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ALKALI-INDUCED SIEVING EFFECT IN Ni ON SILICA CATALYSTS

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It is suggested that the addition of potassium nitrate to a Ni/SiO_2 precursor results, after reduction, in a blocking of nickel particles by a K-containing compound. The potassium film is supposed to act as a molecular sieve: it is permeable to a small molecule (H_2) and inhibits the access of large molecules to the nickel.

Keywords: Alkali promoter, potassium, Ni on silica catalysts, decoration, sieving effect

The addition of alkali promoters to heterogenous catalysts has long been known to improve their properties [1]; this is the case for catalysts involved in reactions of major industrial importance such as ammonia synthesis, oxidation of SO_2 into SO_3, dehydrogenation of ethylbenzene into styrene, epoxidation of ethylene... In spite of its economic importance, however, little is known on the mechanism of the influence of alkali addition.

Our laboratory has focused its researches on model catalysts consisting of nickel carried on silica promoted with alkali compounds [2–6]. In the course of this study, we have shown that the alkali compound is ionic [2] (K^+, Na^+ ...) and associated with a counteranion. According to the results of a selective extraction method [4,7], the alkali promoter consists mainly of alkali silicate. This is at variance with the case of Na and K vapodeposited on Ni(111), which are under the form of $K^{\delta+}$ ($Na^{\delta+}$) with δ varying from 0.5 to 0 as the coverage increases [5], and which are not associated to an anion. Furthermore, we have studied CO chemisorption on both systems [5,6]: all things being equal, the vibration frequency of CO adsorbed on Ni(111) precovered with vapodeposited alkali metals is lower for K than for Na. The reverse is observed for promoted Ni/SiO_2: The smaller the ionic radius of the alkali promoter (Na) the lower the CO wavenumber. On the analogy of organometallic compounds, this was interpreted assuming a direct electrostatic interaction between the oxygen atom of adsorbed CO and the ionic alkali in the promoted Ni/SiO_2 while an indirect interaction via the metal would be prevailing for the case of Ni single crystal precovered with vapodeposited alkali metals.

Table 1
The addition of potassium to Ni/SiO_2 catalysts does not result in large change of Ni particle size and of saturation magnetization. The amount of chemisorbed gas however, is decreased. The larger the size of the adsorbing molecule, the smaller the adsorbed volume.

	Ni/SiO_2	$K-Ni/SiO_2$
D electr. microsc. (nm)	3.92	5.45
D' magnetism (nm)	4.06	6.19
Average $(D+D')/2$ (nm)	3.99	5.82
BET surface area (m^2/g)	190	40
Ni areas [a] (m^2/gNi)	75	51
M_s (emu/g)	52.7	52.7
VH_2 10 T, 300 K (mlNTP/gNi)	40	20.5
VO_2 10 T, 300 K (mlNTP/gNi)	38	15
VCO 1 T, 300 K (mlNTP/gNi)	47.3	5.4
VC_2H_6 1 T, 300 K (mlNTP/gNi)	6	0.0

[a] assuming a spherical shape

For the case of alkali-promoted Ni/SiO_2 if the oxygen atom of adsorbed CO interacts with the ionic alkali, and if the carbon of CO is chemically bonded to Ni, as suggested by the decrease of Ni magnetization observed upon CO chemisorption [2], then it can be speculated that the alkali-containing phase is near the metal surface. This behaviour can give rise to a loss of accessibility of metal particles to gas chemisorption.

In this note we describe results obtained on potassium-promoted Ni/SiO_2 which suggests strongly that alkali compounds also decorate Ni particles. Moreover it is speculated that it induces a sieving effect, inhibiting the access of larger molecules to the nickel surface.

Experiments were conducted on solids described elsewhere [2–4]. Let us recall that the $Ni(OH)_2/SiO_2$ precursor is obtained by reacting silica aerosil from Degussa with a nickel nitrate hexammine solution (24% Ni by weight). The K-containing solids are prepared by adding the precursor to a KNO_3 solution (2.2 wt% K). The solids were treated in flowing hydrogen at 923 K to make the reduction of nickel complete and then outgassed at 723 K. Morphological characterization by electron microscopy and magnetic measurements (assuming a superparamagnetic behavior) reveals that the addition of potassium increases by about 50% the Ni particle size (table 1). The chemical interaction between Ni and the potassium phase is likely to be small since the saturation magnetization of Ni, M_s, is not altered by K addition [2] (if all the surface nickel atoms were chemically interacting with the promoter, we would expect a variation of magnetization which would be of the order of magnitude of the dispersion, i.e 25%).

Gas chemisorption experiments were carried out in a volumetric apparatus. In table 1 the volume of gas adsorbed at room temperature under 10 Torr by unpromoted and promoted Ni/SiO_2 catalysts can be compared. From this table, it can be seen that potassium inhibits more or less completely ethane adsorption while the amount of H_2 chemisorption is decreased by only about 50%. O_2 and CO adsorptions are intermediate. As a first step it can be tentively assumed that this situation results from some dramatic electronic modification of Ni properties induced by the alkali addition which could lead to a selective change in bond strength between Ni and adsorbates. This hypothesis, however, is not in good keeping with the fact that M_s is not altered by potassium addition (table 1). Furthermore, unpublished calorimetric measurements reveal that the initial heats of chemisorption of H_2 and CO are almost unchanged by potassium addition [8], making this interpretation unplausible and confirming that the electronic state of surface nickel atoms is not perturbed to a large extent. Alternatively, it can be assumed that the accessibility of adsorbing molecules to the nickel surface is hindered by potassium and that this hindrance is sensitive to the size of either the ensemble required for chemisorption or of gaseous molecules. This can be made more quantitative by defining the gas accessibility, a, in K-promoted catalysts as the ratio of the volume of adsorbed gas on K-Ni/SiO_2 to that on unpromoted Ni/SiO_2 after proper correction for Ni size effects:

$$a = \frac{V_2}{V_1} \frac{D_2}{D_1}$$

where V, D stand for volume of adsorbed gas, diameter of Ni particles, and subscripts 1 and 2 refer to unpromoted and promoted catalysts, respectively. As can be seen from table 2, the accessibility thus obtained is not the same for all gases and the larger the size of the adsorbing molecule, the smaller the accessibility a.

Another molecule, H_2S, the size of which is intermediate between that of CO and C_2H_6, was put to the test. Volumetric techniques, however, are not ap-

Table 2
The accessibility of Ni in K-Ni/SiO_2 calculated from volumetric methods (a, data of table 1) are in agreement with that obtained from data of table 3 (a', based on the decrease of saturation magnetization). The larger the size of adsorbing molecules, the smaller the accessibility. This result suggests that alkali addition to Ni/SiO_2 induced a sieving effect never reported so far.

	Volumetric method a	Magnetic method a'	Size of molecule adsorbing molecule	
			length (nm)	width (nm)
H_2	0.75	1.05	0.31	0.24
O_2	0.58	0.43	0.39	0.28
CO	0.16	0.20	0.42	0.37
H_2S		0.07	0.436	0.40
C_2H_6	0.0	0.0	0.526	0.46–0.49

propriate to measure the volume of adsorbed H_2S on Ni since a part can be adsorbed on the alkali phase. To estimate the accessibility of Ni surface to H_2S chemisorption, the decrease of the saturation magnetization, ΔM_s of nickel upon chemisorption was measured. This technique was first used by Carter et al. [9] for the case of hydrogen chemisorption on Ni/SiO_2. It is assumed that each surface Ni atoms interacting with adsorbates loses its contribution to the ferromagnetism. Thus the relative decrease of saturation magnetization upon adsorption, $\delta = \Delta M_s/M_s$, is a measure of the fraction of Ni atoms involved in chemisorption and gives directly the fraction of surface atoms (dispersion) when a monolayer is formed and when all surface atoms are accessible. Carter et al. [9] have checked that when using hydrogen chemisorption on Ni/SiO_2 under one atmosphere at room temperature, the results thus obtained are in good agreement with data of X-ray line broadening. For our case this method gives $\delta = 25\%$ for H_2 chemisorption on Ni/SiO_2. If this value is taken as a measure of the nickel dispersion, it corresponds to the fraction of surface nickel atoms of a Ni cubooctahedron having an equivalent diameter of 3.84 nm. This is in good agreement with electron microscopy data (3.92 nm) and magnetic data assuming that Ni particles are superparamagnetic (4.06 nm). Now if a fraction of the Ni surface is not accessible to chemisorption, for example because of the presence of a potassium compound on the Ni surface, the relative decrease of saturation magnetization δ_2, is smaller. The ratio δ_2/δ_1 corrected from Ni size variation due to K addition, gives a reasonable estimation of the accessibility of Ni to gas chemisorption

$$a' = \frac{\delta_2}{\delta_1} \frac{D_2}{D_1}.$$

This method was used for the chemisorption of H_2, O_2, CO and extended to the case of H_2S which interacts with Ni and the K-containing phase. The results are shown in table 3. The dispersion of Ni in unpromoted Ni/SiO_2 obtained from O_2 and CO chemisorption by this method is in good agreement with that obtained from hydrogen experiments (23, 25.3 and 25%, respectively), thus

Table 3
The relative decrease of saturation magnetization of Ni upon chemisorption gives an estimation of the fraction of Ni atoms involved in chemisorption

$\delta = \Delta M_s/M_s$ (%)		
	Ni/SiO_2 δ_1	$K\text{-}Ni/SiO_2$ δ_2
H_2	25	18
O_2	23	6.8
CO	25.3	3.4
H_2S	50	2.4
C_2H_6	11	< 0.2

extending the validity of this method to these adsorbates. The larger value of $\delta_1 = \Delta M_s / M_s$ obtained for the case of H_2S chemisorption reflects the fact that H_2S adsorption on Ni is corrosive and attacks both the external Ni layer and atoms in the bulk [10]. The smaller value corresponding to ethane adsorption on Ni/SiO_2 can be explained in the following way: Ethane adsorption on Ni needs large ensembles composed of at least 6 adjacent Ni atoms. It is understandable that such an adsorption leaves free Ni atoms more or less isolated which cannot be used for further ethane adsorption.

It can also be noticed that ethane adsorption on Ni/SiO_2 is only 15% of hydrogen adsorption when measured by chemisorption while it is 44% when measured by magnetic measurements. This is due to the fact that the decrease of saturation magnetization per adsorbed molecule is smaller for the case of hydrogen [11] (1.5 and 4–4.8 Bohr magneton per adsorbed molecule for hydrogen and ethane, respectively).

The accessibility of Ni atoms to gas chemisorption in K-promoted Ni/SiO_2 catalysts, a', calculated from magnetism variations can be compared with that obtained from volumetric method in table 2, where the sizes of adsorbate molecules have also been reported. As can be seen the agreement between both methods is satisfying. As a first step, it can be speculated that the decrease of accessibility of promoted nickel when going from H_2 to C_2H_6 results from ensemble effects: the nickel surface would be partially blocked by patches of promoter; adsorption of molecules involving small ensembles of nickel atoms would be less hindered than adsorption requiring large ensembles. The size of the ensemble can be estimated from the "bond number", i.e. the number of nickel atoms which are demagnetized per adsorbed molecule [2,10,11]. For H_2, O_2 and CO chemisorption, the ensemble sizes are nearly the same (ca. 2 Ni atoms) while the loss of accessibility reported in table 2 decreases by a factor 5 when going from H_2 to CO. Thus, it seems reasonable to discard the hypothesis of an ensemble effect.

Results of table 2 show unambiguously that the larger the size of adsorbing molecules, the smaller the accessibility to Ni in promoted catalysts. To account for this observation, it can be assumed that the K-containing phase decorates nickel particles. Leaching experiments with water and alcohol to remove selectively potassium compounds have shown [7] that a significant part of the potassium forms a stable silicate. This potassium compound layer would be microporous. The pore aperture would be larger that 0.24 nm (Ni is nearly completely accessible to H_2 chemisorption) and smaller than 0.46 nm since ethane adsorption is nearly completely inhibited. The situation thus described is similar to that of metal particles encaged into zeolites where catalytic phenomena related to the metallic phase are modified by molecular sieving effects [12]. We are now examining how far the alkali-induced sieving effects depend on the amount of alkali, the reduction temperatures and the chemical nature of the support and of the alkali.

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