

Gas phase hydrogenation of acetonitrile on Raney nickel catalysts: reactive hydrogen

F. Hochard *, H. Jobic, J. Massardier, A.J. Renouprez

Institut de Recherches sur la Catalyse, CNRS, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France

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Abstract

Catalytic hydrogenation of acetonitrile on Raney nickel has been studied in gas phase. The chemisorption of hydrogen has been followed by TPD and inelastic neutron scattering; these techniques indicate the presence of both weakly and strongly adsorbed hydrogen. Kinetic studies and pulse experiments show that only weakly adsorbed hydrogen, localised on top of the nickel atoms and on C_{3v} symmetry sites, is active for the hydrogenation. Acetonitrile and reactive hydrogen are weakly adsorbed on Raney nickel, and compete for the same site. Conversely, amines more strongly adsorbed than acetonitrile, but on different sites, do not constitute a poison for the reaction.

Keywords: Acetonitrile; Hydrogen; Hydrogenation; Inelastic neutron scattering; Raney nickel; Thermodesorption

1. Introduction

Hydrogenation of nitriles is an important method for the industrial preparation of various amines. The industrial process of nitrile hydrogenation is generally performed in the liquid phase in the presence of metallic catalysts under high hydrogen pressures. Because of the high reactivity of partially hydrogenated reaction intermediates, a mixture of primary, secondary and tertiary amines is usually obtained [1]. However, the distribution of the hydrogenation products depends on the catalysts [2,3], the properties of the starting nitrile and also the reaction conditions: pressure of the reactants, nature of the solvent [4].

In order to obtain information on the reaction mechanism and especially on the influence of the

reactants, hydrogen and nitrile, we have studied the hydrogenation of acetonitrile on Raney nickel catalysts in gas phase, at atmospheric pressure. The use of gas phase reaction should avoid problems connected with the nature of the solvent and/or to transport limitations, in contrast with the liquid phase hydrogenation employed in industrial processes. Furthermore, chemisorption studies can be investigated in the same conditions as during hydrogenation. These simplified reactions conditions are required to determine the factors governing the selectivity (for primary amines) at the microscopic scale, by classifying the strength of the adsorption sites for the reactants and reaction products. This is achieved by inelastic neutron scattering spectroscopy (INS) and thermodesorption (TPD).

* Corresponding author.

2. Experimental

Preparation of catalysts

The Raney nickel catalysts used in this work were prepared by a standard procedure [5]. It consists in adding slowly the Ni–Al alloy doped with small amounts of Fe and Cr [6] to a 6 M sodium hydroxide aqueous solution. The mixture was kept for two hours at boiling temperature, then treated with a 6 M NaOH solution for two hours. It was then washed with decreasing concentration NaOH solutions (6 M, 3 M, 2 M, 1 M). The catalyst was kept under a NaOH 1 M solution until use.

This Raney nickel develops a specific surface area of $130 \text{ m}^2 \cdot \text{g}^{-1}$, measured by nitrogen adsorption at the liquid N_2 temperature, after degassing two hours at 373 K.

2.2. Chemisorption of hydrogen by inelastic neutron scattering spectroscopy

The wet Raney nickel was evacuated by cryopumping to 10^{-8} kPa at 373 K, and maintained one hour at this temperature. The powder (66 g) was transferred, under vacuum, into a cylindrical aluminium container.

2.1.1. Neutron spectroscopy

The experiment was carried out at the Laue Langevin Institute, in Grenoble, using the beryllium-filter detector spectrometer IN1B [7]. This spectrometer is installed on the hot source of neutrons (graphite at 2000 K). The frequency range $250\text{--}2600 \text{ cm}^{-1}$ was covered with a Cu (220) monochromator plane. With this monochromator,

the energy resolution $\Delta E/E$ is of the order of 5%. All the experimental spectra are shifted up in energy because of the beryllium-filter transmission function, but the frequencies quoted below have been corrected for this effect. It must be recalled that in INS, all the vibrational modes are active and that their intensity is proportional to the number of scattering nuclei in the neutron beam.

2.3. Reaction studies

2.2.1. Continuous flow apparatus for kinetic measurements

The reaction kinetics for the gas phase hydrogenation were studied in a flow reactor operated at atmospheric pressure. High purity CH_3CN was used in the experiments ($\geq 99.9\%$, Aldrich). All gases were purified using a Chrompack Oxygen Filter, hydrogen was further dried by a Chrompack Moisture Filter. Acetonitrile was hydrogenated over ≈ 20 mg of Raney nickel catalyst. The catalyst was first washed, then weighed by picnometry and loaded into a Pyrex reactor to form a fixed bed. The catalyst was then pretreated for 6 h at room temperature under nitrogen flow (10 l/h). After degassing, the reactor was heated at the reaction temperature (373 K) under the same nitrogen flow, the temperature increasing by $2^\circ\text{C}/\text{min}$. Once this required temperature was reached and stabilized, the reactants were introduced. A preliminary kinetic study was performed to choose the conditions (mass of catalyst, flow, partial pressures) avoiding mass and heat transfer limitations. The kinetic measurements were performed under CH_3CN and H_2 partial pressures of respectively 2.2 and 50 kPa and 48.8 kPa of helium used as carrier gas. Gas flow rates were controlled with mass flow controllers, the total flow rate was 10 l/h. The reaction has been performed at rather low temperature (373 K) to avoid side reactions such as acetonitrile decomposition, coke deposition and others occurring at higher temperature (> 423 K) [8,9]. The general test conditions adopted in kinetic measurements are summarized in Table 1.

Table 1
General test conditions for the gas phase hydrogenation of acetonitrile

Weight of catalyst:	≈ 20 mg
Total gas flow rate:	10 l/h
Temperature of the reaction:	373–423 K
Partial pressure of hydrogen:	2.5–50 kPa
Partial pressure of acetonitrile:	0.7–2.5 kPa
Total pressure:	102 kPa
$\text{H}_2/\text{CH}_3\text{CN}$ ratio:	$\approx 20\text{--}133$

Every twenty minutes, the reaction products and acetonitrile were analyzed by flame ionization chromatography. The analysis under N_2 flowing was carried out on a column ($2\text{ m} \times 1/8\text{ in.}$) filled with 28% Pennwalt 223 + 4% KOH on Chromosorb R 80–100. An integrator HP3396A was used for automatization of analysis and data acquisition. The conversion is defined by the following relation:

Conversion (%)

$$= \frac{\text{acetonitrile}_{\text{in}} - \text{acetonitrile}_{\text{out}}}{\text{acetonitrile}_{\text{in}}} * 100$$

The selectivities have been calculated from peak areas taking into account the different sensitivity factors in the flame ionization detector. The selectivity, for the product i , is therefore defined as:

Selectivity^{*i*} (%)

$$= \frac{\text{Corrected area}^i}{\sum_{i=1}^3 (\text{area of all corrected peaks})}$$

where the sum over corrected peaks is made for ethylamine, diethylamine and triethylamine.

Temperature programmed desorption (TPD)

Temperature-programmed desorption of adsorbed hydrogen and acetonitrile was performed in an ultra-high vacuum system including an oil diffusion pump, a liquid nitrogen trap (Fisons Instruments) and a mass spectrometer. Samples were treated first in a flowing apparatus at 373 K, under the reactant mixture, transferred to the TPD apparatus, and evacuated down to 10^{-8} kPa before the TPD experiments.

3. Results

3.1. Neutron spectroscopy of hydrogen chemisorbed on Raney nickel

In a previous INS study of hydrogen adsorption performed on an undoped Raney nickel [10], the

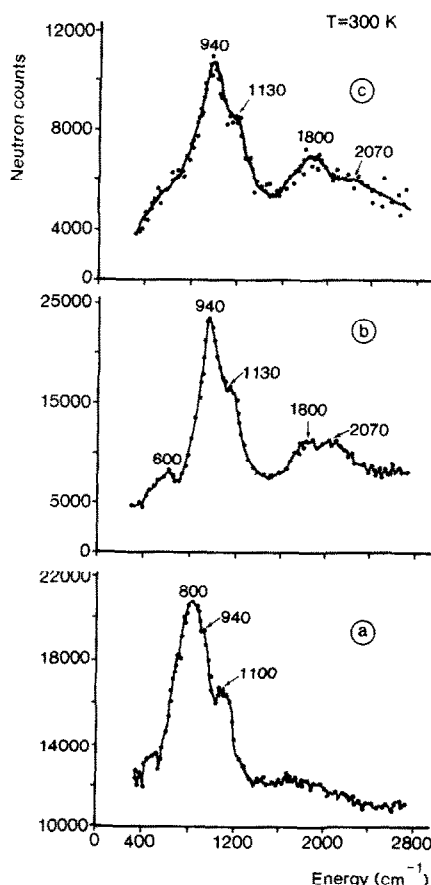


Fig. 1. INS spectra of hydrogen adsorbed on doped Raney nickel: (a) residual hydrogen, after desorption at 373 K under vacuum; (b) spectrum obtained after adsorption of 1.35 kPa of H_2 (the spectrum of residual hydrogen has been subtracted); (c) spectrum obtained after adsorption of hydrogen at atmospheric pressure (spectra (a) and (b) have been subtracted).

adsorption at several pressures was performed after outgassing the sample at 520 K. The surface was then free from hydrogen as shown by the totally flat neutron spectrum. But in the meantime, a structural modification has occurred inducing a decrease of surface area from 130 to $40\text{ m}^2 \cdot \text{g}^{-1}$. In the present case, outgassing at only 373 K leaves on the surface 25 to 30% of the amount of hydrogen which was originally present but does not produce any structural modification.

All the INS spectra were recorded at 300 K. The spectrum shown in Fig. 1 (a) is obtained after subtraction of the background produced by the aluminium container and the phonons due to the nickel sample. It represents the spectrum of a

doped Raney nickel catalyst desorbed at 373 K under vacuum. Two intense bands at 800 and 1100 cm^{-1} are observed. These vibrations are due to residual hydrogen. The intense peak at 800 cm^{-1} and the weaker peak at 1100 cm^{-1} are due mainly to the antisymmetric (*E* symmetry) and to the symmetric (A_1 symmetry) stretching modes of hydrogen atoms adsorbed on sites of nearly C_{3v} symmetry, located on the (110) nickel faces [10,11]. The weaker contribution observed at 940 cm^{-1} is assigned to hydrogen adsorbed on C_{3v} sites, on (111) nickel faces. This species has two vibrational modes: the antisymmetric located at 940 cm^{-1} and the symmetric observed near 1130 cm^{-1} [11]. These vibrational peaks overlap with the modes due to the species adsorbed on the (110) nickel faces.

Fig. 1 (b) is obtained after hydrogen adsorption under 1.35 kPa pressure and subtraction of the contribution of residual hydrogen (Fig. 1 a). In this spectrum, the main peaks are observed at 940 and 1130 cm^{-1} and are thus due to the vibrations of hydrogen atoms adsorbed on the C_{3v} sites. This is the main species which has always been observed on Raney nickel [11,12]. An additional weak peak is observed at 600 cm^{-1} , and is tentatively assigned to the symmetric stretching mode of an hydrogen atom bonded in a four-fold site, in agreement with a frequency observed on the (100) Ni faces [13]. The broad band observed at 2070 cm^{-1} is due to the combination and the harmonics of the two most intense modes. The band centred at 1800 cm^{-1} would correspond to the stretching vibration of on top hydrogen. The bending mode of this species is expected between 800 and 1130 cm^{-1} , and is thus hidden by the more intense features due to multiply bonded hydrogen.

Fig. 1(c) is the INS spectrum obtained after hydrogen adsorption on Raney nickel under atmospheric pressure and subtraction of the spectra (1b) and (1a). The main features are an intense peak at 940 cm^{-1} with a shoulder at 1130 cm^{-1} and a large band centred at $\approx 1800 \text{ cm}^{-1}$ with a shoulder at 2070 cm^{-1} . Therefore, when the pressure of hydrogen is increased, there are no

dramatic changes in the INS spectra, but a gradual increase of intensity is observed.

In summary, after evacuation at 373 K we observed that 30% of the total hydrogen uptake remains on the surface. This residual hydrogen is adsorbed on the (110) and (111) nickel faces. Terminal hydrogen is only detected upon readorption of hydrogen, at higher pressure. This shows that the multi-bonded species present at low coverage are more strongly adsorbed than linear hydrogen. This last type of hydrogen ($\approx 15\%$) would complete the surface coverage to reach saturation.

3.2. Kinetic study

Acetonitrile hydrogenation is very exothermic and therefore the kinetic studies have to be performed under large helium flow (10 l/h) and at low conversion ($\leq 10\text{--}15\%$). To study the order with respect to hydrogen, its pressure was varied between 2.5 and 50 kPa with a constant nitrile pressure of 2.5 kPa. The order with respect to acetonitrile was measured for a nitrile pressure ranging from 0.7 to 2.5 kPa and an hydrogen pressure of 50 kPa. In such conditions, the reaction leads mainly to ethylamine (selectivity ≥ 0.95). Positive apparent orders with respect to hydrogen (1.2 ± 0.1) and acetonitrile (0.55 ± 0.05) have been determined.

The apparent activation energy for the formation of ethylamine measured between 373 and 423 K is about $75 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$.

3.2.1. Acetonitrile pulse experiments

Some additional experiments have shown that hydrogenation does not occur when a pulse of acetonitrile flows on a catalyst only covered by strongly adsorbed hydrogen (adsorption at 100 kPa, evacuation at 300 K). On the contrary, the reaction occurs when the same acetonitrile pulse is contacted with a sample previously covered with weakly adsorbed hydrogen. This is the evidence that only weakly adsorbed hydrogen is reactive for the hydrogenation. These results agree with the kinetic data, which show that reactive

Table 2
Effect of addition products during the hydrogenation of acetonitrile

Hydrogenation of acetonitrile (373 K)	Conversion of acetonitrile (%)	Conversion of diethylamine (%)	Conversion of triethylamine (%)	Selectivity for ethylamine (%)
50 kPa H ₂ 2.3 kPa CH ₃ CN	80	–	–	90
50 kPa H ₂ 2.3 kPa CH ₃ CN + 2.8 kPa diethylamine	80	10	–	80
50 kPa H ₂ 2.3 kPa CH ₃ CN + 1.6 kPa triethylamine	80	–	0	90
50 kPa H ₂ 2.3 kPa CH ₃ CN + 2.8 kPa diethylamine + 1.6 kPa triethylamine	80	10	0	80

hydrogen and acetonitrile are weakly adsorbed on the surface, taking into account their both positive orders. In the same line, another complementary experiment shows that acetonitrile adsorbed on the evacuated catalyst does not react under flowing of hydrogen.

From these two sets of experiments, excluding the poisoning of the surface by acetonitrile, it can be concluded that acetonitrile and reactive hydrogen compete for the same sites but that acetonitrile is more strongly bonded than hydrogen, since it cannot be displaced by hydrogen.

3.2.2. Influence of reactants and products (diethylamine or triethylamine)

When diethylamine is added to the reactants at 373 K, with a partial pressure of 2.8 kPa (the same order of magnitude than the acetonitrile partial

pressure), the conversion of acetonitrile remains unchanged. However, about 10% of the diethylamine is converted (7% in ethylamine and 3% in triethylamine), so the total apparent selectivity of the reaction is decreased. The same experiment was run after addition of triethylamine (partial pressure of 1.6 kPa) during the hydrogenation. No conversion of triethylamine is observed, while the CH₃CN conversion remains unchanged. Thus, the products of the hydrogenation do not inhibit the reaction. These results are given in Table 2.

Finally, TPD experiments were performed to obtain a quantitative evaluation of the adsorption strength of the sites.

3.2.3. Temperature-programmed desorption

The TPD experiments are performed after the reactant mixture has been flowed through the catalyst bed for 30 minutes at 373 K. The reactor is

Table 3
Attribution and sensitivity factor of the characteristics peaks of TPD

<i>m/e</i>	2	41	30	73	86
attribution	hydrogen	acetonitrile	ethylamine	diethylamine	triethylamine
sensitivity	2.2	1.1	1	5.8	0.75

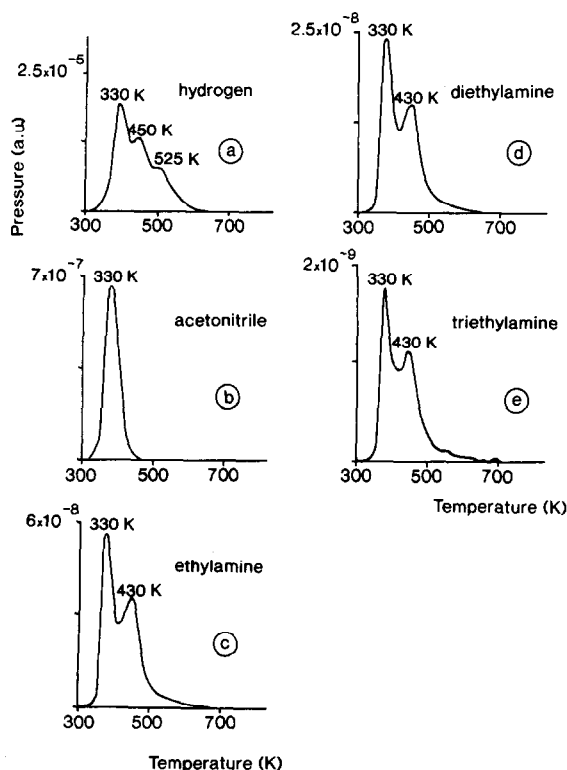


Fig. 2. TPD spectra of (a) hydrogen, (b) acetonitrile, (c) ethylamine (d) diethylamine, (e) triethylamine on doped Raney nickel.

then closed, disconnected from the flow apparatus, and connected to the TPD instrument. The reactor is then evacuated down to 10^{-8} kPa. Thus, only the species irreversibly adsorbed on the catalyst are analysed during the temperature raise from 300 to 670 K, with a linear rate of 50 K/min. The mass spectrometer analyses simultaneously the selected fragments of the desorbed species (2, 41, 30, 73, 86). Their attribution and relative sensitivity with respect to the n-butane are given in Table 3, [14,15], and Fig 2a, 2b, 2c, 2d, 2e show the results. The main desorbed species are hydrogen, followed by acetonitrile, two orders of magnitude smaller. The amount of amines is three or four orders of magnitude smaller than H_2 .

The TPD curve of hydrogen (Fig. 2a), shows three peaks at 330, 450 and 525 K, while only one peak is found for acetonitrile, desorbed under molecular form at 330 K (Fig. 2b). The products of hydrogenation, ethylamine, diethylamine and triethylamine, present the same TPD features,

with a peak at 330 K and a smaller one at 430 K (Fig. 2c, 2d and 2e).

4. Discussion

In agreement with earlier data [10,18], inelastic neutron scattering experiments indicate that there are both weakly and strongly bound hydrogen on Raney nickel. However on this doped nickel, the linear form is already detected for a pressure of 1.5 kPa whereas it was observed in smaller proportion and above 10 kPa in the previous work [10] which was performed on an already sintered metal. This difference can be attributed to a reduction of the number of corner and edge atoms during the thermal treatment performed at 520 K in the previous study. Weakly adsorbed hydrogen evolved at 330 K in TPD is the reactive hydrogen, as already mentioned by Barbier et al. [16]. This hydrogen is adsorbed on top of the nickel atoms *and* on C_{3v} sites on the (111) nickel faces. Hydrogen weakly adsorbed on C_{3v} sites has the same geometry as more strongly adsorbed hydrogen but with a reduced interaction energy. The fact that the vibrational frequencies do not shift within experimental accuracy for the same adsorption site, means that the frequencies are more sensitive to the shape of the potential well than to the binding energy.

Acetonitrile is desorbed without dissociation at 330 K, in agreement with the results of inelastic neutron scattering [17] and LEED [19] in which no C–H bond breaking of acetonitrile has been observed up to 393 K, unlike benzene [20]. Moreover, it was demonstrated [17] that acetonitrile is adsorbed parallel to the surface, with a slight rehybridisation and in interaction with several Ni atoms. Acetonitrile is thus weakly adsorbed on one type of site, with a desorption energy close to that of reactive hydrogen. As mentioned above, reactive hydrogen occupies two type of sites (multibonded and linear), whereas acetonitrile only competes for polyatomic sites. But, in agreement with the kinetic study, acetonitrile would be

more strongly adsorbed than hydrogen, since it is not displaced by reactive hydrogen.

The slightly above unity positive order observed for hydrogen could be explained by its role during the reaction. In fact, part of the hydrogen is used to regenerate the surface of the catalyst during the reaction. Indeed, the presence of methane and ethane during hydrogenation has been evidenced by thermodesorption, indicating that hydrogen would eliminate carbon deposits from the surface by formation of these products. Also a large deactivation of the catalyst (30% within 3 h) is observed if the hydrogen pressure is lower than 10 kPa. Hydrogen playing two roles, hydrogenation of acetonitrile and regeneration of the surface, the actual order with respect to this reactant in the hydrogenation of the nitrile itself is unknown and could even be negative. This hypothesis of a negative order with respect to hydrogen can be discarded because only weakly adsorbed hydrogen is active during the pulse experiments where the regeneration process can be neglected.

An alternative explanation for these both positive orders has to be considered, taking into account that the reaction is performed at 373 K, that the coverage by both reactive species may be far from the saturation and also that the regeneration process is slower than the hydrogenation. In that case, a Horiuti–Polanyi mechanism [21] can be invoked leading to a rate equation of the form:

$$r = k_1 (\theta_{\text{H}_2})^2 \theta_{\text{aceto}}$$

assuming that θ_{imine} can be neglected, this leads to:

$$r = \frac{k_1 K_2 P_{\text{aceto}} K_1 P_{\text{H}_2}}{[1 + K_2 P_{\text{aceto}} + (K_1 P_{\text{H}_2})^{1/2}]^3}$$

where k_1 is the rate constant for the addition of hydrogen leading to the imine and K_1 , K_2 the equilibrium adsorption–desorption constants for hydrogen and nitrile, respectively. In the hypothesis where $K_1 < K_2$, corroborated by the absence of reaction when the surface has been precovered by nitrile, the order with respect to hydrogen

would be close to 1 and that with respect to acetonitrile positive but lower than 1.

Two desorption peaks for the amines have been observed at 330 and 430 K. The first peak with a maximum at 330 K is probably due to the direct hydrogenation of acetonitrile. During its thermodesorption this molecule reacts immediately with weakly adsorbed hydrogen to form amines. Indeed, the peaks at 330 K attributed to the amines are observed at a temperature lower than the reaction temperature, which clearly demonstrates that they result from hydrogenation of acetonitrile, the products being mainly evolved in the gas phase above 330 K. Therefore, most of the products of hydrogenation are desorbed simultaneously as soon as formed, but a small proportion is readsorbed on more energetic sites, probably acid sites, resulting from the presence of alumina. This explains the peaks located at 430 K related to the desorption of the different amines from these sites. The absence of influence of amines in the reactants on the conversion of the nitrile indicates that acetonitrile and amines do not compete for the same sites, as evidenced by the TPD experiments; so the products of the hydrogenation do not constitute a poison for this reaction.

5. Conclusion

On Raney nickel catalysts, both weakly and strongly bonded atomic hydrogen were detected by TPD and inelastic neutron scattering. But only weakly adsorbed hydrogen is active for hydrogenation. Moreover, a molecular desorption of acetonitrile is observed at the hydrogenation temperature. Acetonitrile and reactive hydrogen compete for the same sites, while amines and acetonitrile are adsorbed on different sites. Thus hydrogen diffusion on the surface would be the main factor governing the activity, while the desorption rate of ethylamine with respect to the condensation rate with the intermediate primary imine would control the selectivity. Indeed, imine and ethylamine desorption occur as soon as they

are formed, as evidenced by the TPD results. This will be discussed in a forthcoming paper.

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