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The role of bulk H and C species in the chain lengthening of Fischer–Tropsch synthesis over nickel

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This work documents the possible role of bulk species (dissolved H and C atoms) in the Fischer–Tropsch reaction. This has led us to study the sorption (adsorption or absorption) of hydrogen when increasing the pressure from 0.1 to 5 MPa, the selectivity toward C_{2+} hydrocarbons in carbon monoxide hydrogenation at 5 MPa total pressure, and the amount of nickel carbide formed in the course of the reaction over unsupported nickel, Ni/SiO_2, Ni/TiO_2 and Ni/Cr_2O_3 catalysts. Increasing the hydrogen pressure results in a subsequent sorption which is found to be proportional to the nickel dispersion, and can be attributed either to a completion of the surface hydrogen adlayer (8%) or to a formation of a hydrogen sublayer. No relationship could be found between the selectivity towards C_{2+} hydrocarbons and the quantity of sorbed hydrogen. A correlation between this selectivity and the amount of nickel carbide formation was demonstrated, suggesting that the active phase which leads to C_{2+} hydrocarbons is nickel carbide, or that carbon atoms of subsurface sites participate in the homologation reaction.

Keywords: Fischer–Tropsch synthesis, nickel, hydrogen sorption at high pressures, carbide formation, magnetic methods

1. Introduction

Heterogeneous catalysis can be considered as a typical surface phenomenon. The importance of bulk species as reactants, however, is now recognized. The classic example is provided by oxides where bulk O^{2-} ions play a prominent role in oxidation reactions [1]. In the field of catalysis by metals the active role of bulk species is well documented: the mechanism of carbon formation on nickel-based reforming catalysts involves diffusion through the metal particle [2–4]. Evidence of the reactivity of bulk hydrogen atoms in the hydrogenation of CH_3 groups adsorbed on Ni(111) to form methane has been provided by Ceyer and coworkers [5]. Similar conclusions were reached by this group for ethylene hydrogenation on Ni(111): bulk H atoms, migrating from the bulk to the surface, hydrogenate adsorbed ethylene to ethane whilst surface-bound H atoms do not react [6]. Baerns and coworkers [7] have shown that the formation of formyl species from CO hydrogenation over Pd-based catalysts occurs via the interaction of adsorbed CO with hydrogen dissolved in the Pd bulk, most probably from subsurface sites. In this context, we have speculated that dissolved species such as H or C atoms, from subsurface or from the bulk, might play some role in the Fischer–Tropsch reaction. This has led us to quantify the amount of excess sorbed hydrogen when the hydrogen pressure increases from 0.1 to 5 MPa over a series of nickel catalysts achieving very different selectivities towards C_{2+} hydrocarbons and to measure the extent of bulk carbide formation in the course of CO hydrogenation. In this paper, we show that the amount of sorbed hydrogen is roughly proportional to the dispersion of the nickel particles and that no direct correlation can be found between this amount and the selectivity. In contrast, an interesting relationship is observed between the bulk carbide formation and the chain growth probability.

2. Experimental

The methods of preparation and the morphological characteristics of the precursors have already been described partially elsewhere [8]. The unsupported $Ni(OH)_2$ precursor was obtained by removing ammonia from a solution of nickel nitrate hexammine [9]. Supported nickel catalysts were prepared by adding supports (SiO_2, TiO_2, Cr_2O_3, MgO) to a solution of nickel nitrate hexammine [8,10,11].

A $Ni–Cu/SiO_2$ catalyst with a $Cu/(Ni + Cu)$ atomic ratio of 15% was prepared using the same procedure, starting from a solution of nickel and copper nitrate hexammine [12]. The reduction of 0.1 g of precursors was carried out in flowing hydrogen ($4\ \ell\ h^{-1}$) for 15 h by linearly raising the temperature at $2\ K\ min^{-1}$. The final temperatures which were selected to ensure a nearly complete reduction of the catalysts [8] are listed in table 1.

The dispersion of nickel catalysts was estimated by using various complementary techniques. The unsupported nickel catalyst obtained by reduction of $Ni(OH)_2$ at 573 K demonstrates a BET surface area of $10\ m^2\ g^{-1}$. Assuming that an area of $0.065\ nm^2$ is associated with

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Table 1
Morphology of reduced catalysts

Catalyst	Metal (wt%)	Reduction temp. (K)	D_M (nm)	v_{H_2} [a] (ml NTP g^{-1} Ni)	Dispersion Δ (%)		
					D_M	v_{H_2}	CCS
Ni/SiO_2	15	923	4.3	37	26	24	34
$Ni–Cu/SiO_2$	15	945	3.8	–	29	–	–
Ni/MgO	15	948	9.4	23	13	15	–
Ni/TiO_2	11.3	633	[b]	–	–	–	2.5
Ni/Cr_2O_3	13.3	635	[b]	–	–	–	6

[a] Under 1316 Pa at 300 K.

[b] Not superparamagnetic at 300 K; D_M cannot be calculated [14].

each surface nickel atom [13], the dispersion of the unsupported nickel powder is found to be 1.5%.

Surface average nickel particle diameters, D_M, were obtained from magnetic measurements at room temperature in an electromagnet providing fields up to 2 T (20 kOe), according to a procedure described elsewhere [14,15]. This method has been validated by comparison with transmission electron microscopy data [8]. The relationship between dispersion Δ and diameter has been established assuming a cubo-octahedral shape. Accordingly if m is the number of atoms in the edge of the cubo-octahedron, the total number and the number of atoms, N_T and N_S, respectively, are given by the following equations:

$$N_T = \tfrac{10}{3}(m-1)^3 + 5(m-1)^2 + \tfrac{11}{3}(m-1) + 1\,, \qquad (1)$$

$$N_S = 12 + 10m(m-2)\,. \qquad (2)$$

Dispersion Δ can be straightforwardly obtained by

$$\Delta = N_S/N_T\,. \qquad (3)$$

The weight of a sphere containing N_T metal atoms is given by

$$\frac{AN_T}{\mathcal{N}} = \frac{\pi D^3}{6}\rho\,, \qquad (4)$$

where ρ is the specific weight, D the diameter of the equivalent sphere, A the atomic weight and $\mathcal{N}$ the Avogadro number. For nickel, eq. (4) can be written as

$$D\ (\mathrm{nm}) = 0.273 N_T^{1/3}\,. \qquad (5)$$

Eqs. (5) and (3) establish a relationship between diameter and dispersion.

Some hydrogen adsorption experiments were performed in a conventional volumetric apparatus after outgassing at 570 K for 1 h. Dispersion is calculated from the volume of adsorbed hydrogen, v (ml TPN g^{-1} Ni) assuming the surface stoichiometry $H–Ni_S$, by

$$\Delta = \frac{2vA\mathcal{N}}{22414\mathcal{N}} = 0.00524v\,. \qquad (6)$$

Dispersion measurements can also be achieved using a method initially proposed by Carter, Cusumano and Sinfelt [16], termed the CCS method. This is based on the fact that each chemisorbed hydrogen atom effectively erases the contribution of a nickel atom to the magnetization. The ratio $(M_{S0} - M_{S1})/M_{S1}$, where M_{S1} and M_{S0} are saturation magnetizations under one atmosphere of hydrogen and after desorption, respectively, gives directly the dispersion. The saturation magnetization is obtained by plotting the magnetization measured at room temperature as a function of the reciprocal field strength, $1/H$, and extrapolating at $1/H = 0$. The CCS method is particularly adapted for the case of decorated nickel particles, in the SMSI state for example (Ni/TiO_2), where the nickel surface is not completely accessible to gas chemisorption.

Details on catalytic testing conditions ($T = 513$ K, $P = 5$ MPa, $H_2/CO = 2$, space velocity = 10 000 h^{-1}) can be found in ref. [17].

The influence of the hydrogen pressure on the magnetization of nickel was carried out in an amagnetic stainless steel cell [18] allowing both the reduction at atmospheric pressure and the characterization of the metal phase (fraction of zero-valent ferromagnetic nickel and the dispersion) at increasing hydrogen pressures (up to 7 MPa) by magnetic measurement without sample transfer through air. The same cell was utilized to study carbon deposits formed during CO hydrogenation in conditions similar to those prevailing during catalytic tests ($T = 513$ K, $P = 5$ MPa, $H_2/CO = 2$, space veclocity = 10 000 h^{-1}, reaction time = 4 h). After reaction, the cell was purged with helium at reaction temperature and then cooled down at room temperature. An in situ magnetic measurement was performed then. Carbon deposits were removed by reduction under flowing hydrogen (4 $\ell\ h^{-1}$) at a temperature of 573 K sufficently high to ensure the removal of carbon interacting with nickel [18,20]. From these experiments, only methane could be detected [18]: no substantial amounts of water or carbon oxides, indicative of a possible NiO formation were observed by mass spectroscopy. After hydrogenation a new magnetic measurement was carried out.

3. Results

3.1. Catalyst morphology

The morphological characteristics of the reduced catalysts are summarized in table 1. For Ni/SiO_2 the amount of adsorbed hydrogen at 300 K at 1316 Pa does not correspond to saturation. Under 0.1 MPa the volume of adsorbed hydrogen is 1.22 times larger [19]. The latter value was used to calculate the dispersion, which is found to be in good agreement with the one obtained from D_M. In the following the average value, viz. 25%, is used. The CCS method leads to a figure ca. 30% in excess. The difference might be attributed to the fact that the adsorption of one hydrogen atom decreases magnetization by more than the magnetic contribution of one nickel atom [14]. The agreement between the CCS method on the one hand and other methods on the other hand is sufficiently satisfying to justify its application to Ni/TiO_2 and Ni/Cr_2O_3 catalysts. A correction similar to that used for Ni/SiO_2 was performed to estimate v_{H_2} at 0.1 MPa for Ni/MgO catalysts. This results in a dispersion in good accordance with that deduced from D_M measurement. The average value, 14%, will be used in the following.

3.2. CO hydrogenation

Table 2 reports the catalytic properties of the nickel-based catalysts. As can be seen, unsupported nickel gives rise to a mixture of methane, the most abundant reaction product, C_{2+} hydrocarbons (mainly C_2–C_6), methanol and $C_{2+}OH$ (C_2–C_5). When deposited on silica, nickel turns into a selective methanation catalyst, as already observed [18,20]. Magnesia as a support promotes methanol formation, chromia $C_{2+}OH$ and titania C_{2+} hydrocarbons. Copper addition to nickel results in an increase of the methanol selectivity and a decrease of the C_{2+} selectivity [17]. The sequence of the C_{2+} selectivities, directly related to the chain lengthening probability, is the following:

$$SiO_2 < MgO, Cr_2O_3 < \text{unsupported} < TiO_2\,. \quad (7)$$

This sequence is comparable to that observed on similar samples under different experimental conditions ($P = 0.1$ MPa, $H_2/CO = 3.75$) where alcohols were practically not formed [8]:

$$SiO_2 < MgO < \text{unsupported} < TiO_2, Cr_2O_3\,. \quad (8)$$

Table 2
Catalytic properties of Ni-based catalysts in CO hydrogenation [a]

Catalyst	CO conv. (%)	Selectivity (%)				
		CH_4	C_{2+}	MeOH	$C_{2+}OH$	CO_2
Ni/SiO_2	1	96	1.5	2	0.1	0
Ni–Cu/SiO_2	1.1	84	0.6	15	0	0
Ni/MgO	0.12	47	13.7	33	6.3	0
Ni/TiO_2	0.28	46	31	20	3	0
Ni/Cr_2O_3	1.5	53	14.7	24	8.4	0
unsupp. Ni	0.8	59	27	10.5	3	0

[a] $T = 513$ K, $P = 5$ MPa, $H_2/CO = 2$, space velocity 10 000 h^{-1}, catalyst weight 0.1 g, measured after 4 h of reaction.

It can be questioned whether the mechanism of methane formation in the Fischer–Tropsch reaction is the same as that described by Johnson et al. [5] for methyl species adsorbed on Ni(111) and whether sequence (7) is related to absorbed hydrogen atoms. This has led us to study the sorption of hydrogen at increasing pressure using magnetic methods.

3.3. Sorption of hydrogen at high pressure

Hydrogen atoms absorbed in bulk nickel decrease the saturation magnetization which goes to zero for a H/Ni ratio equal to 0.7 [21]. The magnetic moment of one nickel atom being equal to 0.6 Bohr magneton (BM), this means that the absorption of one hydrogen atom into bulk nickel results in a decrease of the saturation magnetization of 0.86 BM/H atom. This value is very similar to that observed for surface hydrogen chemisorption: the latter is found to be 0.7 BM/H atom (1.4 BM/H_2 molecule) as reported [22] for Ni/SiO_2 catalysts. Magnetic methods are thus well adapted for measuring hydrogen sorption in conditions where other techniques, such as volumetry, would not be very sensitive. However, it does not allow discrimination between absorption and adsorption.

Figure 1 shows the variation of magnetization measured at 1 T with time when the hydrogen pressure first increases from 0.1 to 5 MPa then decreases to 0.1 MPa. As can be seen, magnetization first decreases, then goes back to the initial value within ca. 20%, showing unambiguously that a substantial hydrogen sorption occurs

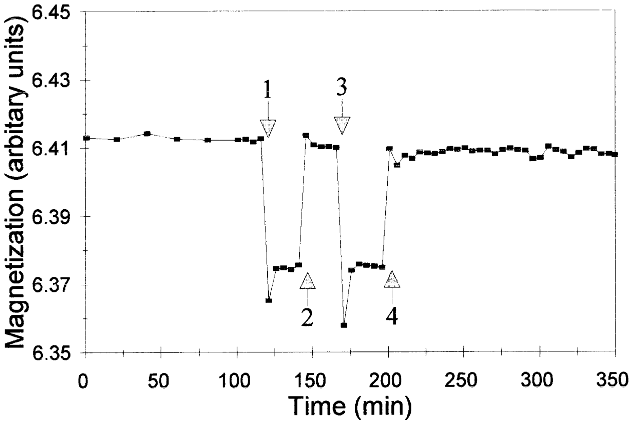

Figure 1. Variations of the magnetization of Ni/Cr_2O_3 measured at 1 T (arbitrary units) with time. The arrows indicate changes of the hydrogen pressure (0.1–5 MPa; 5–0.1 MPa; 0.1–5 MPa; 5–0.1 MPa; 1, 2, 3, 4, respectively).

when the pressure increases, followed by a corresponding reverse phenomenon when the pressure goes back to 0.1 MPa. At least three similar cycles were carried out, giving six $\Delta M/M$ values from which an average figure was calculated. Figure 1 also illustrates the sensitivity of the magnetic method: for the case of Ni/Cr_2O_3, relative variations as small as 0.51% are obtained with good accuracy.

Figure 2 shows the variation of $\Delta M/M$ with nickel dispersion. As can be seen, to a first approximation, $\Delta M/M$ is proportional to nickel dispersion, irrespective of the nature of the support. This trend is not altered by alloying nickel with copper (experiments on Ni–Cu/SiO_2 were designed on the basis of a report [23] indicating that addition of Cu to Ni might change deeply the amount of bulk hydrogen). Complementary experiments were carried out over a sodium-promoted Ni/SiO_2 catalyst [18] reduced at 614 K. Dispersions measured by magnetism and hydrogen chemisorption were found to be 23 and 16%, respectively. Increasing the hydrogen pressure to 5 MPa results in a decrease of magnetization of 2.3%; this is in acceptable agreement with the data of figure 2, showing that alkali promotion does not change the general trend either. Data of figure 2 suggest that the sorption of hydrogen which occurs when the pressure increases from 0.1 to 5 MPa, is a surface phenomenon.

Figure 3 shows the variations of $\Delta M/M$ as a function of the logarithm of the pressure. A linear relationship is achieved, indicating that the amount of sorbed hydrogen varies as P^a. A similar equation was observed for hydrogen chemisorption over a Ni/SiO_2 catalyst in the range 1.3–30 kPa, with $a = 0.035$ at room temperature [19]. This value is of the same order of magnitude as that deduced from the data in figure 3, assuming that the decrease of saturation magnetization per sorbed hydrogen atom is 0.7 BM, viz. $a = 0.017$. These data confirm that hydrogen sorption resulting from an increase of pressure from 0.1 to 5 MPa is likely to be related to a surface phenomenon.

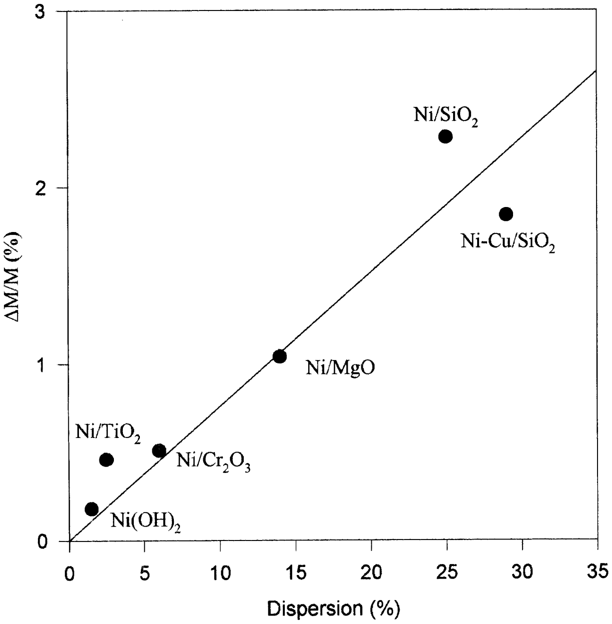

Figure 2. Variation of $\Delta M/M$, the relative change of magnetization of nickel-based catalysts when the hydrogen pressure varies according to 0.1–5–0.1 MPa cycles.

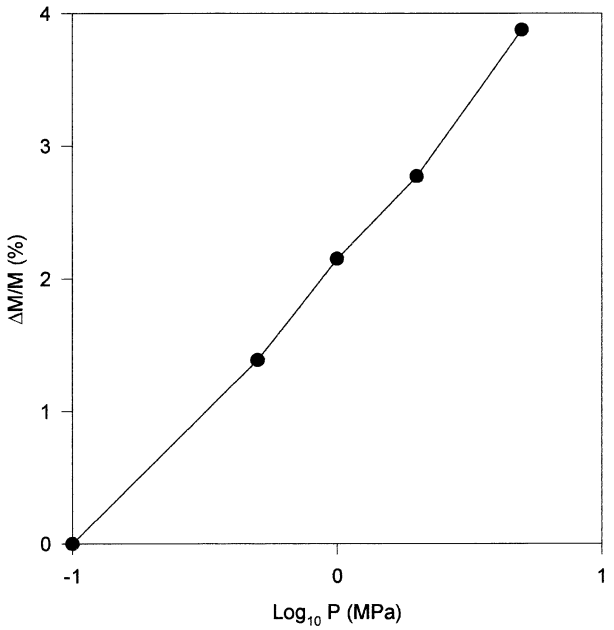

Figure 3. Variation of $\Delta M/M$, the relative change of magnetization of a Ni/SiO_2 catalyst with the logarithm of the hydrogen pressure, expressed in MPa.

3.4. Carburation of Ni in the course of the CO/H_2 reaction

Table 3 shows the change of the fraction of ferromagnetic nickel before and after CO/H_2 reaction and after hydrogenation of the used catalyst. As can be seen, after hydrogenation, the fraction of ferromagnetic metal lost during the reaction is restored. We have shown elsewhere [18] that the decrease of f occurring after reaction has to be related to the formation of carbon deposits chemically interacting with the metal phase. These surface and bulk carbides are not ferromagnetic.

The extent of carbidization of the nickel phase is given by the difference between f_0 before reaction or after hydrogenation (an average value is taken) and after reaction, f_1.

To assess the depth of carbidization (the number of nickel sublayers which cease from participating in ferromagnetism upon carbide formation) it is worthwhile to compare the latter with dispersions (table 1). The number n of nickel sublayers involved in the carbidization is calculated from the ratio $(f_0 - f_1)/\Delta$ shown in table 3. The n sequence,

Table 3
Fraction of ferromagnetic nickel before and after CO/H_2 reaction, and after hydrogenation of the aged catalyst

Catalyst	f, fraction of ferromagnetic Ni (%)			n
	before reaction [a]	after reaction [b]	after hydrogenation [c]	number of carbided sublayers
Ni/SiO_2	68	52	72	0.7
unsupp. Ni	97	92	98	3.7
Ni/TiO_2	97	88	95	3.2
Ni/Cr_2O_3	97	91	95	0.85

[a] Under hydrogen at 300 K, after reduction.
[b] Same catalytic conditions as in table 2.
[c] At 573 K for 2 h in flowing hydrogen.

$$SiO_2 < Cr_2O_3 < TiO_2 < \text{unsupported}\,, \qquad (9)$$

is very similar to sequence (7) for chain lengthening probabilities, owing to uncertainties on magnetic measurements and dispersion. This is in quite good agreement with conclusions drawn from a study of sodium addition to Ni/SiO_2 catalyst: in the presence of this promoter, a simultaneous increase of the selectivity toward C_{2+} hydrocarbons and of the carbidization of the nickel phase was observed [18].

4. Discussion

As shown in figure 2, hydrogen sorption, observed when the pressure increases from 0.1 to 5 MPa, is a surface phenomenon. It could be related to a completion of the first layer, quite compatible with dispersion: according to the slope of figure 2 this would represent ca. 8% of the first layer. Accordingly, hydrogen adsorption at 0.1 MPa would underestimate dispersion by a factor of 1.08.

Alternatively, hydrogen sorption occurring as the pressure increases can be due to the formation of a partial hydrogen sublayer. So far, magnetic methods do not allow discrimination between both hypotheses. They just discard the hypothesis of the formation of noticeable amounts of hydrogen atoms dissolved into the whole bulk of nickel. This situation is not conclusive with regards to the initial question initiated by the experiments of Ceyer et al. [5,6].

Fortunately, the carbiding experiments are much less ambiguous: an interesting correlation is observed between the chain lengthening probability and the depth of carbiding of nickel catalysts in the course of the catalytic reaction. As a first stage, nickel carbide can be considered as the active phase, leading mainly to C_{2+} hydrocarbons, whilst metal nickel would lead to methane. This explains why $S_{C_{2+}}$ increases. Alternatively, another hypothesis can be considered. Carbon atoms of sublayers, C_{subl}, might participate directly in the homologation reaction according to a mechanism similar to that proposed by Ceyer for the methane formation from surface methyl groups, $CH_{3\,surf}$ and bulk hydrogen atoms, H_{bulk} [5]:

$$CH_{3\,surf} + H_{bulk} \rightarrow CH_{4\,gas} \qquad (10)$$

The equivalent reaction would be

$$CH_{3\,surf} + C_{subl} \rightarrow \overset{\diagdown}{\underset{\diagup}{-}}\mathrm{C}{-}CH_3 \qquad (11)$$

It can be noted that the ethylidyne species is an isomer of the vinylic species $\mathrm{H{-}\underset{|}{C}{=}CH_2}$ which has been recently proposed as an intermediate in the Fischer–Tropsch synthesis [24].

5. Conclusion

This work has shown that increasing the hydrogen pressure over Ni-based catalyst from 0.1 to 5 MPa results in a subsequent sorption proportional to the metal dispersion, attributable either to a completion of the surface adlayer, or to the formation of a partial hydrogen sublayer. No relationship was found between the selectivity toward C_{2+} hydrocarbons in CO hydrogenation and the extent of this subsequent sorption. In contrast, a relation between this selectivity and the extent of carbide formation in the reaction course was demonstrated: the larger the amount of nickel carbide, the higher the chain lengthening probability. This suggests that carbon atoms of subsurface sites are involved in the homologation mechanism.

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