Regeneration of Ni / SiO_2 poisoned with carbon disulfide

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The poisoning effect of carbon disulfide on a model nickel/silica catalyst and the regenerating role of both pure hydrogen and 2-butyne + hydrogen are reported. The treatments induce the elimination of sulfur and promote a recovery of the catalytic activity; irreversible adsorbed sulfur still remains on the catalyst.

Keywords: regeneration; poisoning; nickel/silica catalyst

1. Introduction

In spite of the industrial importance of regeneration, few attempts to regenerate sulfur-poisoned nickel catalysts have been published. Few results have been reported about the removal of sulfur linked to nickel using hydrogen streams at different temperatures [1–4]. Aguinaga and Montes [5] proposed a method for the regeneration of thiophene-poisoned nickel catalysts with sequential oxidation–reduction treatments using mixtures with low oxygen partial pressure and pure hydrogen respectively, separated by argon stream purging. All sequential steps were performed at 773 K.

Rostrup-Nielsen [6], using H_2O/H_2 mixtures at 973 K, removed 80% sulfur from nickel catalysts used for methanation. These satisfactory results were, however, obtained with methanation catalysts, which have low metal dispersion and are very resistant to sintering. The operational conditions in which the regeneration treatments used for methanation catalysts were carried out would provoke a dramatic sintering on highly dispersed Ni catalysts used for selective hydrogenation reactions.

On platinum, Oudar et al. [7,8] detailed a mechanism of sulfur displacement from highly to less energetic adsorption sites by poly-unsaturated molecules, like butadiene, in the presence of hydrogen.

The objective of this paper is to describe the poisoning effect of carbon disulfide on a model silica-supported nickel catalyst during the hydrogenation of styrene, and the regenerating role of both pure hydrogen and 2-butyne in the presence of hydrogen, on the poisoned catalyst.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by impregnation of a non-microporous, high surface area, silica (Aerosil Degussa, 200 $m^2\ g^{-1}$) with an aqueous solution of nickel hexamine nitrate, as described previously [9]. The preparation conditions allowed one to obtain a highly loaded catalyst with a well dispersed metallic phase and a quite narrow particle size distribution. To obtain these metallic properties, the catalyst was activated as follows:

(i) heating under argon stream at 5 K min^{-1} up to 673 K and keeping this temperature during 2 h;

(ii) cooling back to room temperature;

(iii) heating at 3 K min^{-1} under hydrogen flow, up to 873 K and maintaining that temperature for 6 h.

2.2. Catalyst characterization

Nickel dispersion and reduction degree were determined by magnetic measurements which were carried out using an electromagnet having a magnetic campus

(H) of 21 kOe. The specific magnetization (M_S) was measured by means of the Weiss axial extraction method. M_S is proportional to the amount of reduced ferro-magnetic metal, and the degree of reduction can be calculated by comparing with the total amount of metal [9].

XPS data were obtained using a Shimadzu ESCA 750 electron spectrometer and processed with a Shimadzu ESCAPAC 760 data system. The C 1s line at 285.0 eV was taken as an internal standard and was used to correct possible deviations caused by electric charge of the samples. The samples were introduced in the preparation chamber of the XPS equipment following the operation procedure described by Mallat et al. [10], in order to protect the samples from exposure to air.

STEM-EDX characterization was carried out with a high-resolution VG HB 50S scanning transmission microscope, operated at 100 kV and fitted with a Tracor energy dispersive X-ray spectrometer. The method was used to determine the ratio S/Ni of the unpoisoned, poisoned and regenerated catalysts. Each sample was analyzed under different conditions in order to obtain both general and local analyses. In that latter condition, it has been possible to analyze single nickel particles on top of the silica carrier.

Catalytic activity was determined in a stirred tank reactor operated at 22 kg cm^{-2} hydrogen pressure, $W/F = 0.02$ g h ml^{-1}, 353 K and stirring velocity 700 rpm, as previously described [11]. The catalyst weight was 1 g. No diffusional limitation was observed under these conditions [12]. Analyses of reactant and products were carried out chromatographically using FID and a 6 m DC-200 column. The activity per exposed metal atom was calculated from the conversion versus time curves.

The selective hydrogenation of styrene to ethylbenzene was used as the test reaction. A 5% styrene in toluene solution (I) or the same solution containing 100 ppm carbon disulfide (Carlo Erba R.P.E.) (II) were used as feedstocks.

Regeneration procedures:

With pure hydrogen: After measuring the activity in the presence of feed II, the reactor was drained, the temperature increased to 473 K under a hydrogen pressure of 20 kg cm^{-2} and the catalyst treated under these conditions for 10 h. Then, the temperature was decreased, the poison-free feed introduced and the catalytic activity measured under standard conditions.

With 2-butyne and hydrogen: As in the preceding case, the reactor was drained off after the determination of the activity with the poisoned feed II; a solution of 300 ppm of 2-butyne in toluene was introduced into the reactor by means of a liquid-pump, without contacting the catalyst with the atmosphere. The temperature was then increased to 473 K under a hydrogen pressure of 1.5 kg cm^{-2}, with agitation, and these conditions were maintained for 5 or 10 h. The treatment is a batch process, and a $W/V = 0.0022$ g cm^{-3} was used, where V is the volume of the 2-butyne solution used. The 2-butyne containing feed was then drained off, the temperature decreased and the poison-free feed (I) introduced. The catalytic activity of the regenerated catalyst was finally determined. For comparative purposes, the same procedure was followed using toluene alone, instead of toluene +300 ppm 2-butyne, under the same temperature and hydrogen pressure.

3. Results

The Ni content of the catalyst, as determined by chemical analysis, was 20.9%. The reduction degree and the nickel dispersion, measured by magnetic measurements were 100 and 25% respectively. This corresponds to a particle size close to 4.5 nm, a value in good agreement with TEM observations.

The activity in the selective hydrogenation of styrene to ethylbenzene for the unpoisoned, poisoned and regenerated catalysts, expressed as relative activity (related to the unpoisoned catalyst), is presented in table 1. Each datum is the average of five runs; the standard deviation is ±0.005. Values were obtained at the steady state. In order to investigate whether the results may be affected by slow deactivation due to carbon formation, runs of 30 h length were performed in the absence of poisons. The activity remained always constant. Thus, deactivation due to carbon formation during the activity tests may be neglected.

It can be observed that, in the presence of 100 ppm CS_2, there is an important decrease in activity. Toluene, under a 1.5 kg cm^{-2} H_2 pressure does not display any regeneration capacity, which would have been assigned to a washing effect of toluene. Also, there is no regeneration effect under a hydrogen pressure of 1.5 kg cm^{-2}.

Both 2-butyne in the presence of 1.5 kg cm^{-2} hydrogen pressure and pure hydrogen under a pressure of 20 kg cm^{-2} produced a regeneration of the poisoned catalyst, of the same order of magnitude. An increase of the time of exposure to 2-butyne + hydrogen, from 5 to 10 h did not induce a better regeneration effect. Under the present conditions of regeneration, an irreversible nickel poisoning by CS_2 still exists. It has been verified that

Table 1

Relative activity of unpoisoned, CS_2-poisoned and regenerated catalysts in the selective hydrogenation of styrene

Catalyst	Relative activity
without poison	1.00
100 ppm CS_2	0.09
regenerated toluene	0.09
regenerated 2-butyne, 5 h ($P_{H_2} = 1.5$ kg cm^{-2})	0.21
regenerated 2-butyne, 10 h ($P_{H_2} = 1.5$ kg cm^{-2})	0.22
regenerated H_2, 1.5 kg cm^{-2}	0.09
regenerated H_2, 20 kg cm^{-2}	0.22

the regeneration treatments did not produce significant modification of the nickel particle size, as seen by TEM.

XPS analyses of the poisoned catalyst, show a S 2p peak at 161.4 eV, which may be assigned to sulfur of CS_2 adsorbed at the surface or to a nickel–sulfur bond. The C 1s peak was detected at 285.0 eV, with FWHM = 2.1 eV. As the binding energy of C 1s, in molecular CS_2, is 286.9 eV [13,14], the presence of molecularly adsorbed CS_2, at the catalyst surface, can be neglected.

The S/Ni ratios, collected by STEM-EDX analyses, are shown in fig. 1, for the different catalysts. A small amount of sulfur appears on the freshly reduced catalyst. After poisoning, a large increase in the S/Ni ratio is observed; this ratio is similar for large areas and isolated nickel particles, suggesting that the poisoning of nickel is rather homogeneous and that the adsorption of CS_2 on the support is not important. The S/Ni ratio has decreased after regeneration with hydrogen under 20 kg cm^{-2} and even lower after regeneration with 2-butyne + 1.5 kg cm^{-2} hydrogen pressure.

4. Discussion

According to the results shown in table 1, both hydrogen at a pressure of 20 kg cm^{-2} and 2-butyne in the presence of a small pressure of hydrogen are effective for the regeneration of Ni/silica catalyst poisoned by CS_2, during the selective hydrogenation of styrene. A decrease in the S/Ni ratio, after regeneration treatments, is observed all over the catalyst, indicating thereby that sulfur has been eliminated from the catalyst and that it is not only redistributed/redispersed on the active phase.

According to the XPS results of the poisoned catalyst, molecular CS_2 is not present on the catalyst surface; it can be considered that sulfur interacts with Ni particles to form surface and subsurface Ni_xS_y species which are not active for the hydrogenation reaction or which have an intrinsic activity very much lower than purely metallic nickel surface. It has been previously reported that the adsorption of CS_2 on nickel, even at room temperature, is dissociative and highly corrosive [9].

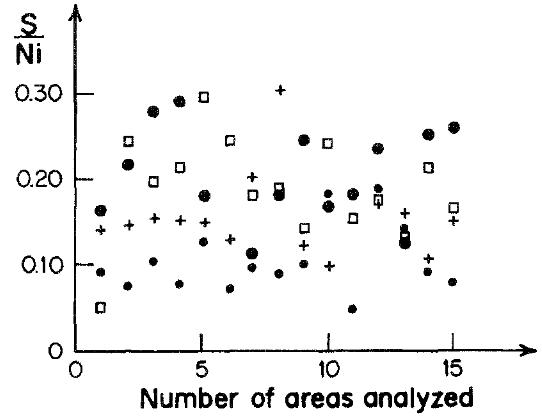

Fig. 1. Sulfur–nickel ratios from STEM/EDX analysis: (•) Ni/SiO_2 simply reduced; (●) Ni/SiO_2 after poisoning with CS_2; (□) Ni/SiO_2 poisoned with CS_2 and regenerated with H_2 (20 kg cm^{-1}); (+) Ni/SiO_2 poisoned with CS_2 and regenerated with 2-butyne.

The treatment of the poisoned catalyst with 2-butyne together with a very low pressure of hydrogen, produced a hydrogenation activity recovery of about 22%. The semi-quantitative results from STEM/EDX also show that some sulfur have been eliminated due to the treatment with 2-butyne. Oudart et al. [7] working with a Pt(110) surface, observed that starting from an ordered sulfur–metal surface, sulfur atoms are removed by non-saturated molecules like butadiene when hydrogen is present, from hollow sites to the sites where hydrogen dissociation takes place, and on which they are randomly adsorbed. Adsorption isotherms provided Oudart et al. [7] additional information on the sulfur–sulfur interactions and on the decrease in the sulfur–metal binding energy, induced by the presence of the unsaturated organic molecule. The identification of alkylthiols in the desorption spectrum reflected the formation of hydrogenated compounds containing both sulfur and carbon on the platinum surface. In accordance with the results of Oudart et al. [7], we can consider that, after butyne adsorption, there is a decrease in the binding energy of sulfur, which facilitates its elimination, through association with hydrocarbon fragments after a consecutive or parallel hydrogenation.

The treatment under hydrogen at high pressure and 673 K also produced a recovery in the activity of nickel catalyst poisoned by CS_2. It can be supposed that under such conditions, a part of the adsorbed sulfur, or of sulfur present as Ni_xS_y surface compound, may be eliminated as H_2S.

Although the recoveries of the hydrogenation activity produced by both H_2 at 20 kg cm^{-2} and 2-butyne, in the presence of H_2, are almost the same, STEM/EDX analyses show that 2-butyne eliminates more sulfur than hydrogen from the catalyst. This may indicate that, after 2-butyne treatment, carbonaceous materials still exist on the catalyst surface, thus producing a decrease in activity, in spite of a better sulfur elimination. Alternatively, a larger content of subsurface sulfur could be present in the nickel phase treated with a higher hydrogen pressure.

5. Conclusions

Treatments with either pure hydrogen at a pressure of 20 kg cm^{-2} and at 473 K or 2-butyne in the presence of hydrogen of a CS_2 poisoned Ni/silica catalyst induce an elimination of sulfur from the catalyst and promote a recovery of the catalytic activity during the selective hydrogenation of styrene. Under the conditions presently used for the catalyst regeneration, irreversibly adsorbed sulfur still remains in the catalyst. Due to the mild conditions used for catalyst regeneration, no modifications on Ni dispersion were observed, this being an advantage of the proposed regenerating procedure.

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