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Nanonickel particles supported on silica. Morphology effects on their surface and hydrogenating properties

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We have studied a whisker-like nickel phase supported on silica and obtained by the reduction of nickel acetate in aqueous hydrazine media. Under H_2/300 °C flow, the obtained phase remains stable when the reduction is carried out at 70 °C for 2 h whereas it totally tranforms to spherical-like particles when the reduction is performed at 80 °C for 30 min after a gradual heating from room temperature. It is shown that the whisker-like nickel phase adsorbs and stores more hydrogen than the spherical-like nickel particles. It also exhibits a higher activity in the gas phase hydrogenation of benzene (3–4 times greater). In acetylene hydrogenation, it strongly favors the cylotrimerization process to benzene at the expense of the processes to linear C_2–C_4 hydrocarbons. This work is a direct demonstration of the influence of the metal phase morphology of nickel supported catalysts on their surface and catalytic properties.

KEY WORDS: nickel; whiskers; morphology; catalyst; benzene; acetylene; hydrogenation; adsorption.

1. Introduction

The challenge in the preparation of supported metal catalysts is the control of the morphology, i.e. size and shape, of the final materials. Indeed, it is well established that the method of preparation influences the performances of a given catalyst, as a result of changes in the electronic and structural properties of the active phase [1–7]. The catalyst materials are usually prepared by *in situ* reduction of a metal salt or oxide. An alternative method used to obtain supported catalysts with well-defined metal particles is the preparation *via* metal colloids.

In recent years, a great deal of attention has been paid to metal nanoparticle research due to their unusual properties as compared to those of the bulk metal. At the nanoscale, metal particles exhibit unusual electronic, optical, magnetic and chemical properties due to their extremely small size and large surface to volume ratio [8–10]. They have potential applications as advanced materials [8–10] and also have been utilized in heterogeneous catalysis [11–15]. The chemical route of preparation of such materials is of specific interest since it allows better structural control on the microscopic level [16–18]. The chemical methods have generally involved the reduction of the relevant metal salt in the presence of stabilizers which prevent the nanoparticles from agglomerating [19–21].

We have undertaken a systematic study of nickel metal nanoparticles (%Ni<5%) prepared by reduction of nickel acetate by hydrazine in aqueous media and supported on silica of low surface area (15 $m^2\ g^{-1}$) [22–25]. Preliminary experiments showed that no reduction occured with silica of high surface area [23]. In addition, nickel supported catalysts have been concerned with high surface area supports and metal loadings. Also the use of silica of low surface area and low metal loadings in the preparation of nickel based catalysts was expected to give rise to an important contribution to the existing corpus of literature on Ni/SiO_2 systems. The reduction led to metal crystallites of mean particle size increasing (3–20 nm) with increasing nickel loading (1–5%). The chemisorptive and catalytic properties of the supported particles prepared have also been studied. It was shown that they stored more hydrogen and were more active in benzene hydrogenation than conventional catalysts [24]. Their reactivity was also different from that of classical catalysts in acetylene cyclotrimerization under hydrogen atmosphere [25].

In a recent work, we showed that, strikingly, the fresh non-classical nickel phase was of whisker-like morphology only for low metal loadings (<2%Ni), whereas various shapes, mainly spherical, were obtained for higher loadings [23]. The whisker phase is believed to form through nanoparticle coalescence in interaction with the support. In addition, after a hydrogen thermal treatment, the whiskers-like phase transformed to various nanoparticle shapes. These findings prompted us to study the stability and surface and hydrogenating properties of a whisker-like nickel phase as a function of the mode of preparation. The metal surface properties of the catalysts prepared were examined by H_2-adsorption and temperature programmed desorption (H_2-TPD). Their hydrogenating capability and selectivity were tested in the gas phase hydrogenation of benzene to cyclohexane or of acetylene to benzene. The catalyst

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structure was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques.

The test-reactions used are of both practical and fundamental interest. Indeed, the hydrogenation of aromatics is of major importance in the production of diesel fuels [26]. Benzene hydrogenation has been chosen as the model aromatic feedstock [27–29]. In academic research, this reaction is considered as model reaction in heterogeneous catalysis by metals where metal–support interactions are involved [27–30]. As to selective hydrogenation reactions, they have been employed for several decades to eliminate dienes and acetylenic compounds in hydrocarbon feedstocks [31,32]. Acetylene and ethylene undergo several surface reactions and selected product(s) can be formed through selected reaction conditions and metal surfaces [32–35]. It was shown that benzene can be formed in acetylene hydrogenation [25,35].

2. Experimental section

2.1. Catalyst preparation

The catalysts (1%Ni content) were prepared [24] by reducing a suspension of nickel acetate (≥99.0%, Fkuka) supported on silica (Chempur, 99.99%, 15 m^2 g^{-1}, grains of 325 mesh) by an excess aqueous hydrazine (Fluka, 24–26%, ≥99.0%) at pH = 10–12 under argon atmosphere. Two procedures were used for the obtention of nanoparticles:(i) in the first one, as previously reported [23], the suspension of the supported precursor was stirred for 20 min at room temperature then hydrazine solution was added at once. The reaction mixture was slowly heated (4 °C min^{-1}) from room temperature to 80 °C, then maintained at this temperature for 0.5 h; (ii) in the second one, the suspension of the supported precursor was slowly heated from room temperature to 70 °C. At this temperature, hydrazine solution was added at once. The resulting suspension was maintained at the same temperature for 2 h. The materials obtained were denoted Ni/SiO_2(PRG) and Ni/SiO_2(ISO) for programmed temperature and isothermal reduction procedures, respectively. They were filtered, washed several times with water until neutral pH was obtained, dried at 60 °C under vacuum then stored under argon.

2.2. Equipment

The nickel content of the catalysts was determined on a Varian AA1275 atomic absorption spectrophotometer. XRD patterns were recorded with a classical $\theta/2\theta$ diffractometer using CuK_α radiation. The electron microscopy images were obtained with a Phillips CM20 STEM after placing a drop of the nanoparticle suspension on the carbon coated copper grid. Hydrogen chemisorption or tests experiments were carried out in fixed bed microreactors equipped with Hewlett Packard AT M200 TCD or 5730A FID gas chromatographs respectiveley. The chromatographs were fitted with molecular sieve or TCEP (2 m, 1/8 in.) and Sterling (3 m, 1/8 in.) columns, respectively. MTI or Kontron software were used.

2.3. Procedures for chemisorption and catalytic testings

The fresh samples (100 mg) were slowly heated in the reactor in pure H_2 flow to 300 °C, maintained at this temperature for 2 h and purged under argon flow for 2 h [until no hydrogen (<1 ppm v/v) was detected in the exit gases]. It was then cooled under argon atmosphere to room or reaction temperature for chemisorption or testing studies, respectively. For the chemisorption experiments, a 100 ppm H_2/argon flow was injected in the reactor every 2 min at room temperature. After saturation, the sample was purged under argon flow. It was subsequently heated in programmed temperature to 700 °C with a heating rate of 10 °C min^{-1} in order to desorb hydrogen previously adsorbed. For testing experiments, the reactor was continuously fed at a flow rate of 50 mL min^{-1} with the required reactant mixture (1%C_6H_6/H_2 or C_2H_2 /H_2/He : 5/20/75). The reproducibility of the reaction rates was ±3%. The carbonaceous species deposited on the catalyst surface during acetylene hydrogenation were analyzed according to the following procedure. After 3 h of working, the used sample was *in-situ* cooled to room temperature, swept with helium for 2 h then flowed under hydrogen in programmed temperature to 500 °C at a heating rate of 10 °C min^{-1}. At the outlet of the reactor the C_1^+ gaseous products formed were trapped in liquid air. They were analyzed by gas chromatography (with the same columns as above) after heating the liquid air trap to room temperature. Methane was directly analyzed by gas chromatography. It appeared above 300 °C.

The freshly prepared catalysts do not adsorb hydrogen and are inactive in the hydrogenation reactions without a hydrogen thermal pre-treatment [24]. This is ascribed to the embedding effect of the organic matrix, stemming from the acetate fragment of the metal salt precursor and remaining on the catalyst surface after the aqueous reduction of nickel. This matrix hinders the access of the nickel active sites. After the hydrogen treatment, the organic matrix is removed (mainly as methane or/and carbon monoxide), and leads to the liberation of the metal active sites, thus rending the catalyst active.

3. Results and discussion

3.1. Catalyst characterization

The fresh catalysts exhibited an almost flat XRD signal for the nickel phase. Therefore, the metal particle size was estimated less than 2–3 nm. This size was not changed after a H_2 treatment of the catalysts at 300 °C for 2 h, as indicated the XRD spectra obtained. The TEM study showed that nickel was in *fcc* structure. In addition, strikingly, it also showed interesting features on the stability of the particle shape under the reducing atmosphere.

As previously reported [23], the reduction of supported nickel acetate by aqueous hydrazine, at 80 °C for 0.5 h and after a gradual heating from room temperature, led to a fresh Ni^0 phase with a whisker-like shape [Ni/SiO_2(PRG) catalyst]. After the hydrogen thermal treatment, the whisker shape completely transforms into Ni^0 particles with various shapes, mainly spherical. When, the reduction is isothermally carried out at 70 °C for 0.5 h, without pre-heating [Ni/SiO_2(ISO) catalyst], the Ni^0 phase obtained is also of whisker-like type as shown in figure 1a. However, in this case, the whisker phase remains stable after the hydrogen thermal treatment and no other shapes are observed (see figure 1b). Thus, after the thermal pre-treatment, either whisker-like or mainly spherical shapes can be obtained, depending on the mode of reduction of the precursor. The whiskers were about 20 nm length and 3 nm width before or after the hydrogen treatment. These various shapes induced very different surface and catalytic properties as reported below.

3.2. Reactivity towards hydrogen

Hydrogen chemisorption is one of the most widely used method to probe the chemical surface properties of metal supported catalysts [36]. Thus, for classical supported nickel catalysts reduced by gaseous hydrogen, it is admitted that the amount of adsorbed hydrogen is a good estimation of the metal dispersion. In addition, these catalysts give rise to H_2-TPD profiles comprising two or more reduction peaks as a result of the formation of several active sites [36]. Moreover, the amounts of desorbed hydrogen are generally greater than that previously adsorbed at room temperature. The additional amounts arise from hydrogen molecules dissociated on the metal phase then incorporated on the support or at the metal–support interface during the H_2-treatment [36–39]. This is the so-called hydrogen spillover [37].

A similar behavior was observed by our non-classical nickel catalysts after the hydrogen thermal treatment. The amount of hydrogen adsorbed depends on the shape of the nickel phase (table 1). The Ni/SiO_2(ISO) whisker phase adsorbs more hydrogen than the Ni/SiO_2(PRG) spherical-like particles:937 against 742 μmol g_{Ni}^{-1}.

The H_2-TPD of the catalysts prepared was also carried out. After the hydrogen adsorption at room temperature as described above, the materials were purged under argon flow then heated gradually to 700 °C. The temperature profiles obtained (figure 2) show that hydrogen desorption comprised two domains denoted type I (below 300 °C) and type II (above 300 °C), respectively. All the peaks are shifted to lower temperatures for the metal whisker-like phase in the Ni/SiO_2(ISO) catalyst. This phase exhibits a broad peak of type I centered at 100 °C with shoulders at 85 and

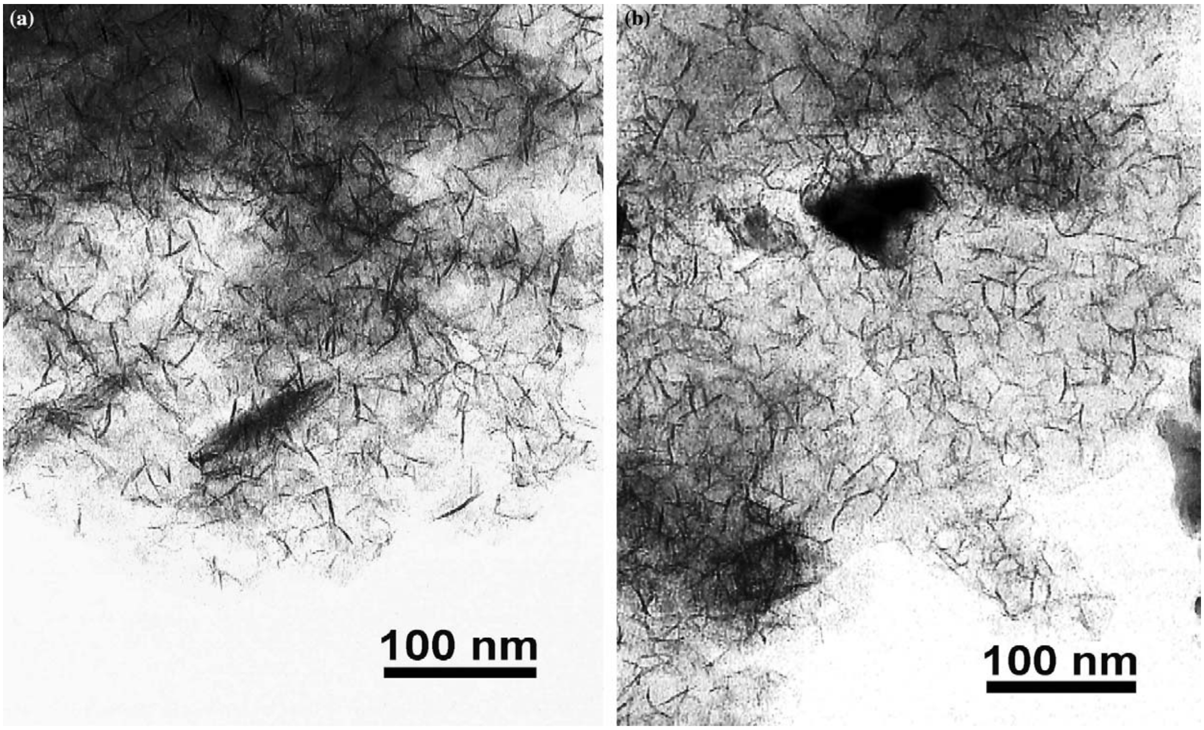

Figure 1. TEM micrographs of [Ni/SiO_2(ISO)]:(a) fresh sample; (b) after H_2/300 °C/2 h pre-treatment.

Table 1
Amounts of hydrogen chemisorbed, TOF's and energy of activation in benzene hydrogenation for the Ni/SiO_2 catalysts

Catalyst	% Ni	Adsorbed $H_2(\mu mol \cdot g_{Ni}^{-1})$	Desorbed H_2 $(\mu mol \cdot g_{Ni}^{-1})$	TOF's (75 °C (s^{-1}))	E_a (kJ mol^{-1})
Ni/SiO_2(PRG)	1.1	742	1210	0.033	44.7
Ni/SiO_2(ISO)	1.0	937	1587	0.089	24.1

Pre-treatment:H_2/300 °C/2 h.

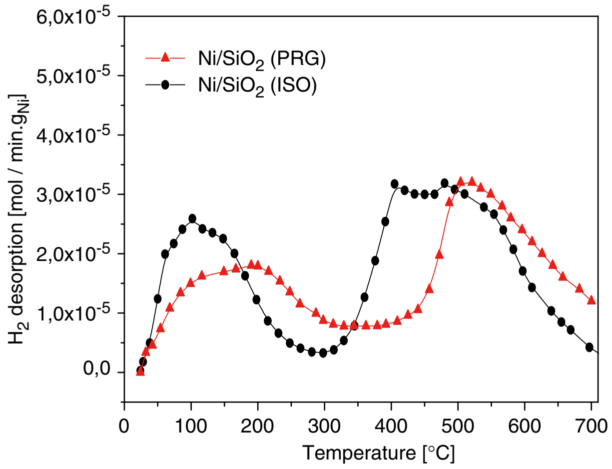

Figure 2. H_2-TPD of the Ni/SiO_2 catalysts after hydrogen adsorption at room temperature. Pre-treatment:H_2/300 °C/2 h.

160 °C, respectively and two peaks of type II at 410 and 495 °C, respectively with a shoulder at 565 °C. The supported spherical-like particles of Ni/SiO_2(PRG) show a plateau with two underlying peaks at low temperatures (100 and 190 °C, respectively) and a large dissymetric peak at a higher temperature (525 °C). The temperature peaks were ascribed to hydrogen weakly (type I) or strongly (type II) attached to the nickel active sites [24]. The high temperature peaks are believed to be due to the desorption of hydrogen spillover, more strongly bonded to the catalyst surface [24,36–39].

Hydrogen stored is ascribed to spilt-over species, namely the dissociation of H_2 on the metal sites then migration to the support of the hydrogen species formed from the metal [24,36–39]. For a given catalyst, the amount of stored hydrogen depends on the number of acceptor sites of the support [36–39]. This means that the Ni/SiO_2(ISO) catalyst contains a greater number of hydrogen storage sites than the Ni/SiO_2(PRG) catalyst. The hydrogen acceptor sites might have been formed during the preparation steps of the catalysts. Thus, whisker nickel is more reactive towards gaseous hydrogen than spherical nickel at room as well as high temperature. The exact nature of the hydrogen acceptor sites is still an open question [36–39].

3.3. *Gas phase hydrogenation of benzene*

In benzene hydrogenation both catalysts selectively produced cyclohexane. The activity increases with the reaction temperature and reaches a plateau then decreases. Strikingly, the whiskers phase was more active:in the conditions used, it converted benzene to cyclohexane to 100% from 120 °C whereas at this temperature the spherical-like particles gave a conversion of 50% only (figure 3). The maximum of conversion was lower (70%) and occurred at a higher temperature (from 140 °C) for spherical nickel. At low temperatures (<120 °C) the activity is 3–4 times greater for Ni/SiO_2(ISO) (figure 3). The turnover frequency (TOF), calculated at about 10% of conversion, was 3 times greater for the whisker-like phase (table 1). The Arrhenius plots show the changes of the reaction rate with rising temperature and were used for activation energies calculations (table 1). Whisker particles exhibit a lower energy of activation (24.1 kJ mol^{-1}) as compared to spherical-like particles (44.7 kJ mol^{-1}).

The existence of a temperature dependent aromatic molecule hydrogenation maximum on classical nickel based catalysts is now well established [24,28,29]. It is ascribed to a decrease in the surface coverage by the aromatic with increasing temperature which, at some point, results in a decrease in the reaction probability

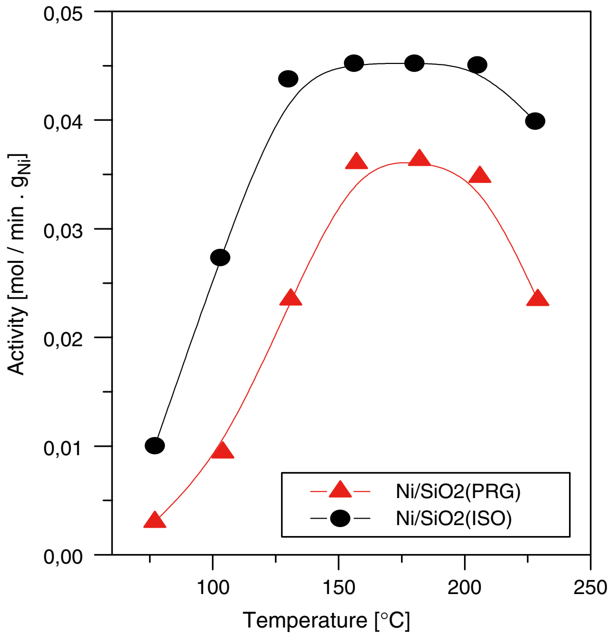

Figure 3. Activity in benzene hydrogenation for the Ni/SiO_2 catalysts. Pre-treatment: H_2/300 °C/2 h. m_{CAT} = 50 mg; F = 50 mL min^{-1}; C_6H_6/H_2 = 1%.

[24,28,29]. However, the observed maximum could also be accounted for by the competitive adsorption of the benzene and hydrogen reactant molecules [40,41]. This could also be the case for the present catalysts, as suggested a kinetic study of benzene hydrogenation over a set of non-classical nickel catalysts prepared by hydrazine reduction of supported nickel acetate [42].

The low value 24.1 kJ mol^{-1} for the activation energy of Ni/SiO_2(ISO) may be ascribed to kinetic limitations. Indeed, the existence of the maximum of activity(figure 3) and the great ratio (5–7) between the highest and the lowest activity in the range reaction temperature examined, allows one to exclude the existence of diffusion limitations for both catalysts. Moreover, we recall that the apparent energy of activation can be considered as the difference between the true energy of activation of the rate determining step and the energy of adsorption of the reactant molecules or intermediates in previous steps. Also, the experimental activation energies found (table 1) did account for the chemisorption reactions involved in the overall determining processes. Therefore, it can be conjectured that a high benzene adsorption energy could explain the lower experimental activation energy observed for the whisker nickel.

Sensitivity of reactions to the surface structure is an important and widely discussed point in heterogeneous catalysis [27–30,43,44]. It is based on the correlation between the variation of the TOF's as a function of the particle size. In the case of benzene hydrogenation on nickel catalysts, the structure sensitivity of the reaction is still an open question [27–29]. The controversy lies in the uneasy determination of the concentration of the active sites [29,43]. In the present experiments, the results obtained strongly indicate the intervention of the shape of the metal particles in the determination of the surface chemical processes, that is the reaction is structure sensitive. To our knowledge, this is the first direct establishment of the structure sensitivity of benzene hydrogenation on nickel catalysts comprising a whisker-like phase.

3.4. *Acetylene cyclotrimerization under hydrogen atmosphere*

We have previously studied the performances of conventional and non-conventional nickel catalysts supported on silica of low and high surface area in acetylene cyclotrimerization to benzene in the presence of hydrogen [25]. We showed that several factors favor benzene formation, among them low conversion and small metal particle size.

In acetylene hydrogenation over Ni/SiO_2(PRG) or Ni/SiO_2(ISO) catalysts, ethylene, benzene, ethane and butane were formed. The study of the effect of the reaction temperature on the catalyst activity showed that the whisker phase was more active at low temperatures (≤60 °C)/low conversions (<10%). Remarkably (*see* figure 4), in these conditions, the whisker phase strongly favored acetylene cyclotrimerization to benzene (54.6%) at the expense of the monohydrogenation to ethylene (23.5%) and produced only small amounts of C_2 and C_4 alkanes (21.9%). In contrast, the spherical nickel particles gave important and equal amounts of mono (43.8%) and dihydrogenation (37.5%) products and only small amounts of benzene (17.6%).

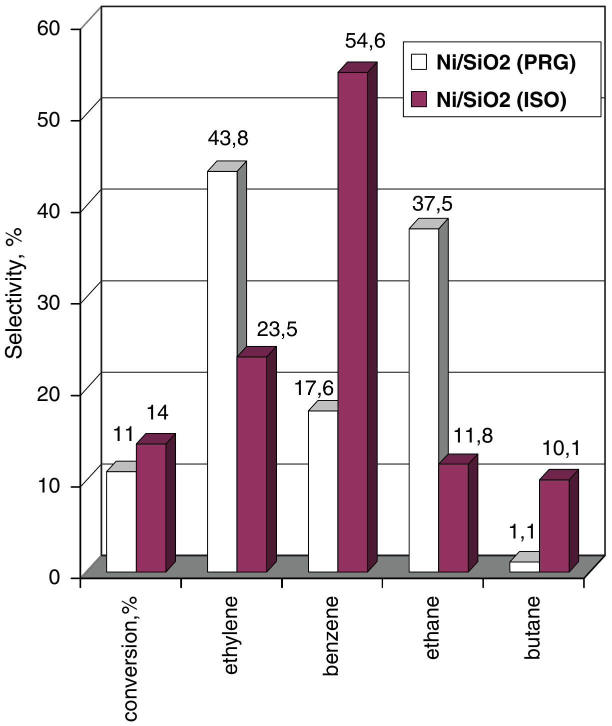

Figure 4. Activity in acetylene hydrogenation at 60 °C for the Ni/SiO_2 catalysts. Pre-treatment:H_2/300 °C/2 h. m_{CAT} = 100 mg; F = 50 mL min^{-1}; $C_2H_2/H_2/He$ = 5/20/75, respectively.

The better selectivity to benzene of Ni/SiO_2(ISO) as compared to Ni/SiO_2(PRG) was correlated to coke deposit. That's why we studied the amount (expressed as μmol of equivalent acetylene per g_{Ni}) and chemical composition of the carbonaceous species deposited on the catalyst surface using the TPRS technique. The used catalyst was submitted to a hydrogen flow in programmed temperature and the removed entities were collected in a cold trap at the outlet of the reactor (*see* Experimental section). The results obtained show that the whisker-like phase gives a greater quantity of coke than the spherical-like particles:2160 against 788μmol C_2H_2/g_{Ni}. These amounts correspond to 1.15 or 0.53 equivalent monolayer, respectively. This confirms that the whisker nickel phase contains active sites in a greater number or/and with a higher reactivity than the spherical-like particles. On the other hand, the chemical composition of the carbonaceous species deposited also depends on the shape of the nickel phase (figure 5). The whisker-like phase mainly retains aromatic (benzene + toluene + higher aromatics ≈ 70%) at the

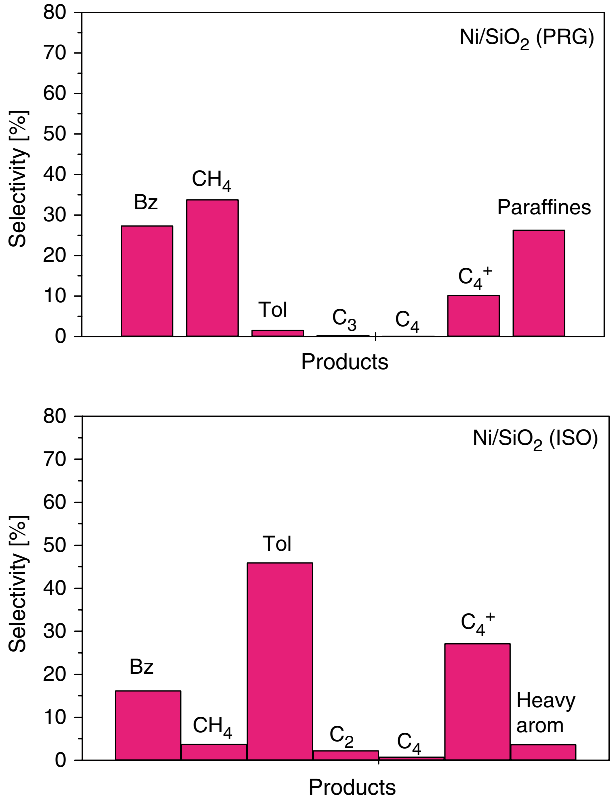

Figure 5. Chemical composition of the carbonaceous surface species deposited in acetylene hydrogenation (see Figure 4 for reaction conditions) after 3 h of working for Ni/SiO$_2$(PRG) (a) and Ni/SiO$_2$(ISO) (b) catalysts.

expense of alkane (C^{4+} ≈30%) species. Contrary to this, the spherical-like nickel particles selectively adsorb alkane (methane + paraffinic products ≈ 60%) at the expense of aromatic (benzene ≈ 25%) species.

From the above study, it appears that wisker nickel is more prone to produce aromatics under hydrogen atmosphere as compared to spherical nickel. More strikingly, the former phase is much more poisoned than the latter. The poisoned sites are most probably those where the undesirable by-products are formed, namely ethane and butane. Consequently, poisoning favored the reaction paths to the benzene and ethylene valuable products.

These results are in good accordance with the literature data in selective hydrogenation reactions. Indeed, hydrogenation of acetylene to ethylene is generally accompanied by the formation of ethane, oligomers and carbon deposit. For Pd-based catalysts, it is generally accepted that the metal surface is extensively covered by hydrocarbon molecules and that the hydrocarbon overlayer ensures the high selectivity of alkene formation [45,46]. The reaction would take place on a primary, irreversibly adsorbed layer. This was also shown for Ni/Al$_2$O$_3$ catalysts [47]. In this case, acetylene mainly produced ethylene and coke (whiskers and amorphous coke). By-products were methane and ethane. The coke formed enhanced the ethylene yield by poisoning three atom arrangements, the active sites for methane and, partly, ethane by-products. Because of this, acetylene is considered as reaction 'apparently sensitive' to structure [48]. In our case, the formation of benzene probably involves an ensemble of surface atoms [49]. Also, it can be stated that acetylene cyclotrimerization in hydrogen atmosphere is a structure sensitive reaction on nickel supported catalysts. Our results stress on the effect of the metal phase shape on the activity and coke deposit of nickel based catalysts in aceylene hydrogenation. They also show that the carbon deposit, in turn, plays an important role the reaction selectivity.

4. Conclusions

This work is the direct demonstration of the influence of the metal phase morphology of nickel supported catalysts on their surface and catalytic properties. The thermal stability under hydrogen atmosphere of a nickel whisker-like phase depends on the method of preparation. Whisker nickel adsorbs and stores more hydrogen than spherical nickel. It is also more active in benzene hydrogenation and more selective to benzene in acetylene cyclotrimerization. Benzene hydrogenation and acetylene cyclotrimerization are shown to be structure sensitive reactions. Finally, the method of preparation used allows better control of the final materials morphology which, in turn, control their physical and chemical properties.

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