



Selective hydrogenation of nitrocyclohexane to cyclohexanone oxime with H₂ on decorated Pt nanoparticles

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ABSTRACT

A Pt catalyst has been designed to convert nitrocyclohexane into cyclohexanone oxime under mild hydrogenation conditions (4 bar of H₂, 383 K, and solvent-free media). It has been found that the partial reduction of the nitro group to the oxime function is promoted by Pt nanoparticles decorated with TiO_x species, being cyclohexanone the main undesired by-product. A reaction scheme has been proposed that explains the process and active sites involved with the formation of the different reaction products. Based on that, a further chemical modification of the catalyst with sodium cations has allowed to increase the selectivity to cyclohexanone oxime to ~85% at 95% conversion. The final catalyst can be recycled and TON values of, at least, 13,000 can be obtained.

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1. Introduction

Nylon-6 has become an important reference in the industrial production of polymers, and the demand has expanded in the last years. ϵ -caprolactame, precursor of Nylon-6, is currently manufactured using cyclohexanone as starting reactant, which is converted into cyclohexanone oxime and finally rearranged to give the lactam in a three step process [1,2]. Based on this approach, much effort has been done on the study of Beckmann rearrangement reactions of oximes to the corresponding lactams [3–8]. Though cyclohexanone can be obtained by hydrogenation of phenol, the preferred industrial route involves the direct oxidation of cyclohexane. However, the aerobic oxidation of cyclohexane to cyclohexanone limits the whole efficiency of the process owing to the low yields per pass achieved (~8%) using homogeneous cobalt catalysts [9] or up to ~10% with Co-HZSM-5 [10]. Furthermore, the need of hydroxylamine to produce cyclohexanone oxime introduces another sensitive reaction step in the classical process, which can be improved by *in situ* generation of hydroxylamine [11].

Alternative processes for the production of ϵ -caprolactame have been searched and recently [12] a different route has been proposed that involves the hydrogenation of nitrobenzene to cyclohexylamine followed by controlled oxidation of the amine to produce the cyclohexanone oxime. This clever method becomes limited by the long reaction times required (10 days) and the yield of oxime achieved (~60%). An alternative method for the produc-

tion of cyclohexanone oxime was reported by DuPont [13,14]. It was based on the one step hydrogenation of nitrocyclohexane into cyclohexanone oxime at 35 bar and 413 K with a supported Pd catalyst in the presence of PbO salts. In this process, relatively high pressures and environmentally unfriendly PbO salts were required to produce moderated yields (~70%) of cyclohexanone oxime. Nevertheless, for carrying out this interesting process nitrocyclohexane has to be produced. Recent publications [15,16] have taught the possibility to nitrate cyclohexane under mild conditions (343–356 K) giving up to 91% selectivity to nitrocyclohexane. The advances in nitration technology has made us to reconsider the direct transformation of nitrocyclohexane into cyclohexanone oxime and have designed an easy recyclable lead free (Pt–Na)/TiO₂ solid catalyst which works in a solvent free media under milder reaction conditions (4 bar) than the DuPont process [13,14]. This objective represents an important scientific challenge since the Pb additive, which can give toxic by-products, seems to be responsible for the low activity of the Pd catalysts (high reaction pressures required), but at the same time is responsible for raising the catalyst selectivity from less than 25% to ~70%.

2. Experimental

2.1. Catalysts preparation

A commercial sample of 5% Pd on active charcoal was provided by Sigma-Aldrich. 1.5% Au on TiO₂ was synthesized by the World Gold Council using a deposition–precipitation procedure [17]. On the other hand, 0.2% Pt/C, 1% Pt/Al₂O₃, and 0.2% Pt/TiO₂ catalysts were prepared by the incipient wetness technique, using H₂PtCl₆

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Table 1
Catalytic results in the hydrogenation of nitrocyclohexane using different metal-based catalysts.^a

Catalysts	$T_{\text{reduction}}$ (K)	Catalyst (mg)	Time (min)	%Conversion (NCH)	%Selectivity					
					CHA	CHO	CHone	CHCHA	DCHA	CHCHone
1.5% Au/TiO ₂ ^b	673 ^c	150	105	9	35.2	22.8	43.0	1.0	n.d.	n.d.
1% Pt/Al ₂ O ₃ ^a	723	100	40	70	80.1	2.0	8.9	3.0	4.0	2.0
5% Pd/C ^b	723	15	195	97	84.9	4.9	4.7	2.5	n.d.	3.0
0.2% Pt/C ^b	723	100	80	85	70.0	18.0	5.0	6.5	n.d.	0.5
0.2% Pt/TiO ₂ ^b	473	150	100	97	31.8	5.4	14.2	4.0	40.6	4.0
0.2% Pt/TiO ₂ ^b	723	250	80	95	5.0	65	23.0	5.0	n.d.	2.0
0.2% Pt/TiO ₂ ^c	723	200	900	96	3.5	69.6	21.8	3.1	n.d.	2.0
0.2% Pt/TiO ₂ ^{c,d}	723	200	880	95	3.4	84.5	8.6	2.0	n.d.	1.5

NCH—nitrocyclohexane; CH—cyclohexylamine; CHO—cyclohexanone oxime; CHone—cyclohexanone; CHCHA—cyclohexyl-cyclohexylidene amine; DCHA—dicyclohexylamine; CHCHone—2-cyclohexylidene-cyclohexanone.

^a Reaction conditions: $T = 393$ K, $P_{\text{H}_2} = 10$ bar; feed composition: 75% ethanol, 25% nitrocyclohexane (mol%).

^b $T = 413$ K; $P_{\text{H}_2} = 15$ bar; feed composition: 75% ethanol, 25% nitrocyclohexane (mol%).

^c $T = 383$ K; $P_{\text{H}_2} = 4$ bar; feed composition: 100% nitrocyclohexane (mol%).

^d Catalyst doped with 6000 ppm of Na.

^e Catalyst calcined at 373 K under flow air.

hexahydrate as Pt. As an example, 20 mL of an aqueous solution containing 53.1 mg of H₂PtCl₆·6H₂O were impregnated on 10 g of TiO₂ (Degussa, P-25) to prepare the 0.2 wt% Pt/TiO₂ catalyst. After a perfect mixing of the corresponding slurry, the sample was dried at 373 K during 5 h.

All the catalysts, with the exception of the Au/TiO₂ system, were treated under H₂ flow (50 mL/min) at a selected temperature before performing the catalytic tests (see Table 1).

The sodium containing titanium decorated Pt/TiO₂ catalyst was prepared by impregnating the 0.2% Pt/TiO₂ sample reduced at 723 K with different amounts of Na (sodium acetate as precursor). As an example, to prepare 10 g of the material doped with 6000 ppm of Na, 20 mL of an aqueous solution containing 214.1 mg of CH₃COONa must be used. After homogenizing the resulting gel, the material was dried at 373 K during 6 h before the catalytic test.

2.2. Kinetic experiments

Catalytic experiments were performed in reinforced glass reactors equipped with temperature and pressure control. For each reaction, 1 mL mixture of reactants and solvent, if required, was placed into the reactor (2 mL capacity) together with an appropriate amount of catalyst. Nitrocyclohexane comes from Sigma-Aldrich Company with purities above 96%. 1,3,5-trimethylbenzene was always used as external standard for the determination of conversions and yields. Details on the composition of the feed and amount of catalyst for the different experiments can be found in Table 1. After sealing the reactor, air was purged by flushing twice with 10 bar of hydrogen. Then, the autoclave was heated up to the required temperature and finally it was pressurized with H₂ at the selected set point. During the experiment, the pressure was maintained constant and the stirring rate was fixed at 1000 rpm (magnetic stirring). Aliquots (~50 μ L) were taken from the reactor at different reaction times. The product composition was determined by means of gas chromatography, once the catalyst particles were removed from the solution by centrifuging at 12,000 rpm. The products were identified by GC-MS and also by comparison with commercially pure products (Sigma-Aldrich Company).

For recycling experiments, the catalyst was recovered, washed with ethanol, and dried at 373 K during 12 h. Only experiments with mass balances >95% were considered.

2.3. TEM measurements

Electron Microscopy data were collected in a JEOL2010-FEG TEM/STEM microscope, equipped with a Field Emission electron

source and an objective lens with C_s value of 0.5 mm. Operating this microscope at 200 kV allows recording HREM images with a point-to-point resolution of 0.19 nm. These images were digitally recorded on a 1024 \times 1024 CCD camera. HREM image analysis was performed using routines implemented in the software plugins of Digital Micrograph. High Angle Annular Dark Field Images (HAADF) were obtained using an electron probe with a diameter of 0.5 nm and diffraction camera length of 10 cm. For the HAADF detector mounted on this microscope this would correspond to effective detector radii of 60 mrad (inner radius) and 160 mrad (outer radius). Under these conditions the image contrasts in the HAADF images would allow detecting the presence of subnanometer-sized platinum particles supported on titania.

To reveal subtle details of the surface composition of the Pt nanoparticles in the Pt/TiO₂ catalysts, nanoanalysis by STEM-EELS has been performed. Electron Energy Loss spectra were acquired in the so-called spectrum-line mode using a GIF2000 spectrometer. For these experiments a fine, 0.5 nm diameter, electron probe was scanned along predefined paths of the catalysts, starting at positions located on the supports, passing through the particle-support interface, then bulk positions in the particle and particle surface and ending in vacuum. At specific points of each path, separated at a distance slightly larger than the probe size, i.e. 0.7 nm, Electron Energy Loss spectra covering the range of energy losses characteristic of the elements present in the support were collected (O-K and Ti-L_{2,3} edges). Acquisition times in the range 3–5 s per spectra and a dispersion value of 0.3 eV were used.

The simultaneous analysis of the collection of EELS spectra obtained in this way and the HAADF signal allows establishing the spatial distribution of Ti species in the catalysts and, more in particular, the presence of submonolayer TiO_x species on the surface of the metal particles, which could have eventually migrated during the synthesis or activation of the catalysts.

Electron microscopy specimens were prepared by depositing small amounts of the catalyst powders onto holey-carbon coated 3-mm Cu-grids. To avoid contamination problems, the grids were dipped directly into the catalyst powders and excess sample removed by gentle blowing.

3. Results and discussion

3.1. Partial hydrogenation of nitrocyclohexane to cyclohexanone oxime on Pt and Pt decorated nanoparticles

We have recently found that the adsorption and reactivity of nitro compounds on metal catalysts is strongly dependent not only on the nature of the metal [18], but also on the crystallite size

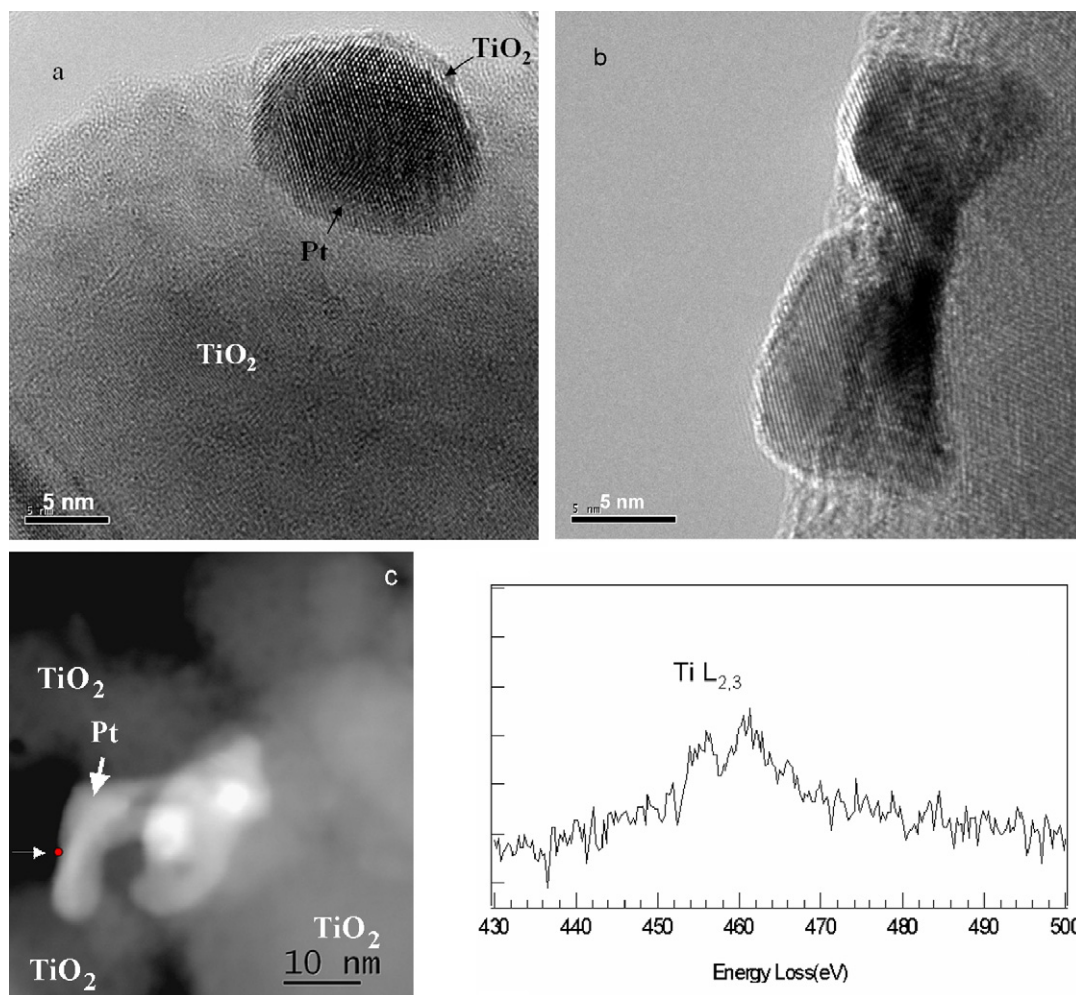


Fig. 1. HRTEM images of Pt/TiO₂ samples treated at 723 K (a) and 473 K (b) under H₂ flow. TiO_x species can be observed decorating the surface of Pt particles when the reduction process is carried out at 723 K, as also evidenced by a STEM-EELS analysis (c).

and the way the reactant interacts with the support [19,20]. More specifically, it was reported that Au/TiO₂ was able to transform 1-nitro-1-cyclohexene into cyclohexanone oxime with excellent selectivity (~90%) in the presence of H₂ [18,21]. However, as far as we know, there is not yet any feasible process to produce this starting reactant at an industrial scale and it would be highly desirable to develop an equivalent green and profitable route using a more accessible substrate such as nitrocyclohexane. Unfortunately, we have seen (Table 1) that Au/TiO₂ is inactive when reacting nitrocyclohexane. Thus, when more active hydrogenation catalysts such as Pt/Al₂O₃, Pt/C or Pd/C were used, very low selectivities to cyclohexanone oxime were obtained, and the complete reduction of the nitro group to the corresponding amine was the main reaction occurring (see Table 1).

It is known [19,20,22–27] that the activation of nitroaromatics onto metallic nanoparticles strongly depends on the nature of the support, the metal crystallite size, and the presence of other additives, which become decisive for the final activity and selectivity of the catalyst. Taking into account that an improvement in the selective hydrogenation of nitrocyclohexane to cyclohexanone oxime was observed when depositing PbO on Pd in the DuPont process [13,14], we thought that TiO_x decorated Pt could also be used as a more active and selective catalyst for producing cyclohexanone oxime by hydrogenation of nitrocyclohexane, while avoiding the use of lead.

It is well known in the literature [28–32] that the surface of Pt particles in Pt/TiO₂ can be decorated with TiO_x species by treating

the material at 723 K with H₂. Thus, we have prepared Pt/TiO₂ treated at two different temperatures (473 and 723 K) under H₂ flow. The presence of TiO_x moieties on the top of Pt crystals was evidenced on the sample reduced at 723 K by means of HRTEM measurements (see Fig. 1a). This fact was confirmed with a STEM-EELS analysis (Fig. 1c), which shows that a partial coverage of the active phase has been produced. On the contrary, Ti features were completely absent on the Pt nanoparticles of the sample reduced at 473 K, indicating that no decoration has occurred in this case (Fig. 1b).

The catalytic reduction of nitrocyclohexane on the Pt/TiO₂ catalysts treated at low (473 K) and high (723 K) temperatures shows that selectivity to cyclohexanone oxime increases from 5% to 65% when the Pt particles are decorated with TiO_x species (see Table 1), indicating that the partial coverage of Pt nanoparticles strongly decreases the complete hydrogenation of the substrate to the amine compound (cyclohexylamine). With this catalyst, and after optimizing the reaction conditions, it was possible to reach the selectivity levels of the DuPont process (70%) at high conversions of the nitrocycloalkane, but working under much milder reaction conditions, i.e. 4 instead of 35 bar of H₂, in a solvent-free media, and avoiding the use of unfriendly PbO salts. The resultant Pt/TiO₂ catalyst is recyclable (see Table 2) and gives a TOF ~ 300 h⁻¹ (mol_{converted} mol_{Pt}⁻¹ h⁻¹, calculated with respect to total Pt atoms in the sample) and TON > 13,000.

Table 2

Catalytic results during the nitrocyclohexane hydrogenation (TON, TOF, and selectivity to the oxime at complete conversion of nitrocyclohexane) using the decorated Pt/TiO₂ after two consecutive recycles.

Experiment	Selectivity _{oxime} (%)	TOF (h ⁻¹)	Accumulated TON (mol _{converted} mol _{Pt})
1st use	70	303	3328
2nd use	68	291	7741
3rd use	65	274	13289

3.2. Reaction scheme

Results from Table 1 and Scheme 1 shows that besides cyclohexanone oxime (CHO), other products such as cyclohexylamine (CHA), cyclohexanone (CHone), cyclohexyl-cyclohexylidene amine (CHCHA), dicyclohexylamine (DCHA), and 2-cyclohexylidene-cyclohexanone (CHCHone) are usual by-products of the nitrocyclohexane hydrogenation. Results from Fig. 2 indicate that, when using 1% Pt/Al₂O₃ catalyst, cyclohexanone appears as a primary unstable product, while the shape of the curves for cyclohexanone oxime (CHO), cyclohexylamine (CHA), dicyclohexylamine (DCHA), and cyclohexyl-cyclohexylidene amine (CHCHA) indicates that they are secondary unstable products, being cyclohexylamine the predominant. However, the relative proportion of the different products is not only a function of the level of conversion, but also depends on the nature of the catalysts (Table 1). Then, while samples based on Al₂O₃ or C produce cyclohexylamine as the main reaction product, large amounts of cyclohexanone and dicyclohexylamine are observed with the undecorated Pt/TiO₂ catalyst. In this later case, it is possible to see that dicyclohexylamine is the

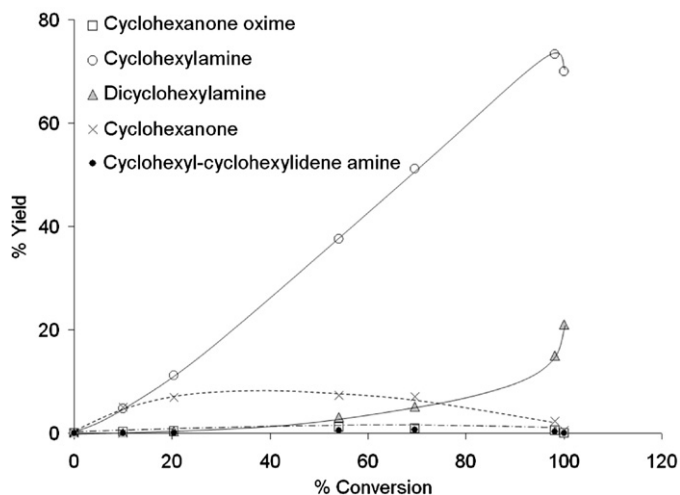
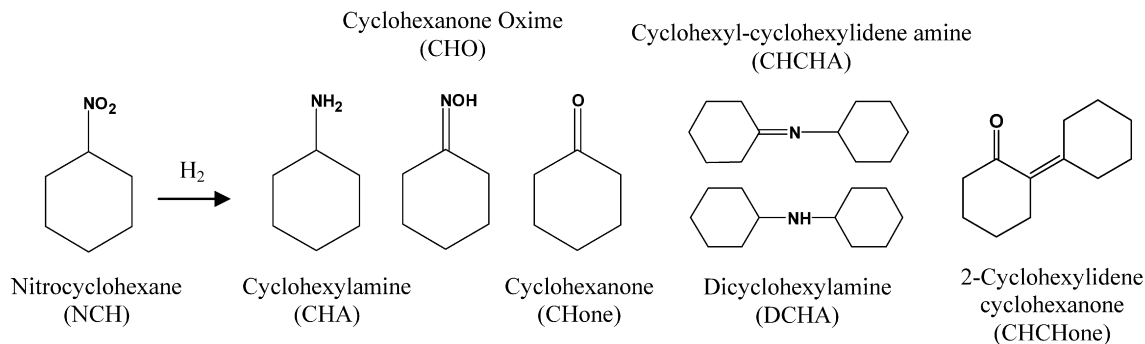


Fig. 2. Distribution of products as a function of the conversion level during the hydrogenation of nitrocyclohexane using the 1% Pt/Al₂O₃ catalyst.



Scheme 1. Principal reaction products detected during the hydrogenation of nitrocyclohexane with different Pt, Pd, and Au catalysts.

unique stable product, formed at high conversion levels (Fig. 3). On the contrary, cyclohexanone oxime, cyclohexylamine, and cyclohexanone appear as primary unstable products, and cyclohexyl-cyclohexylidene amine as secondary unstable products. Nevertheless it should be thought that, from a mechanistic point of view, cyclohexylamine and cyclohexanone require several reaction steps to be produced from nitrocyclohexane and they were expected to appear as secondary products, unless the intermediates react before desorbing from the catalyst surface. In fact, one could consider that while cyclohexylamine could be produced by consecutive hydrogenation reactions [33,34] through cyclohexylhydroxylamine as intermediate (see Scheme 2a), cyclohexanone could be produced by hydrolysis of cyclohexanone oxime [35–38] with the water formed during the first hydrogenation step (see Scheme 2b). After this, and when the amine and ketone compounds are produced, the formation of cyclohexyl-cyclohexylidene amine, dicyclohexylamine, and small traces of 2-cyclohexylidene could be easily explained taking into account the sequence of reactions given in Scheme 3.

When Pt nanoparticles were decorated by TiO₂ species (catalyst reduced at 723 K), a drastic decrease of the concentration of cyclohexylamine (inhibition of the complete hydrogenation of nitrocyclohexane) can be observed, but important amounts of the cyclic ketone are still produced (Table 1 and Fig. 4). The formation of larger amounts of cyclohexanone by using Pt/TiO₂ (either decorated or not) in comparison with catalysts based on Al₂O₃ or C suggests that the presence of TiO₂ promotes the hydrolysis of cyclohexanone oxime. In fact, it is well known that this reaction

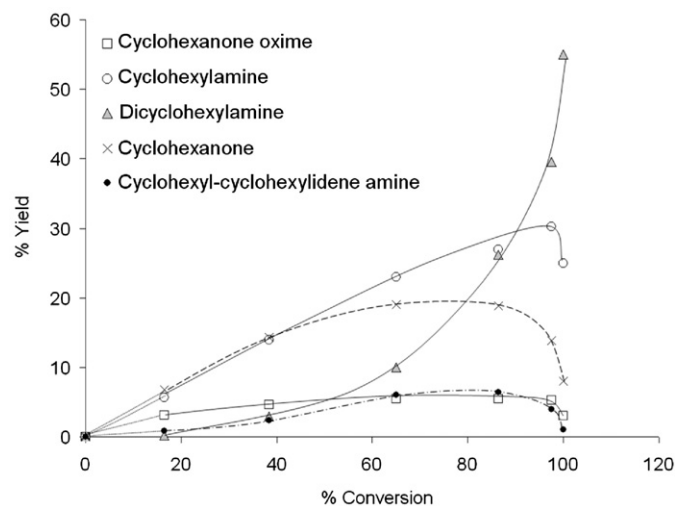
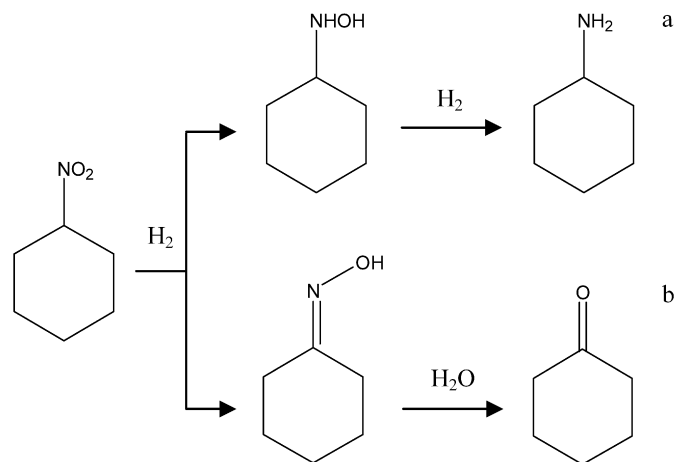


Fig. 3. Distribution of products as a function of the conversion level during the hydrogenation of nitrocyclohexane using the undecorated 0.2% Pt/TiO₂ catalyst (reduced at 473 K).



Scheme 2. Potential reaction pathway to form cyclohexylamine and cyclohexanone oxime during the hydrogenation of nitrocyclohexane.

may be catalyzed either by Brønsted or Lewis acid sites [35–37], and TiO_2 can support certainly introduce certain acid character into the reaction media [39–41]. In order to check if the formation of cyclohexanone is directly formed by hydrolysis of cyclohexanone oxime on decorated Pt/TiO_2 , cyclohexanone oxime was reacted, in the presence of decorated Pt/TiO_2 and stoichiometric amounts of water, and in absence of H_2 . Then results in Fig. 5 show that

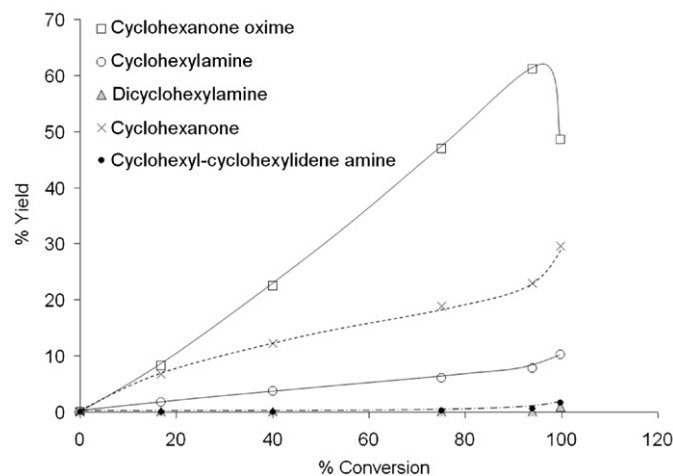


Fig. 4. Distribution of products as a function of the conversion level during the hydrogenation of nitrocyclohexane using the decorated 0.2% Pt/TiO_2 catalyst (reduced at 723 K).

when this reaction was carried out with the decorated Pt/TiO_2 catalyst, low conversion of the oxime is observed after 5 h, indicating that this compound is stable against hydrolysis when in absence of H_2 . Thus, we can conclude that the formation of cyclohexanone during the hydrogenation of nitrocyclohexane must occur through a catalytic route other than the direct hydrolysis of cyclohexanone oxime by water given in Scheme 2. To this respect, it has been reported that cyclohexanone oxime can also be reduced with H_2 in the presence of certain metal-based catalysts, forming either cyclohexylamine or cyclohexanone [42–44]. In this alternative mechanism (see Scheme 4), cyclohexanone would be initially reduced to an unstable intermediate (cyclohexylimine), which could be a further hydrogenated to give the amine, or hydrolyzed giving the cyclic ketone as reaction product. In our case, we believe that the formation of large amounts of cyclohexylamine, and cyclohexanone, as well as the formation of the corresponding condensation products, observed when cyclohexanone oxime is reacted with H_2 in the presence of water and the decorated Pt/TiO_2 catalyst (see Fig. 5), will be in favor of the reaction scheme given in Scheme 4. Furthermore, the fact that cyclohexylhydroxylamine has not been detected in any experiment, clearly suggests that, in our case, Scheme 4 can also explain the formation of cyclohexylamine, better than the reaction route proposed in Scheme 2a.

Taking into account the above discussion we can propose a general reaction scheme (Scheme 5) that can explain the products observed and the potential reaction intermediates.

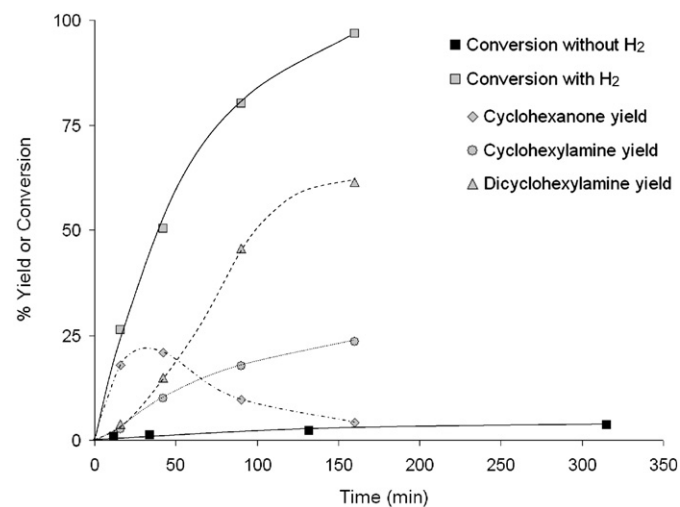
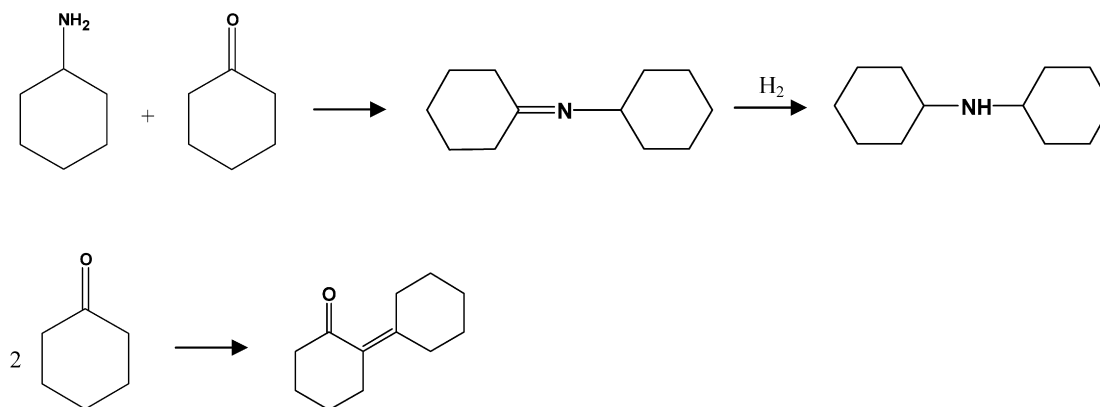
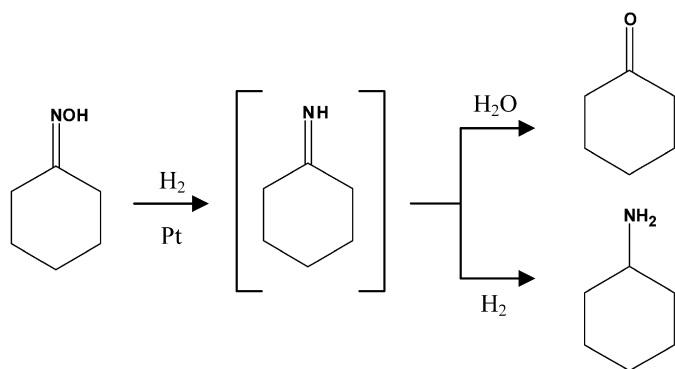


Fig. 5. Stability of cyclohexanone oxime in the presence of the decorated Pt/TiO_2 catalyst, and water (molar ratio oxime/ H_2O = 1). No hydrolysis of the oxime is observed in absence of H_2 .



Scheme 3. Formation of condensation by-products through binary reactions involving cyclohexylamine and cyclohexanone.



Scheme 4. Reaction Scheme proposed by Rylander et al. for the catalytic hydrogenation of cyclohexanone oxime with Nickel Raney Catalysts.

3.3. Improving the catalytic behavior of decorated Pt/TiO₂ catalysts by decreasing the formation of cyclohexanone

The practical absence of cyclohexylamine when nitrocyclohexane is reduced with the decorated Pt/TiO₂ catalyst (see Table 1), indicates that though cyclohexanone oxime can be further hydrogenated through the route suggested in Scheme 4, this is strongly inhibited in the presence of a nitro functionality. This fact is in complete agreement with previous literature about the role of the metal-TiO₂ interphases for preferential activation of the NO₂ group in the presence of other chemical functions [19,25] owing to the preferential adsorption of the nitro group. Thus, while TiO₂ is required to decorate the Pt and in this way to control the hydrogenation of nitrocyclohexane avoiding further reduction of cyclohexanone oxime, TiO₂ is responsible for the hydrolysis of cyclohexanone oxime leading to cyclohexanone. At this point, it becomes then necessary to preserve the desired hydrogenation sites of the titanium decorated Pt, while removing the acid sites of the support responsible for the formation of cyclohexanone. To do this, we have doped the catalyst an alkali cation [45–48]. Then the decorated Pt/TiO₂ catalyst was impregnated with increasing amounts of CH₃COONa (from 1500 to 15,000 ppm Na) and the resultant samples were tested for the hydrogenation of nitrocyclohexane. Catalytic results in Fig. 6 show that, for the optimum Na content (~6000 ppm), selectivity to cyclohexanone oxime can be increased from 69% (no Na doping) to 85% at high conversion levels. A further increase in Na⁺ decreases the yield of cyclohexanone while produces an increase in cyclohexylamine formation, with a final

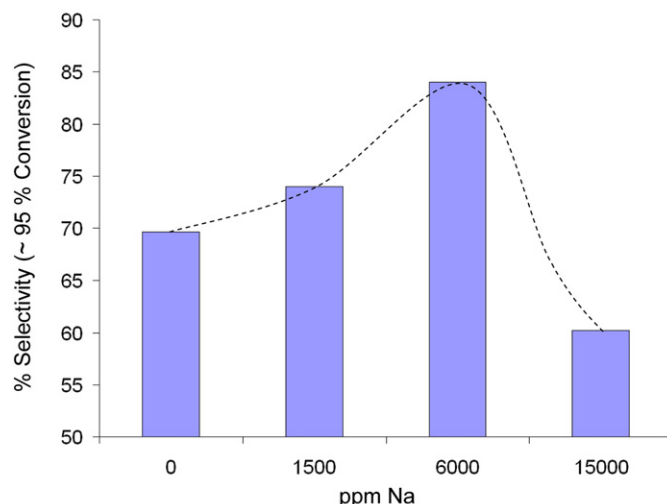
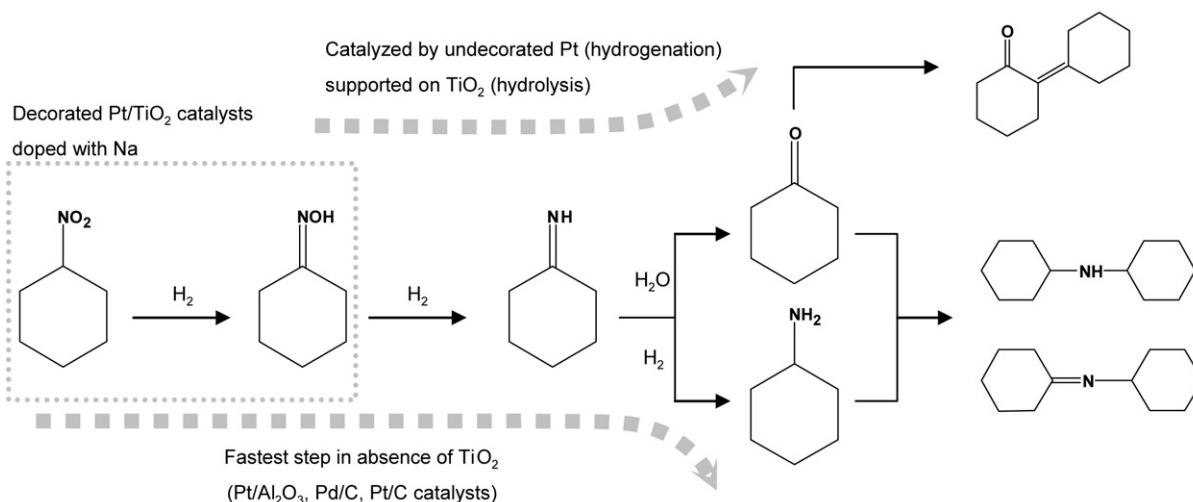


Fig. 6. Effect of Na content on the surface of decorated Pt/TiO₂ catalysts for the selective hydrogenation of nitrocyclohexane to cyclohexanone oxime.

decrease in the selectivity to cyclohexanone oxime. In other words, it appears that when the Na content is too high, the efficiency of the titanium decoration effect to promote the partial reduction of the nitro group is partially lost. Thus, it can be speculated that the doping method must be accurately controlled to reach an optimal balance between a low number of acid Ti⁴⁺ species (to avoid hydrolysis reactions), and a sufficient number of Pt/Ti boundaries (to avoid a complete hydrogenation of the nitro group). As a result of the optimization process, the selectivity to cyclohexanone oxime can be raised to ~85%, improving the previous results reported by DuPont with Pd/Pb catalyst, while working under greener and much milder reaction conditions (and 4 bar of instead of 35 bar) and in a solvent free media.

4. Conclusion

We have shown that it is possible to selectively reduce nitrocyclohexane to cyclohexanone oxime with a titanium decorated Pt catalyst containing an optimized level of alkaline. In this catalyst the TiO_x decoration avoid the complete hydrogenation of nitrocyclohexane to cyclohexylamine, while the alkaline avoids the formation of cyclohexanone by inhibiting the hydrolysis of the cyclohexanone oxime intermediate. These results can give a new chance



Scheme 5. General reaction scheme during the hydrogenation of nitrocyclohexane with H₂ using different metal-based catalytic systems.

to the DuPont process that was used at demonstration scale, but which had to be operated at lower yields, harder reaction conditions and a less environmentally friendly catalyst.

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