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# Hydrodenitrogenation on Pt/silica–alumina catalysts in the presence of $H_2S$: Role of acidity

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## Abstract

The effect of the support acidity on the HDN activity of a series of Pt/silica–alumina catalysts was investigated. Catalyst containing 1 wt.% of Pt supported on silica–aluminas with silica content varying between 10 and 50 wt.% were prepared by incipient wetness impregnation. The acidity was characterized by IR spectroscopy of adsorbed pyridine and isooctane hydrocracking and a good correlation with the silica content of the supports was observed. All the catalysts presented similar metal dispersion as measured by hydrogen chemisorption. The conversion pathway of 1,4-tetrahydroquinoline (1,4-THQ), used as model molecule for HDN study, on Pt/silica–alumina catalysts was similar to the one previously reported for sulfided catalysts, having as main steps the complete saturation of this molecule followed then by C–N bond scission to form completely denitrogenated products. Hydrogenation and HDN activities increased with the Brønsted acidity of the catalysts. As the thiotolerance of these catalysts does not seem to be affected by the support acidity, it is proposed that the 1,4-THQ activity increase would be related to a bifunctional mechanism involving neighboring Pt sites and Brønsted sites of the silica–alumina support.

*Keywords:* Hydrodenitrogenation; Metallic catalysts; Platinum; Silica–alumina; Acidity

## 1. Introduction

The removal of sulfur and nitrogen compounds by hydrotreating is a major refining process which is adapted in terms of process approach, operating conditions and catalysts according to the feedstock to be processed, product specifications and demand [1,2]. The most abundant heteroatom in petroleum cuts is usually sulfur but when shifting from light to heavier crudes or coal derived oils the nitrogen content in the fuel increases. A great variety of nitrogen compounds have been identified in liquid fossil fuels [3]. They are responsible for imparting instability and color degradation to final products and for poisoning acidic and metal catalysts in refinery processes. Actually, hydrodenitrogenation (HDN) processes are devoted to the treatment of lube oils and diesel to improve their stability, to hydrocracking or to FCC feeds pre-treatment to avoid the poisoning of acid sites of catalysts and to naphtha treatment for catalytic reforming process. Compared to sulfur compounds, heterocyclic nitrogen compounds like quinoline and indol are more difficult to remove and require more severe conditions in terms of hydrogen pressure, temperature and space velocity.

Preferentially Mo or W sulfides promoted by Ni sulfide are utilized in as HDN catalysts [4]. However, the processing of high nitrogen crudes may require an alternative approach when deep HDN is required. In such case a technology based on a two-stage process (involving two reactors) or multiple catalyst beds (within a single reactor) could be used similarly to those proposed for deep hydrogenation of aromatics or deep hydrodesulfurization (HDS) [5,6]. In a two-stage process, the purpose of the initial step is to reduce the sulfur and nitrogen contents (typically below 500 ppm) for processing in the second reactor.

Considering that the first steps in the conversion of aromatic nitrogen containing molecules are hydrogenation reactions [7],

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the use of noble metal-based catalysts can be envisaged in a two stages approach provided the sulfur content is low enough to avoid a strong poisoning of the metallic phase. HDN on noble metal catalysts is less studied as compared to sulfided catalysts and the information available in the literature is quite small. Hydrogenolysis of C–N bonds on metals, in the absence of $H_2S$, has been investigated on model molecules such as methylamine and quinoline [8,9]. Metallic nickel, rhodium and ruthenium supported on alumina or silica were very active even at mild conditions (498–573 K, 1–6 MPa $H_2$ pressure). However, when tested in the presence of $H_2S$ most of the metals presented a strong deactivation and only Pt gave suitable activities [10].

Our group has devoted some effort in studying the effect of the metallic phase and of the support in the HDN and aromatic hydrogenation activities of noble metal based catalysts. In a previous work, it was shown that platinum based catalysts supported on $ZrO_2$ or silica–alumina presented high catalytic activities under low partial pressure of $H_2S$ [10,11] for the conversion of 1,2,3,4-tetrahydroquinoline (1,4-THQ); alumina and Y zeolite supported catalysts were less effective in such a reaction. Experiments carried out with substituted pentylamines indicated that the C–N hydrogenolysis mechanism on platinum based catalysts in the presence of $H_2S$ is similar to the one proposed on metals without $H_2S$ and different than those proposed on sulfides or carbides [12]. A metal assisted displacement mechanism is highly probable, with the intervention of $H\alpha$. However, this mechanism is sensitive to support effect which may modify the electronic properties of small particles of Pt providing more selective catalysts for completely denitrogenated products. In the case of a Pt/silica–alumina, it was observed that support acidity may contribute for the conversion of such molecules since this was the unique metallic catalyst able to convert *tert*-pentylamine, a molecule which does not have any $H\alpha$ [12].

The purpose of the present work is to contribute to a better understanding of the effect of the support acidity in the conversion of nitrogen containing molecules on metallic catalysts. Thus, the activities of Pt catalysts supported on silica–aluminas of different silica contents were measured in the HDN of 1,4-THQ in the presence of a small partial pressure of $H_2S$. These results were correlated with the acidic properties of the catalysts determined by pyridine adsorption and isooctane hydrocracking (HCC).

## 2. Experimental

### 2.1. Catalyst preparation and characterization

A series of commercial silica–alumina samples (Siral from Condea), with silica content varying between 10 and 50 wt.%, was used as support. The samples were previously calcined at 773 K before metal impregnation.

Platinum (1 wt.%) was deposited on the silica–alumina supports (see Table 1) by incipient wetness impregnation using chloroplatinic acid (Johnson Matthey) as metal precursor. After impregnation, the samples were aged for 2 h, then oven dried at 393 K and calcined at 773 K for 1 h. The final catalysts were obtained by reduction under pure hydrogen at 583 K for 6 h and stored under inert atmosphere.

Table 1
Composition of the supports and catalysts and platinum dispersion

| | Support | | | | |
|---|---|---|---|---|---|
| | Siral10 | Siral20 | Siral30 | Siral40 | Siral50 |
| $SiO_2$ content (wt.%) | 10 | 20 | 30 | 40 | 50 |
| Surface area ($m^2$/g) | 352 | 330 | 360 | 374 | 476 |
| Pt content (wt.%) | 1.1 | 1.1 | 1.1 | 1.1 | 1.0 |
| Pt dispersion | 0.66 | 0.68 | 0.70 | 0.70 | 0.57 |
| Pt particle size (nm)[a] | 1.4 | 1.4 | 1.3 | 1.3 | 1.6 |

[a] Calculated according to the dispersion results.

Metal dispersions were measured by hydrogen chemisorption at 373 K by the volumetric method. The total amount of chemisorbed hydrogen was determined by the difference between overall and reversible adsorption isotherms and dispersion was calculated using a H/Pt atom ratio equal to 1. Platinum particle sizes were calculated considering that metallic particles have a cubic geometry with five exposed faces [13].

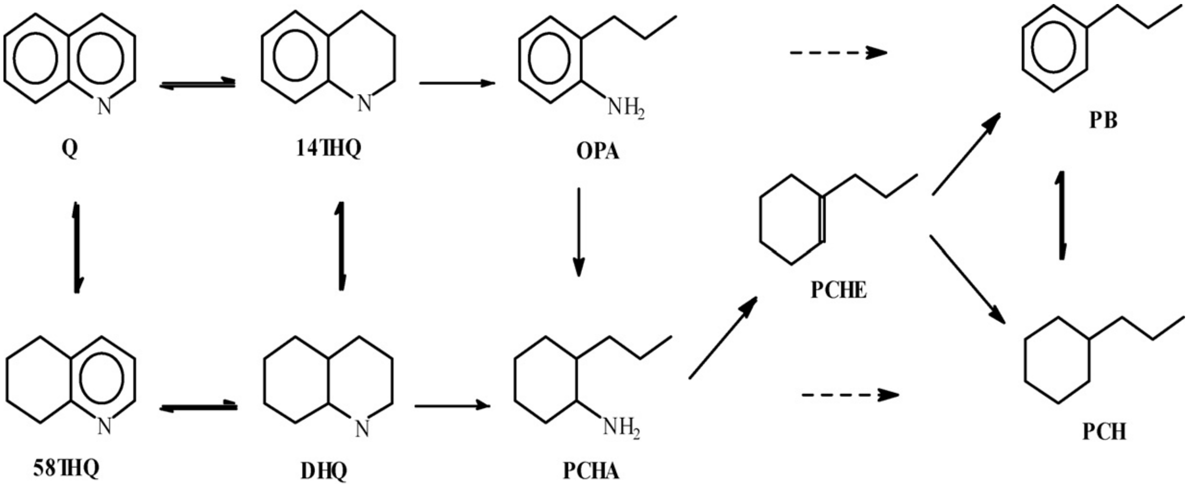
Some used samples (after 1,4-THQ HDN tests) were analyzed by transmission electronic microscopy (TEM), using a JEOL 2010 microscope. After grinding, the catalysts samples were dispersed in methanol by ultrasound and deposited over a copper grid covered with carbon film.

The acidities of the catalysts were evaluated by isooctane hydrocracking and Fourier transformed infrared spectroscopy (FTIR) of adsorbed pyridine. The HCC reaction was carried out in plug-flow microreactor at 523 K and atmospheric pressure. In a typical test, a catalyst weight in the range of 50–75 mg was placed in the reactor, followed by reduction with pure hydrogen at 583 K. Then the temperature was adjusted to the reaction temperature and the catalyst was contacted with a flow of 0.67 ml/s of hydrogen saturated with isooctane (isooctane partial pressure of 1.7 kPa). Reaction products were analyzed in a gas chromatograph equipped with FID detector and HP1 column of 50 m long, 0.2 mm internal diameter and film thickness of 0.2 μm. Catalytic activities were measured after a stabilization period higher than 12 h. Rate constants were calculated considering a first order rate model.

FTIR spectroscopy of adsorbed pyridine was carried out in a Nicollet FTIR spectrometer. Self-supported wafers containing about 30 mg of catalyst were treated at 758 K under vacuum ($1.3 \times 10^{-3}$ Pa) during 16 h then cooled to ambient temperature for recording the reference spectrum. The samples were then exposed to 533 Pa of pyridine at 423 K for 30 min followed by evacuation below $2 \times 10^{-3}$ Pa. Final spectrum was also recorded at ambient temperature and the spectrum of the adsorbed pyridine was obtained by subtraction of the reference spectrum.

### 2.2. HDN catalytic tests

The catalysts were tested in the HDN of 1,4-THQ, a generally accepted model molecule for nitrogen containing oil



Scheme 1. Reaction scheme for the conversion of 1,4-THQ—adapted from Ref. [7]. Q: quinoline; 5,8-THQ: 5,8-tetrahydroquinoline; DHQ: decahydroquinoline; OPA: orthopropylaniline; PCHA: propylcyclohexylamine; PCHE: propylcyclohexene; PB: propylbenzene; PCH: propylcyclohexane. PB, PCHE and PCH correspond to HDN products.

constituents [14], in a gas phase tubular micro-reactor operated in the dynamic mode. In a typical experiment, 0.1 g of pre-reduced catalyst was placed in the reactor and heated in a flow of pure $H_2$ hydrogen up to 623 K. At this temperature, 1,4-THQ was then introduced in the reactor by saturating a hydrogen flow in a high-pressure saturator. Hydrogen sulfide was introduced in the reactor by using a mixture containing 1000 vol. ppm of $H_2S$ in hydrogen. In such a way, the 1,4-THQ and $H_2S$ partial pressures in the reactor were adjusted by an adequate choice of pure hydrogen and $H_2S/H_2$ mixture flowrates and the saturator temperature. All the experiments were carried out at 3 MPa of total pressure, 4 kPa of 1,4-THQ and $H_2S$ partial pressures between 0 and 1500 Pa. After a stabilization period of 12 h (minimum), the reaction products were sampled on-line and analyzed every hour by a FID gas chromatography with a HP1 column (non-polar) of 25 m long, 0.22 mm internal diameter and 0.25 μm of film thickness.

The standard experimental conditions were so chosen as HDN products (PCHE, PB, PCH, see Scheme 1) could be obtained in a not negligible quantity ($T > 573$ K) and thermodynamic equilibrium of dehydrogenation of 1,4-THQ was not displaced too much to quinoline and 5,8-THQ formation [15]. Scheme 1 gives the reaction network of 1,4-THQ in the presence of hydrogen [7]. Under the conditions indicated before, the main reaction products were DHQ for N-containing products and PCH for completely denitrogenated products (HDN products). Heavy products were also formed in minor amounts which were identified by GC–MS analysis as substituted molecules of 1,4-THQ, bicyclohexyls and phenylamines.

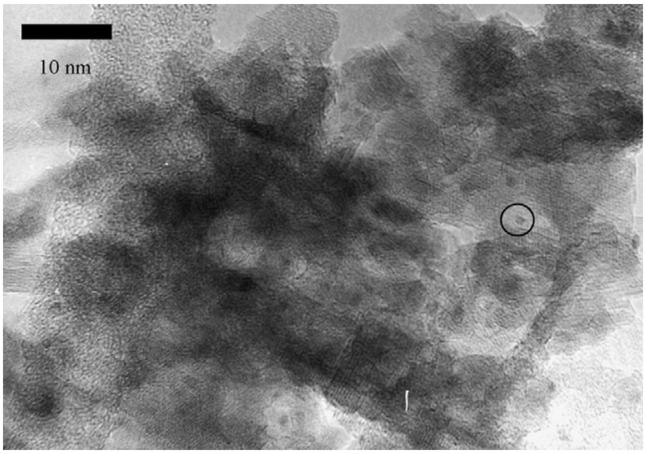


Fig. 1. TEM micrography of Pt/Siral20 catalyst after 1,4-THQ HDN reaction.

The overall conversion $X$ was calculated considering the transformation of all unsaturated heterocyclic nitrogen compounds (quinoline, 1,4-THQ and 5,8-THQ). Rate constants were calculated according to first-order kinetic and conversions were determined within 10% error.

## 3. Results and discussion

Chemical composition and surface area (SA) of the Pt/silica–alumina catalysts are shown in Table 1. For silica contents between 10 and 40 wt.%, the surface areas of the catalysts are quite similar but lower than the one of the support with higher silica content. The platinum content is very close to the theoretical one (1.0 wt.%) and the small variations are within the precision of the chemical analysis method.

### 3.1. Dispersion and acidic properties of the catalysts

The dispersions of platinum on the various silica–alumina supports (shown in Table 1), as calculated from the results of hydrogen chemisorption, were very similar for the supports with silica content in the range of 10–40 wt.% but slightly lower for the one prepared with the Siral 50. The calculated sizes of the platinum particles varied in the range of 1.3–1.6 nm.

Some of these catalysts were examined by TEM after the catalytic test of HDN of 1,4-THQ; as example, a image from the catalyst Pt/Siral20 is shown in Fig. 1. In general, the particle sizes after the catalytic test were similar to the ones shown in

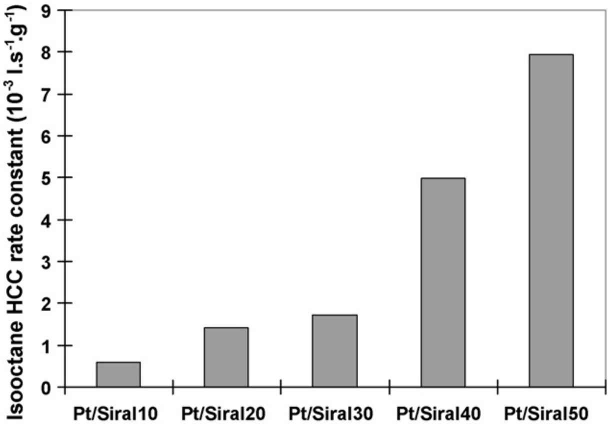


Fig. 2. Isooctane HCC activities of Pt catalysts supported on silica–alumina of different silica contents.

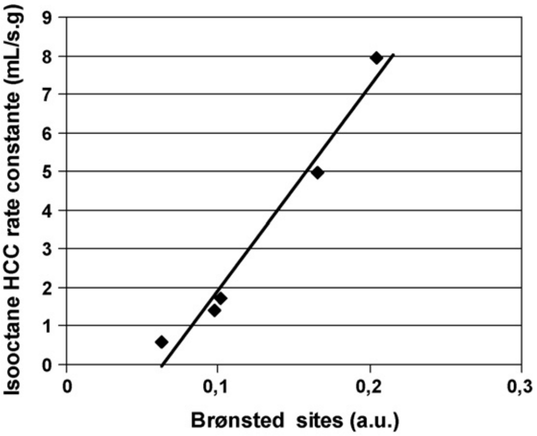


Fig. 4. Relationship between Brønsted acidity and the rate constant of isooctane HCC for the series of Pt on silica alumina catalysts (from Pt/Siral10 on the left up to Pt/Siral on the right).

Table 1, although a few sintered particles were sometimes observed.

Isooctane hydrocracking is usually used as model reaction for measuring the acidity of catalysts. The conversion of this molecule involves a tertiary carbocation resulting in the formation of isobutane and isobutene. The cracking of secondary carbocations, formed after isooctane isomerization, can lead to C3 and C5 products, as reported by Bourdillon et al. [16].

According to this reaction, a large increase in catalytic conversion was obtained with increasing $SiO_2$ content as shown in Fig. 2. The main reaction product was isobutane and very small amounts of C3 and C5 products were observed.

The FTIR spectroscopy of adsorbed pyridine was used to discriminate Lewis and Brønsted acidities of silica–alumina supports and respective catalysts. The IR spectra the silica–alumina supports are shown in Fig. 3 and Table 2 summarizes the integrated surface of the IR characteristic bands of Brønsted sites (1548 $cm^{-1}$) and Lewis sites (1455 $cm^{-1}$), after pyridine desorption at 423 K.

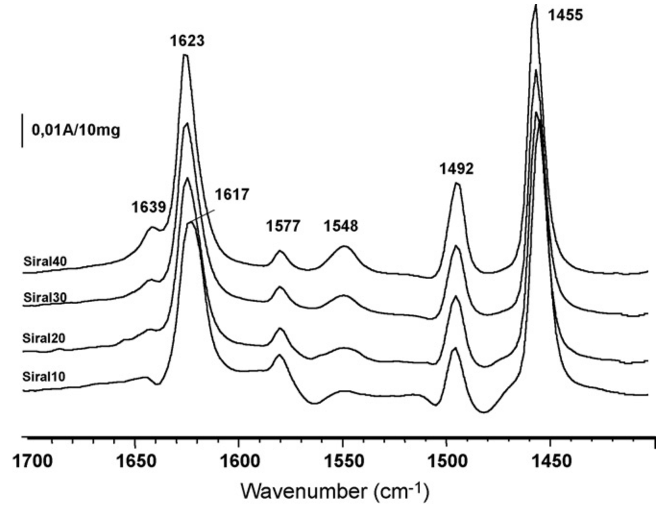


Fig. 3. IR spectra of adsorbed pyridine on Pt/silica–alumina catalysts with different silica contents.

As expected, the concentration of Brønsted acidic sites increases with increasing silica content whereas the concentration of Lewis acidic sites decreases. The introduction of platinum on these supports does not modify significantly the FTIR spectra of adsorbed pyridine and the intensity of the Brønsted and Lewis bands.

Isooctane hydrocracking activity being related to Brønsted sites, a direct relationship between these two characterizations could be drawn, as illustrated in Fig. 4. It is important to consider that the characterization of the acidity of bifunctional catalysts such as Pt/silica–alumina by model reaction requires that the hydrogenation–dehydrogenation activity is not rate limiting. Considering that all catalysts had similar metal content and dispersion, the good relationship between isooctane hydrocracking and Brønsted sites determined by FTIR spectroscopy is an evidence of an adequate measurement of the catalyst acidity. Thus, this silica–alumina series gave us the possibility of checking the influence of the acidity on the catalytic properties of nanoparticles of Pt in HDN reaction.

### 3.2. Catalytic activities in HDN of 1-4THQ

The conversion of 1,4-THQ was initially investigated at 623 K in the presence of 100 ppm of $H_2S$. The overall conversion of 1,4-THQ and the product distribution are shown in Table 3. As mentioned before, the overall conversion $X$ accounts for the transformation of all unsaturated nitrogen containing compounds (1,4-THQ, 5,8-THQ and quinoline),

Table 2
Brønsted and Lewis acidic sites of silica–alumina supports as determined by IR of pyridine

| | Support | | | | |
|---|---|---|---|---|---|
| | Siral10 | Siral20 | Siral30 | Siral40 | Siral50 |
| Brønsted sites[a] | 0.06 | 0.1 | 0.1 | 0.17 | 0.2 |
| Lewis sites[a] | 1.42 | 1.26 | 1.17 | 1.25 | 0.97 |

[a] Integrated surface of characteristic IR bands at 1548 $cm^{-1}$ (Brønsted sites) and 1455 $cm^{-1}$(Lewis sites)—arbitrary units.

Table 3
Conversion of 1,4-THQ on Pt/silica–alumina catalysts at 623 K

| Catalyst | $X^a$ (%) | Product yields (%)[b] | | | | | 1,4-THQ rate constant | |
|---|---|---|---|---|---|---|---|---|
| | | HDN | OPA | PCHA | DHQ | HP | ($\times 10^{-4}$ l/s g)[c] | (l/s atg $Pt_s$)[d] |
| Pt/Siral10 | 49.0 | 19.2 | 3.2 | 2.4 | 20.8 | 3.4 | 10.6 | 29 |
| Pt/Siral20 | 58.6 | 29.0 | 2.9 | 3.0 | 19.6 | 4.1 | 14.4 | 37 |
| Pt/Siral30 | 62.7 | 34.7 | 2.7 | 2.5 | 18.2 | 4.6 | 15.3 | 41 |
| Pt/Siral40 | 63.9 | 37.2 | 2.5 | 1.9 | 17.4 | 4.9 | 15.8 | 42 |
| Pt/Siral50 | 58.4 | 32.8 | 3.0 | 1.9 | 16.8 | 3.9 | 13.2 | 44 |

[a] Overall 1,4-THQ conversion.

[b] See Scheme 1 for abbreviations, HP: heavy products.

[c] Rate constant normalized by catalyst weight.

[d] Rate constant normalized per gram of surface platinum.

since these molecules are considered to be in chemical equilibrium at the reaction conditions.

The conversion of 1,4-THQ with noble metal catalysts followed the same reaction pathway as the one observed with conventional HDT catalysts, as shown in Scheme 1. In general terms, the 1,4-THQ was firstly hydrogenated to DHQ and then completely denitrogenated compounds (HDN compounds) were formed by C–N bond scission. Table 3 shows that DHQ concentration is close for all catalysts, indicating that an equilibrium is reached between all quinolines whereas strong differences are observed on HDN products. Thus, due to the high hydrogenation activities of noble metal catalysts, the rate limiting step is the C–N bond scission to form HDN products, in opposite to the result observed with sulfided catalysts where the formation of DHQ is the slower step [11]. Therefore, the overall conversion $X$ can be considered representative of the catalyst hydrogenation activity.

The overall conversion of 1,4-THQ, as well as the specific rate constant (by weight of catalyst), increased as the support silica content varied from 10 to 40% and then decreased slightly for the catalyst containing the higher silica content. When the rate constants were normalized with respect to the dispersion of the platinum particles (last column of Table 3), there was clearly a correlation with the Brønsted acidity of the catalysts as shown in Fig. 5.

Although the formation of HDN products also increased with the catalyst acidity, the effect of the Brønsted acidity on the hydrogenolysis activity was not straightforward because HDN products are formed by secondary reactions and their yields are strongly dependent on the overall conversion. Nevertheless, it is important to point out that the increase in the HDN product yields was higher than the corresponding increase in the overall 1,4-THQ conversion. The yields of other products as OPA, PCHA and heavy products were not strongly influenced by the catalysts acidity and remained almost constant.

It is generally considered that acidic support enhances the thiotolerance of Pt particles in hydrogenation reactions. According to Gallezot et al. [17], this promotion effect would be attributed to the formation of electron deficient Pt particles which would be more tolerant to sulfur compounds.

This aspect was analyzed by measuring the conversion of 1,4-THQ in presence of $H_2S$ contents varying in the range of 0–500 ppm. The results are illustrated in Fig. 6. After exposure to 500 ppm of $H_2S$, a back point performed for a 100 ppm concentration of $H_2S$ indicates that the poisoning effect of $H_2S$ is reversible at our experimental conditions. The kinetic order with respect to $H_2S$ was found to be −0.43, i.e. close to the one observed with Pt on alumina [10], which is not an acidic support. So, the observed increase of 1,4-THQ activity with

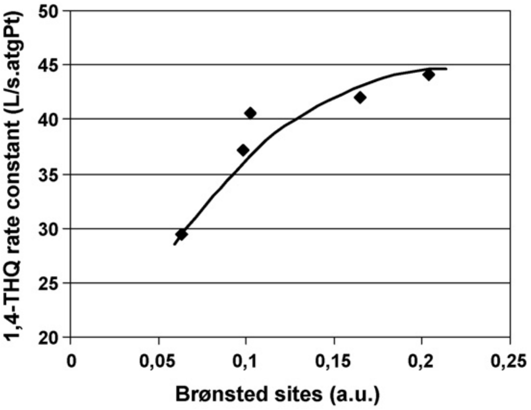


Fig. 5. 1,4-THQ rate constant as function of the Brønsted acidity of Pt/silica–alumina catalysts.

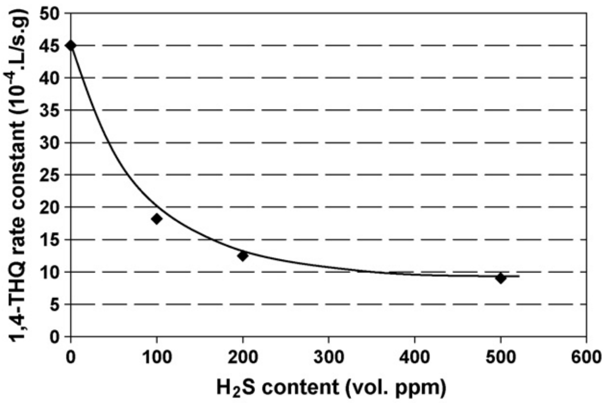


Fig. 6. Effect of $H_2S$ partial pressure on the conversion of 1,4-THQ rate constant with Pt/Siral40 catalyst at 623 K.

support acidity cannot be attributed to a better thiotolerance of the noble metal particles.

In the presence of 1,4-THQ and its reaction intermediates, the contribution of the acidic sites of the support should be attenuated or suppressed due to the strong adsorption of these basic molecules. Nevertheless a promotion effect on the 1,4-THQ conversion is observed. Even if basic molecules and ammonia are formed, the intrinsic acidity of the support and especially Brønsted acidity contributes to enhance the hydrogenation and HDN properties of platinum, probably in a bifunctional mechanism. The basic molecules can be strongly adsorbed on acidic sites in the vicinity of the Pt particles and both metallic and acidic sites may cooperate to proceed to the hydrogenation and hydrogenolysis of the molecule. Hydrogenolysis of C–N bonds on Pt nanoparticles is supposed to proceed via a mechanism analogous to that described for C–C bond scission i.e. a hydrogen deficient intermediate formed upon chemisorption [12,18]. The adsorption of the amine on Brønsted sites close to this metallic site brings a cooperative effect.

Finally, it is interesting to note that the catalytic activity of Pt/Siral40 (or Pt/Siral50) catalysts were about twice higher than that of a conventional hydrotreating NiMoP on alumina catalysts, tested under the same conditions [19].

## 4. Conclusions

In the framework of a two-stage process, i.e. in the presence of a small partial pressure of $H_2S$, Pt on silica–alumina is an efficient HDN catalyst. The acidic properties, and especially the Brønsted acidity, of the support influence greatly the performances of the catalyst. For an almost similar dispersion of Pt particles, activity can be doubled with an increase of acidity. However, this effect cannot be attributed to an electronic effect which would favor thiotolerance. We suggest that we are in presence of a bifunctional mechanism which occurs on neighboring Pt sites and Brønsted sites of the silica–alumina support.

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