ni–K catalysts to ethylenics in CO hydrogenation (Fig. 10) and to cyclohexene in benzene hydrogenation. Ethylenics and cyclohexene can be considered as electron-donor molecules; their bonds with Ni are weakened by potassium and their desorption rates are probably increased, leading to the observed selectivity changes.

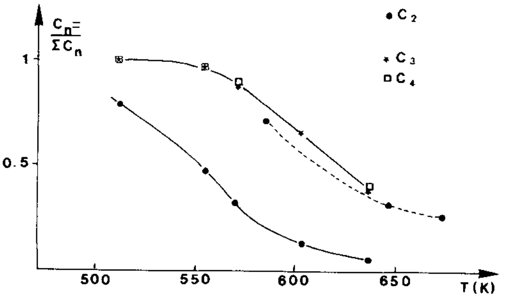

FIG. 10. Selectivity toward olefinics in CO + H$_2$ reaction vs reaction temperature for Ni–K catalysts. (●) C_2H_4 selectivity (full line, space velocity = a; dashed line, space velocity = a × 20). (★) C_3H_6, (□) C_4H_8 selectivities (space velocity = a).

CONCLUSION

From this work, it can be concluded that potassium addition to Ni/SiO$_2$ catalysts, which results in marked changes in the catalytic pattern and in the kinetic parameters similar to those observed on other metals, blocks a certain number of Ni atoms and acts as an electronic modifier of the remaining free Ni atoms. The variations of the true activation energies can be traced to the electron "enrichment" of the metallic phase. This leads to a strengthening of the bond between Ni and (i) adsorbed molecular CO, (ii) the more or less hydrogenated surface carbon intermediate, considered as electronegative, and (iii) adsorbed molecules with a relatively small ionization potential such as ethylenics, but a weakening of the bond strength between Ni and adsorbed hydrogen. However satisfying this rationale may be, it cannot be overlooked that the concept of electron "enrichment" for metals in the solid state is not unequivocal and further work is underway to give more precision on the physical nature of this electronic effect.

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