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Surface Organometallic Chemistry on Metals Applied to the Environment: Hydrogenolysis of $AsPh_3$ with Nickel Supported on Alumina

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The reaction of $AsPh_3$ with Ni/Al_2O_3 at 100 to 200°C under 6 to 30 bars of hydrogen has been followed by kinetic analysis of both the consumption of $AsPh_3$ and the evolution of benzene and cyclohexane as well as magnetic and XRD measurements of the metallic and intermetallic phase(s). The reaction proceeds via complete hydrogenolysis of the As–Ph bonds, with final formation of a well-characterized NiAs alloy (XRD). The mechanism of alloy formation is complex: at low coverage of the nickel surface, stepwise hydrogenolysis of the As–Ph bonds leads to the formation of the surface organometallic fragments $Ni_s[AsPh_x]_y$ (kinetic studies and analytical data). Further hydrogenolysis of these fragments progressively leads to the formation of arsenic "adatoms" which quickly migrate inside the nickel particles to form $NiAs_{0.45}$ amorphous intermetallic phases (XRD and magnetic measurements). The reaction then proceeds slowly up to the As/Ni ratio of unity with formation of the crystalline NiAs "nickeline" phase (XRD). © 2001 Academic Press

Key Words: **arsine removal; triphenylarsine hydrogenolysis on nickel; surface organometallic chemistry on metal; NiAs alloy formation.**

1. INTRODUCTION

The modification of metallic (M) catalysts by selective hydrogenolysis of organometallic compounds ($M'R_x$) leads to a new class of bimetallic catalysts obtained by surface organometallic chemistry on metals (SOMC/M) (1–3). Depending on the reaction conditions of hydrogenolysis, the organometallic complexes may react with the metallic catalyst and keep some ligands to form an organometallic fragment grafted onto the metal surface, transformed into adatoms which poison selectively the metallic surface or finally may be incorporated into the lattice of the particle to give intermetallic compounds or eventually alloys. Interestingly, in most cases, the hydrogenolysis occurs selectively on the metallic surface and not on the catalyst support. These catalysts are very selective in various catalytic reactions, such as hydrogenation of α,β-unsaturated aldehydes into the corresponding unsaturated alcohols (4–7), hydrogenation of acetophenone into 1-phenylethanol (8), dehydrogenation of secondary alcohol into ketone (9), dehydrogenation of isobutane into isobutene (10, 11), or hydrogenolysis of ethyl acetate into ethanol (12–14). We report here that the concept of SOMC/M can be applied to remove organometallic compounds in natural petroleum feedstock which is a new and promising application in the field of clean and environmental chemistry.

The presence of arsine or mercury compounds in crude oil or in raw gas condensates can cause environmental pollution, equipment corrosion, and reduction of catalyst lifetime. It was recently demonstrated that these compounds can be completely removed by feedstock hydrotreatment on nickel-based catalysts, under hydrogen at 160–200°C (15, 16), but the mechanisms and the kinetics of these reactions are not yet understood. This work reports the kinetic and the mechanistic study of the triphenylarsine hydrogenolysis as a model reaction with metallic nickel catalysts. This reaction is not truly catalytic, but deals with chemical processes at surfaces relevant to catalytic deactivation and removal of arsenic.

2. EXPERIMENTAL

2.1. *Monometallic Ni/Al_2O_3 Catalyst*

The γ-Al_2O_3 with a surface area of 200 m^2/g was used as the support. The 18% (w/w) Ni/Al_2O_3 catalyst was prepared by the incipient wetness method. The Ni/Al_2O_3 samples were reduced under flowing hydrogen at 450°C overnight before use. The dispersion of the sample (number of surface nickel atoms, Ni_s, per total nickel atoms, Ni) was measured by hydrogen chemisorption at room temperature under 300 mbar. Assuming the stoichiometry of one H atom chemisorbed per surface nickel atom (Ni_s) (17), the dispersion was found to be close to 0.10.

2.2. *Triphenylarsine Hydrogenolysis on Ni/Al_2O_3*

The reaction of $AsPh_3$ on Ni catalysts was carried out in a stainless steel autoclave, well stirred by a magnet (200 ml)

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in 100 ml of n-heptane, at 100–210°C, under a total pressure of 6–40 bar.

Before the reaction, 117 mg of catalyst was reduced in flowing hydrogen overnight at 450°C. After cooling down to room temperature under hydrogen, the resulting reduced catalyst was suspended in 100 ml of heptane. This suspension of catalyst was placed into the autoclave under argon and then the reactor was pressurized with H_2. The temperature and the pressure of the autoclave were established at the desired values and a known amount of $AsPh_3$ in heptane solution was introduced into the autoclave via a syringe. The $AsPh_3$ concentration $[AsPh_3]$ in the solution and the amount of benzene or cyclohexane evolved were analyzed by gas-phase chromatographic analysis at regular intervals of time (t). In order to exclude the internal diffusion control, all the catalysts were crushed into a fine powder before use. The rate of the reaction was expressed from the slope of the curves $[AsPh_3] = f(t)$. It was checked that the initial rate of the reaction did not depend on the stirring rate and was proportional to the amount of Ni. In all the experiments, the stirring frequency is 5 Hz.

2.3. *Hydrogen Concentration in Heptane*

The hydrogen concentration in heptane was measured at various temperatures and pressures in an autoclave filled with 100 ml of heptane, maintained at the desired temperature and filled with hydrogen to achieve a given equilibrium pressure (P). After 10 min, a known amount of the solution was introduced in a sealed volume which was cooled to the temperature of liquid nitrogen. The quantity of hydrogen dissolved in the sample was measured using a volumetric apparatus. Assuming that, at 77 K and for a pressure lower than 0.01 bar, the quantity of hydrogen dissolved is negligible, it is possible to estimate the quantity of hydrogen according the following expression,

$$[H_2] = k_T(P - P_0),$$

where $[H_2]$ is the concentration of dissolved hydrogen (mol/mol), P is the equilibrium pressure (bar) and P_0 the pressure (bar) in the autoclave before introduction of H_2, and T is the temperature. The values of k_T and P_0 for various temperatures are reported in Table 1. They are in good accordance with the values measured by Brunner (18) for hexane at 25 to 100°C.

2.4. *Magnetic Measurements*

The magnetization (σ) of the samples was measured in an electromagnetic field (H) varying from 0 to 21 kOe at room temperature using the extraction method (19). The magnetization at saturation, σ_s, expressed in Bohr magnetons per Ni(β/Ni), is obtained by extrapolation of the $\sigma = f(1/H)$ curve for $1/H \rightarrow 0$.

The samples were drawn directly from the autoclave, under flowing argon, and placed in the magnetization sample holder, without contact with air. After magnetization measurement, the samples were dried and weighted.

TABLE 1

Concentration of Hydrogen Dissolved in n-Heptane (mol/mol) at Various Temperatures, Following $[H_2] = k_T(P - P_0)$

Temperature (°C), P_0 (bar)	25, 0	100, 1	150, 4	200, 7
k_T (mol/mol/bar)[a]	0.0007	0.0011	0.0013	0.0015
k_T (mol/mol/bar)[b]	0.0007	0.0010		

[a] This work.

[b] For n-hexane, following Brunner (18).

For the monometallic Ni catalyst, the average metallic particle size can be estimated from the $\sigma = f(H)$ curve (20) and the amount of reduced nickel atoms($Ni^{(0)}$) per total nickel atoms (Ni) can be deduced from the magnetization at saturation, σ_s, knowing that the magnetization at saturation of one reduced nickel atom ($Ni^{(0)}$) is 0.62 β(21):

$$Ni^{(0)}/Ni = 1.61\sigma_s.$$

For bimetallic $NiAs_x$ samples, the decrease in magnetization at saturation can be related to the number of bonds formed between Ni and As, assuming that each bond cancels the magnetization of one nickel atom (22, 23).

2.5. *XRD Analysis*

The XRD measurements were performed using a Bruker D 5005 diffractometer with a goniometer θ–θ. The samples were analyzed in the form of a finely crushed powder.

3. RESULTS

3.1. *Triphenylarsine Hydrogenolysis on Ni/Al_2O_3*

Typical kinetics of $AsPh_3$ hydrogenolysis on Ni/Al_2O_3 at 172°C are reported in Fig. 1. With the support alone, there

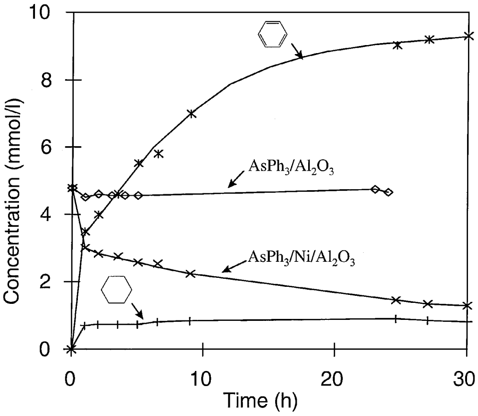


FIG. 1. Kinetics of the hydrogenolysis of $AsPh_3$ on Ni/Al_2O_3 (plain lines), blank experiment with Al_2O_3 (dashed line) at 172°C under 12 bars: (×) $AsPh_3$ consumption; (+) cyclohexane; and (∗) benzene evolution (100 ml of n-heptane, 0.117 g of catalyst, 0.478 mmol of $AsPh_3$($AsPh_3$/Ni = 1.32)).

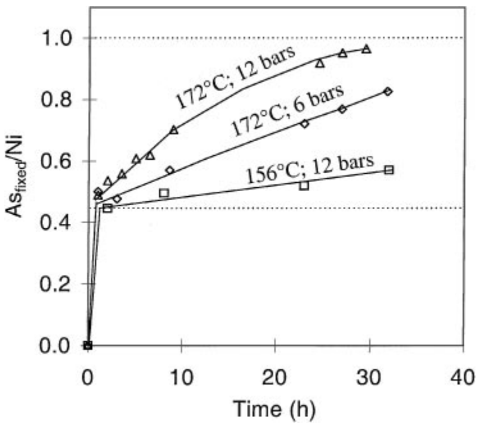


FIG. 2. Influence of the temperature and total pressure on the amount of As fixed on Ni/Al_2O_3 at increasing time of reaction (100 ml of *n*-heptane, 0.117 g of catalyst, 0.478 mMol of $AsPh_3$).

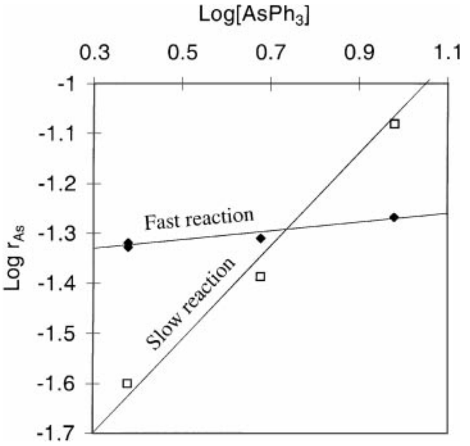


FIG. 4. Logarithm of the reaction rate of $AsPh_3$ hydrogenolysis on Ni/Al_2O_3 as a function of the logarithm of the $AsPh_3$ concentration for the fast (107°C) and the slow (191°C) processes.

is no detectable reaction or adsorption of the organoarsenic compound. With Ni/Al_2O_3, there is consumption of $AsPh_3$ and formation of benzene and cyclohexane. Clearly, the reaction proceeds via two steps. During the first step, the rate of hydrogenolysis of $AsPh_3$ is very fast with formation of benzene (main product) and cyclohexane. After about 1 h of reaction, the rate of $AsPh_3$ consumption sharply decreases and there is formation of benzene selectively. After about 30 h of reaction, the consumption of $AsPh_3$ and the formation of benzene reach a plateau.

The variation with time of $AsPh_3$ fixed by total nickel atom (As/Ni, mol/mol) under different reaction conditions—temperature ranging from 156 to 172°C and hydrogen pressure varying from 6 to 12 bar—are reported in Fig. 2. Apparently, the amount of $AsPh_3$ fixed during the fast uptake is always close to 0.45 As/Ni and does not depend on the temperature or the hydrogen pressure. Yet the total amount of $AsPh_3$ fixed seems to reach a plateau corresponding to 1 As/Ni.

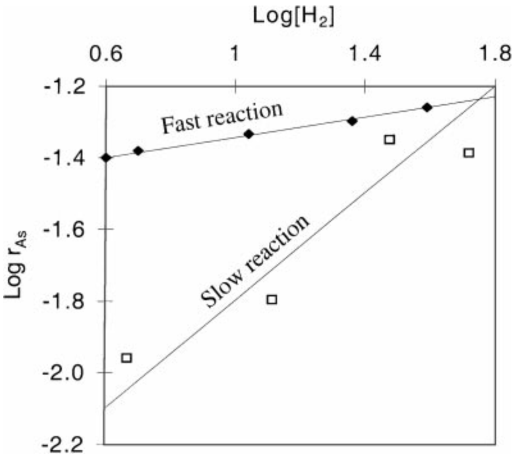


FIG. 3. Logarithm of the reaction rate of $AsPh_3$ hydrogenolysis on Ni/Al_2O_3 as a function of the logarithm of the H_2 concentration for the fast (107°C) and the slow (172°C) processes.

The reaction rates of the two steps are measured from the slope of the $As_{fixed} = f(t)$ curves at $As_{fixed}/Ni = 0$ (fast uptake) and at $As_{fixed}/Ni = 0.45$ (slow uptake). The first step (fast uptake) of the reaction is more than 2 orders of magnitude faster than the second step. The reaction rates of both the fast and the slow $AsPh_3$ uptake increase with the temperature (T), the amount of dissolved H_2, and the $AsPh_3$ concentration. The reaction orders of the fast and slow uptakes with respect to hydrogen and $AsPh_3$ concentrations are deduced from the logarithm curves of Figs. 3 and 4 (Table 2). The apparent activation energies for the fast and the slow uptakes are respectively 23 and 19 $kcal \cdot mol^{-1}$ (Table 2).

The amount of benzene + cyclohexane (C_6) evolved per $AsPh_3$ for As_{fixed}/Ni coverage close to 0.45 and 1 and under the different reaction conditions are reported in Table 3. On average, the quantity of phenyl groups which has reacted to give benzene and cyclohexane seems to be independent of the amount of $AsPh_3$ fixed and slightly lower than 3.

The ratio of cyclohexane/benzene formed seems to be independent of the hydrogen pressure, but increases almost 5 times when the reaction temperature increases from 156

TABLE 2

Reaction Rate (*r*), Apparent Activation Energy (*E*), and Reaction Orders with Respect to H_2 (*n*) and $AsPh_3$ Concentrations (*m*) of Fast and Slow Uptake

	r (mmol mol^{-1} h^{-1})	E (kcal mol^{-1})	n	m
Fast uptake	219[a]	23	0.3	0.15
Slow uptake	4.4[b]	19	0.8	1

[a] Measured at 140°C and 6 bar.

[b] Measured at 156°C and 12 bar.

TABLE 3

Hydrogenolysis of $AsPh_3$ on Ni/Al_2O_3: Effect of Reaction Time, Pressure, and Temperature on the Amount of C_6 (Benzene + Cyclohexane) Formed per As Fixed (C_6/As_{fixed}) and on the Ratio Cyclohexane/Benzene (100 ml of *n*-Heptane, 0.117 g of Catalyst, 0.478 mmol of $AsPh_3$ ($AsPh_3/Ni = 1.3$))

Reaction time (h)	Pressure (bar)	Temp (°C)	As_{fixed}/Ni_t	C_6/As_{fixed}	C_6H_{12}/C_6H_6
2	12	156	0.44	2.7	0.06
100	12	156	0.83	2.7	0.03
1	12	172	0.47	2.4	0.13
30	12	172	0.96	2.5	0.09
1	12	192	0.45	2.4	0.15
10	12	192	0.92	2.5	0.20
0.5	24	192	0.44	2.8	0.25
6	24	192	0.94	2.9	0.22
0.5	40	192	0.47	2.8	0.30
6	40	192	0.98	2.8	0.16

to 192°C (Table 3). On average, the ratio of cyclohexane/benzene is lower after the complete reaction than after the fast uptake period (As_{fixed}/Ni close to 0.45).

3.2. Magnetization Measurements

For the monometallic Ni/Al_2O_3 catalyst, the average metallic particle size deduced from the magnetization measurement is close to 7 nm. Assuming a spherical shape for the metallic particles, the dispersion of the sample becomes close to 10%, in good agreement with the value deduced from hydrogen chemisorption (10%). The amount of reduced nickel in the sample, deduced from the magnetization at saturation, is about 85% since a fully reduced nickel would have Bohr magnetons/nickel of 0.62. If surface nickel atoms (10%), which are covered with hydrogen, are fully reduced but do not contribute to the ferromagnetism of the sample (17), the real degree of reduction of the sample treated at 450°C under flowing hydrogen overnight is close to 95%.

The magnetization values at saturation (M_s) of various $NiAs_x/Al_2O_3$ samples with increasing As/Ni ratios are reported in Fig. 5.

The magnetization at saturation decreases strongly with the amount of As fixed. Above As/Ni of 0.45, the samples do not exhibit ferromagnetic behavior. It is interesting to note that this value coincides with the stoichiometry of the compound obtained at the breaking point of the kinetics curves (end of the fast uptake, $As_{fixed}/Ni = 0.45$), (Fig. 2).

The slope of the magnetization variation versus As content indicates that at the beginning of the reaction, each fixed As cancels the ferromagnetism of about 3 Ni (the slope of the curve in Fig. 5 is equal to 1.86 Bohr magnetons/arsenic fixed, which corresponds to 3 Ni/As grafted).

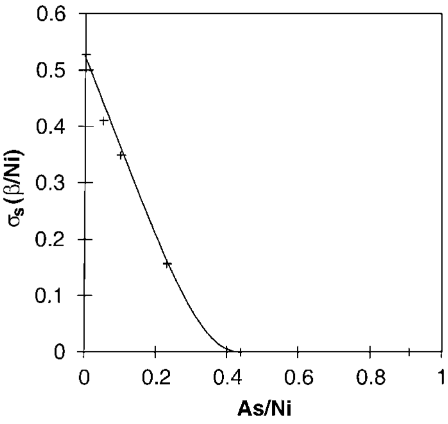


FIG. 5. Variation of the magnetization of nickel with increasing amounts of $AsPh_3$ fixed (172°C, 12 bar H_2).

3.3. X-Ray Diffraction Analysis

The XRD spectra of Al_2O_3 (a) and the differential diffraction spectra, obtained by subtraction of the Al_2O_3 spectrum from that of the reduced Ni/Al_2O_3, are presented in Fig. 6. Clearly, the XRD spectra in Fig. 6b can be assigned to pure crystalline nickel (24). From the broadening of the diffraction bands, it is possible to estimate the metallic particle diameter. The value obtained for Ni/Al_2O_3 is about 7 nm and is in good agreement with the value deduced from magnetization of the starting material.

Two bimetallic samples are obtained by reaction of $AsPh_3$ on Ni/Al_2O_3 at 172°C under 12 bar of H_2 for 1 h ($NiAs_{0.4}/$

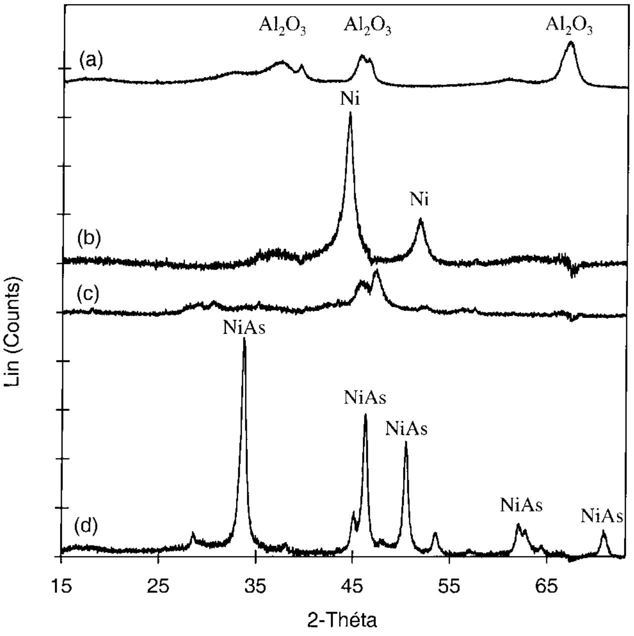


FIG. 6. (a) The XRD spectra of the Al_2O_3 support. (b), (c), and (d) represent respectively the differential diffraction spectra, obtained by subtraction of the Al_2O_3 spectra with those of (b) Ni/Al_2O_3, (c) $NiAs_{0.4}/Al_2O_3$ (172°C, 12 bar H_2 for 1 h), and (d) $NiAs/Al_2O_3$ (172°C, 12 bar H_2 for 24 h).

Al_2O_3) or 24 h ($NiAs/Al_2O_3$). The differential diffraction spectra, obtained by subtraction of the Al_2O_3 spectrum from those of Ni/Al_2O_3 (Fig. 6b), $NiAs_{0.4}/Al_2O_3$ (Fig. 6c), and $NiAs/Al_2O_3$ (Fig. 6d) samples are represented in Figs. 6b, 6c, and 6d. They can be respectively assigned to crystalline Ni (Fig. 6b), amorphous compound (Fig. 6c), and crystalline "nickeline" NiAs (Fig. 6d)(24).

4. DISCUSSION

The reaction path of $AsPh_3$ with Ni/Al_2O_3 can be divided in two steps. For As_{fixed}/Ni lower than ca 0.45, the reaction rate is very fast and the benzene formed is readily hydrogenated to cyclohexane. For $As_{fixed}/Ni = 0.45$, the crystalline Ni structure has completely disappeared and the sample does not exhibit any ferromagnetism. Above As_{fixed}/Ni of 0.45, the rate of the $AsPh_3$ reaction is drastically lowered and the hydrogenation of the benzene formed is not observed. For As/Ni = 1, there is formation of crystalline NiAs nickeline phase and the hydrogenolysis of the As–Ph bonds is stopped.

The dispersion of the Ni/Al_2O_3 starting material is no more than 10%. It is then obvious that the reaction of $AsPh_3$ with Ni/Al_2O_3 at high temperature is not limited to the nickel surface (since one can graft one As per Ni_{total}). Many hypotheses can account for the fact that the amount of fixed arsenic is more than a monolayer on the nickel particle:

—formation of multilayers of As on the surface of the metallic particles as proposed by Margitfalvi *et al.* (25) in the case of the reaction of SnR_4 on Pt surfaces;

—migration of As atoms from the nickel surface to the support surface (spillover of As) (26, 27);

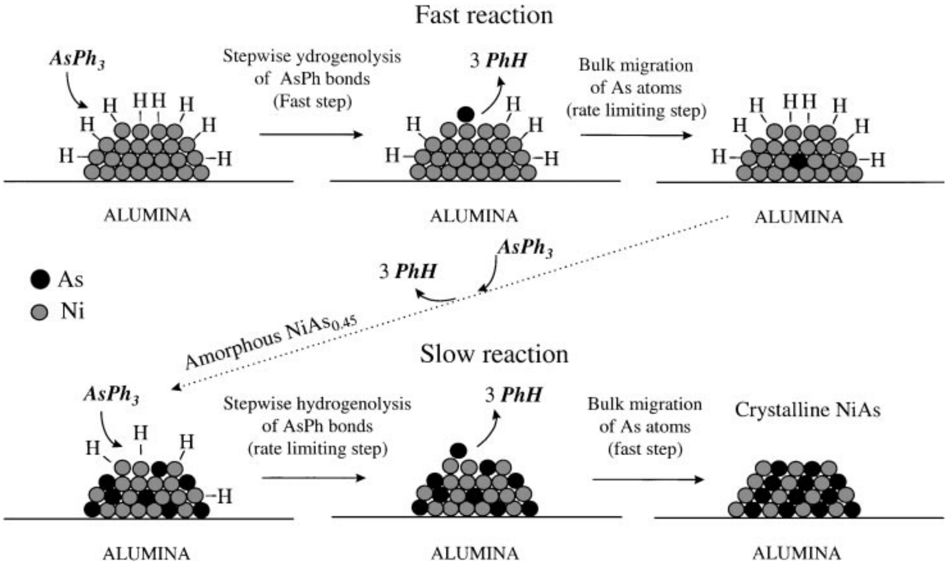
—reaction of $AsPh_3$ on an activated fraction of the alumina surface close to the Ni particles as in the case of $SnBu_4$ on Pt/Al_2O_3 (28);

—migration of As inside the metallic particles.

Among these hypotheses, only the last one must be retained on the basis of magnetic measurement and XRD analysis. The structure of the obtained compound (NiAs) corresponds exactly to the expected stoichiometry, deduced from the amount of As fixed. It is then obvious that the As naked atoms formed by hydrogenolysis of the As–Ph bonds on the $NiAs_x$ surface can readily migrate *inside* the metallic particles, to form, in a first step, an amorphous Ni_xAs_y phase and then, in a second step, the "crystalline" NiAs phase. This process occurs at the relatively low temperature of 170°C, whereas the melting points of solid Ni, As, and NiAs are respectively 1452°C, 818°C, and 1000°C (29); this result must be ascribed to the relatively low size of the aggregate, as observed previously, for the formation of single-phase Ni_3Sn particles at low temperature after CVD process of $Sn(CH_3)_4$ on nickel particles of 7 nm in diameter (30).

For As/Ni lower than 0.45, the rate of $AsPh_3$ consumption is roughly independent of the $AsPh_3$ and H_2 concentration and the apparent activation energy is high (more than 23 kcal/mol). It is then obvious that the rate-limiting step of the reaction of $AsPh_3$ on Ni/Al_2O_3 could not be the hydrogenolysis of the Ph–As bond on the Ni–H surface. More likely, the rate of the reaction must be limited by the rate of diffusion of As atoms from the metallic surface to the bulk, as shown in Scheme 1.

Above As/Ni = 0.45, the ferromagnetism of Ni in the $NiAs_x$ phases is completely canceled. These phases still remain active for the hydrogenolysis of the As–Ph bonds, but



SCHEME 1

the rate of the reaction is almost 100 times lower than for the $NiAs_{(x<0.45)}$ phases. Moreover, the rate of the reaction is approximately proportional to the $AsPh_3$ and H_2 concentrations and the apparent activation energy is lower (19 kcal/mol). It seems that the rate-limiting step of the reaction of $AsPh_3$ on $NiAs_{(x>0.45)}$ phases is the hydrogenolysis of the Ph–As bonds. It is well known that the C–C bond hydrogenolysis on Ni decreases upon dilution with Cu (31). The same "ensemble size effect" could be postulated for As–C bond hydrogenolysis, in addition to an electronic effect of As on Ni (32).

The overall reaction path of $AsPh_3$ on Ni/Al_2O_3 could be schematically represented as in Scheme 1.

5. CONCLUSION

The reaction of $AsPh_3$ with Ni/Al_2O_3 in the 100 to 200°C range under 6 to 30 bar of hydrogen proceeds by complete hydrogenolysis of the As–Ph bonds, with formation of a NiAs alloy. The mechanism of alloy formation is stepwise: at low coverage of the nickel surface, there is a fast hydrogenolysis of three As–Ph bonds with formation of As adatoms which migrate quickly inside the metallic particles to form Ni_xAs_y amorphous intermetallic phases. The benzene formed during the hydrogenolysis of the As–Ph bonds is readily hydrogenated into cyclohexane on the $NiAs_x (x < 0.45)$ phases. The reaction then proceeds up to an As/Ni ratio of 1 with the formation of the crystalline NiAs nickeline phase. This alloy does not exhibit any hydrogenation ability for benzene.

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