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Hybrid organic—inorganic catalysts: a cooperative effect between support, and palladium and nickel salen complexes on catalytic hydrogenation of imines

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Abstract

A method for immobilizing chiral salen palladium and nickel complexes (salen = (R,R)-N',N'-*bis*-(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) on ordered mesoporous silica supports (MCM-41), delaminated ITQ-2 and ITQ-6 zeolites, and amorphous silica has been developed. Hydrogenation of imines was studied with the homogeneous as well as with the heterogenized counterpart catalysts. The high accessibility introduced by the structure of the supports allows the preparation of highly efficient immobilized catalysts with TOFs of 200×10^3 h^{-1}. A moderate acidity in the support increases the catalytic activity by stabilizing the charged transition state and can duplicate the activity of the homogeneous analogues. No deactivation of the catalysts was observed after repeated recycling.
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1. Introduction

One drawback of homogeneous catalysis is the separation and recovering of the catalyst when the reaction is completed. Binding the active metal complexes to insoluble or water-soluble carriers is an attractive strategy allowing separation by filtration or extraction [1]. However, immobilization usually affects negatively the catalytic performance and efforts should be made to design new systems in which a cooperative effect between the solid support and the transition metal complex is established that can increase the activity of the homogeneous catalyst.

In recent years, reactions catalyzed by chiral–salen-based transition metal complexes have become a matter of interest [2]. Chiral–salen complexes have been applied in different kind of reactions such as asymmetric epoxidation [2a–c, 2g], cyclopropanation [2e], aziridination [2f], Knoevenagel

condensation [2h], selective hydrogenation [5g,5h]. In many cases, metal–salen complexes have been immobilized on different materials, such as polymers [3], or inorganic solids, such as silica [4] and zeolites [5]. Their interest is related to the fact that they perform highly selective processes in a multiphase system, in which the catalysts can be easily recovered.

The selective hydrogenation of imines is a reaction of interest in the production of fine chemicals, and the catalysts of choice have traditionally been Ir and Rh complexes [6], even if they require relatively high H$_2$ pressures (~ 80 bar) for carrying out the reaction. There is incentive to design highly active catalysts that can work under much milder reaction pressure and, if possible, to use less expensive metals such as palladium and nickel. We show here that salen Pd and Ni complexes are active catalysts for hydrogenation of imines at 4 bar H$_2$ pressure. Moreover by properly choosing the support it is possible to achieve a two fold increase in activity with respect to the homogeneous counterpart, by means of a cooperative effect of the support.

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Table 1
Textural characteristics of the solid supports

Support	Si/Al	BET surface area (m^2/g)	Micropore surface (t plot m^2/g)	External (or mesoporous) suface area (m^2/g)
Silica	–	540	–	540
MCM-41	∞	1030	0	1030
ITQ-2	∞	830	130	700
ITQ-6	∞	618	10	608
MCM-41	44	900	0	900
ITQ-2	25	810	90	720
ITQ-6	30	546	26	520

2. Experimental

2.1. Materials

The supports were prepared following [7] for MCM-41 and [8,9] for ITQ-2 and ITQ-6. The textural characteristics of the solids are given in Table 1.

2.2. Reactants and methods

The silylating agent 3-triethoxysilylpropylisocyanate was obtained from ABCR. The aldehydes (5-azidomethyl-2-hydroxybenzaldehyde (**1a**) and 5-azidomethyl-3-*tert*-butyl-2-hydroxybenzaldehyde (**1b**)) were prepared as follows: 35.9 mmol of chloroaldehyde precursor was dissolved in 10 ml dimethylformamide at room temperature. Then, sodium azide (37.7 mmol) was slowly added while stirring and maintained until the reaction was completed (6–10 h). The mixture was diluted with 15 ml of water and extracted with ethyl acetate (3 × 10 ml). The combined organic extracts were washed successively with water (10 ml) and brine (10 ml). The organic layer was dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure. The crude was purified by chromatography in silica (hexane–ethyl acetate 6:1) to afford **1a** or **1b** in high yields (90–95%).

N-[(5-Formyl-4-hydroxyphenyl)methyl]-*N*′-(3-triethoxysilylpropyl)urea (**2a**) and *N*-[(3-*tert*-butyl-5-formyl-4-hydroxyphenyl)methyl]-*N*′-(3-triethoxysilylpropyl) urea (**2b**) were prepared as follows: Solutions of the aldehydes **1a** (2 mmol) or **1b** (2 mmol) and 3-triethoxysilylpropylisocyanate (2.1 mmol) were prepared in 40 ml of ethyl acetate at room temperature. Then, slurry of 50 mg of Pd/C (10%) in 2 ml of ethyl acetate was carefully added and the mixture was vigorously stirred overnight under positive H_2 pressure. The slurry was then filtered and the filtrate evaporated in vacuum to afford **2a** or **2b** in almost quantitative yields.

2b: IR (KBr): $\nu = 3350, 1650, 1570$ cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 11.65$ (s, $-OH-$); 9.78 (s, 1H, $-CHO$); 7.35 (s, 1H, arom.); 7.26 (s, 1H, arom.); 4.72 (br. s, $-NH-$); 4.58 (br. s, $-NH-$); 4.24 (d, 2H, PhCH_2NH–); 3.72 (q, 6H, CH$_3$CH_2O–); 3.11 (m, 2H, CH$_2$CH_2NH–); 1.53 (2H, m, NHCH$_2$CH_2CH$_2$Si); 1.32 (9H, s, (CH_3)$_3$C–); 1.15 (t, 9H, CH_3CH$_2$O–); 0.56 (t, 2H, CH$_2$CH_2Si); ^{13}C NMR (CDCl$_3$): $\delta = 197.07$ ($-CHO$); 160.40 ($-NHCONH-$); 158.10 ($=C$–OH); 138.55 ($=C$–CH$_2$NH–); 133.65 ($=CH$, arom.); 130.46 ($=CH$, arom.); 130.11 ($=C$–C(CH$_3$)$_3$); 120.33 ($=C$–CHO); 58.43 (CH_2O–); 43.78 (CONHCH$_2$–); 42.88 (PhCH$_2$NHCO–); 34.83 (C(CH$_3$)$_3$); 29.12 (C(CH$_3$)$_3$); 23.55 (CH$_2$$CH_2CH_2$); 18.26 ($CH_3CH_2$O–); 7.50 ($CH_2$Si–); MS$^+$ (EI) (m/z, %): 454 (M$^+$, 5); 408 (M$^+$–EtOH, 68); 206 (M$^+$–CONH(CH$_2$)$_3$Si(OEt)$_3$, 100); 191 (M$^+$–NHCONH(CH$_2$)$_3$Si(OEt)$_3$, 40); 163 (M$^+$-291, 33).

Imines **I** and **II** used as substrates for the catalytic tests were synthesized according with the method described in the literature [10].

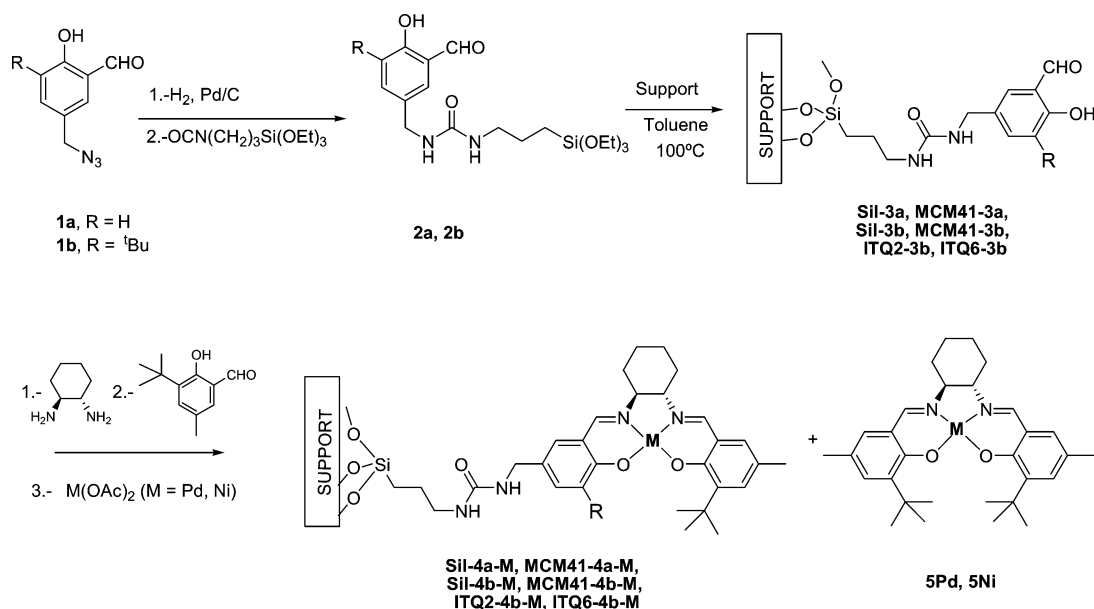### 2.3. Heterogenization of hydroxyaldehydes

Typically, silica or the corresponding MCM-41, ITQ-2, or ITQ-6 (2 g) materials were suspended in toluene (25 ml) and stirred at room temperature for 30 min. Then, a solution of 2 mmol of the triethoxysilylaldehydes **2a** or **2b** in toluene (5 ml) and 400 μl of water were added. The slurry was heated at 100 °C for 16 h and the yellow solid was filtered off and washed successively with toluene, petroleum ether, ethanol, and ether. The solid was dried under high vacuum for 24 h to afford the anchored hydroxyaldehydes **Sil-3a**, **Sil-3b**, **MCM41-3a**, **MCM41-3b**, **ITQ2-3b**, and **ITQ6-3b**.[1]

MCM41-3b: % C: 13.90, % H: 2.63, % N: 1.91 corresponding to 0.78 mmol/g; IR (KBr): $\nu = 3421, 1642, 1564$ cm^{-1}; UV-vis (λ, nm) 425, and 360; ^{13}C NMR (solid): $\delta = 199.29$ ($-CHO$); 160.58 ($-NHCONH-$); 147.84 ($-C$OH); 143.84; 138.13; 130.98; 120.18; 57.45 (CH$_3$CH$_2$O–); 54.29 ($-NHCH_2$Ph–); 42.04 ($-NHCH_2$CH$_2$–); 27.60 ($-CH_2$CH$_2$CH$_2$–); 18.99 (CH$_3$CH$_2$O–); 9.64 ($-CH_2$Si–).

2.4. Preparation of immobilized salen ligands

Typically, stirred slurry of 1 mmol of the corresponding anchored hydroxyaldehydes **Sil-3a**, **Sil-3b**, **MCM41-3a**, **MCM41-3b**, **ITQ2-3b**, and **ITQ6-3b** was prepared in ethanol (10 ml) under argon at room temperature. After 10 min 125 mg (1.1 mmol) of (1S,2S)-1,2-diaminecyclohexane was added and stirred for 16 h. To this slurry, a solution of 211 mg (1.1 mmol) of 3-*tert*-butyl-5-methylsalicylaldehyde in ethanol (5 ml) was added. The resulting mixture was stirred for 4 h at room temperature and then refluxed for an additional 2 h. Then, the mixture was allowed to cool and the deep yellow solid was filtered off and washed thoroughly with ethanol and then with ether. The solid was dried under vacuum to afford the corresponding anchored salen ligands **Sil-4a**, **Sil-4b**, **MCM41-4a**, **MCM41-4b**, **ITQ2-4b**, and **ITQ6-4b**. The loadings were calculated from the elemental analysis data. The filtered solution was concentrated

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[1] Representative data for new materials were included. Experimental and spectroscopic data for all materials could be obtained directly from authors.

Scheme 1

and purified by flash chromatography in silica (hexane–ethyl acetate, 30:1) to afford the free salen ligand.

ITQ2-4b: % C: 10.50, % H: 2.00, % N: 1.96 corresponding to 0.35 mmol/g; IR (KBr): $\nu = 1636, 1564$ cm^{-1}; UV-vis (λ, nm): 374, 268 and 238; ^{13}C NMR (solid): $\delta = 172.01$; 160.35; 138.26; 129.61; 118.39; 72.84; 58.54; 42.35 (NHCH_2CH_2–); 33.87; 28.04 ((CH$_3$)$_3$C–); 15.20; 8.07 (CH_2Si–).

2.5. Synthesis of Pd and Ni complexes

Typically, palladium(II) and nickel(II) complexes were prepared by adding ethanolic solutions of Pd(OAc)$_2$ or Ni(OAc)$_2$ (0.5 mmol/15 ml) to vigorously stirred slurries of the corresponding anchored salen ligands **Sil-4a**, **Sil-4b**, **MCM41-4b**, **ITQ2-4b**, and **ITQ6-4b** (over 0.5 mmol/g) or free salen ligand (0.5 mmol) in CH$_2$Cl$_2$ (15 ml) at room temperature. The resulting mixture was refluxed for 4 h and then concentrated under reduced pressure. The residue was thoroughly washed with ethanol and then with ether and dried in vacuum to afford the heterogenized complexes in almost quantitative yields (Scheme 1). The catalysts prepared in this way were digested in acid (NO$_3$H/HF, 1/1) and the resulting aqueous solutions analyzed by atomic absorption. The materials present metal loadings of 0.1–0.30 mmol-metal/g-support (Table 2).

ITQ6-4b-Pd: % C: 12.69, % H: 1.83, % N: 2.04, % Pd: 1.91 gives 0.18 mmol/g; IR (KBr): 1626, 1555 and 573 (ν_{Pd-O}) cm^{-1}. UV-vis (λ, nm): 400 and 350 ^{13}C NMR (solid): $\delta = 160.02$ (–CH=N–); 137.87; 129.41; 118.30 (–C–CH=N); 72.47 (–CH_2CH–N); 58.67 (–NHCH_2Ph–); 41.65 (NHCH_2CH$_2$–); 33.42; 27.64 ((CH$_3$)$_3$C–); 15.20; 8.52 (CH_2Si–).

MCM41-4b-Ni: % C: 16.98, % H: 2.91, % N: 2.53, % Ni: 0.56 gives 0.10 mmol/g; IR (KBr): $\nu = 1632$,

Table 2
Metal loading in the support

LIGAND	Loadings (mmol-metal/g-support)	
	Pd	Ni
Free[a]	1.52	1.79
Sil-4a	0.21	0.30
MCM41-4a	0.13	0.21
Sil-4b	0.12	0.19
MCM41-4b	0.17	0.10
ITQ2-4b	0.19	0.16
ITQ6-4b	0.18	0.25

[a] Found for **5Pd** · 2EtOH and **5Ni** · 2H$_2$O.

1562, and 576 (ν_{Ni-O}) cm^{-1}; UV-vis (λ, nm): 570, 420, and 365; ^{13}C NMR (solid): $\delta = 159.97$ (–NHCONH–); 156.87 (–CH=N); 153.54 (=C–O–Ni); 136.92; 127.45; 121.75; 119.57; 117.63 (–C–CH=N); 68.73 (–CH_2CH–N); 57.32 (–NHCH_2Ph–); 34.27 (–NHCH_2CH$_2$–); 27.84, 13.04 (–CH$_2$$CH_2CH_2$–); 6.00 (–$CH_2$Si–).

2.6. Analytical techniques

C, H, and N analyses were carried out with a Heraeus and a Perkin–Elmer 240C apparatus. Metal contents were analyzed by atomic absorption using a Perkin Elmer AAnalyst 300 atomic absorption spectrometer and ICP Perkin–Elmer 40. IR spectra were recorded with a Perkin–Elmer spectrum one using KBr wafers. ^{1}H and ^{13}C NMR spectra were taken with a Varian Gemini-200 and Varian XR300 spectrometers operating at 200 and 300 MHz for ^{1}H, and 50 and 75 MHz for ^{13}C, respectively. Diffuse reflectance UV-vis spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. Mass spectra were recorded on a VG 12-250 spectrometer using EI techniques (70 eV). High-resolution ^{13}C NMR or CP/MAS spectra of powdered samples, in some

cases also with a Toss sequence, in order to eliminate the spinning side bands, were recorded at 100.63 MHz, 6.5 µs, 90° pulse width, 1 to 3-ms contact time and 5 to 10-ms recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle (54°44′) was 10–12 KHz. Gas chromatography analysis was performed using a Hewlett–Packard G1800A with an electron ionization detector.

2.7. Reaction procedure

Reactions were carried out in a stirred batch reactor (Autoclave Engineers) of 100-ml capacity at 40 °C and 4 bar of H_2, in the presence of 40 ml of ethanol. The metal/substrate molar ratio varies from 1/1000 to 1/100000. The evolution of the reaction was monitored by GC with a capillary column with methylsilicone (DV-1701) and methylsilicone:*heptakis*-[2,3-dipentyl-6-(*tert*-butylmethylsilyl)-β-cyclodextrine as stationary phase) [11].

3. Results and discussion

3.1. Preparation of immobilized ligands and complexes

In the last years we have developed a modular system combining functionalized ligands with different supports and linkers in order to have a systematic access to a variety of immobilized chiral catalysts [12]. We have applied here this methodology (Scheme 1) to immobilize salen ligands on mesoporous silica supports such as MCM-41, ITQ-2

and ITQ-6 delaminated zeolites, and amorphous silica (see characteristics in Table 1). With respect to the supports, both silica and MCM-41 are short-range amorphous materials containing a large number of silanol groups available for grafting. In the case of MCM-41, however, the material presents a long-range ordering of hexagonal symmetry with regular monodirectional channels of 3.5 nm diameter. On the other hand, ITQ-6 and ITQ-2 delaminated zeolites present both short and long range order, together with a large well-structured external surface (see Figs. 1and 2, respectively) in which the silanol groups act as grafting centers. However, there are structural differences between the two delaminated zeolites. Indeed, in the case of the ITQ-2 there are "cup-like" apertures to the external surface with ∼0.8 × 0.8-nm dimensions, while in the case of the ITQ-6 these cups are less deep (∼0.3 nm). In a previous work and by a molecular dynamics study, we have shown [13] that there is a minimum of potential energy in the void space of the cups, in which the molecules have a high tendency to adsorb. Taking this into account and the fact that the structured silanols are located at the borders of those cups (see Fig. 1), one can envisage a structural model analogous to that presented by Breslow et al. [14] for cyclodextrines, in which the grafted organometallic site is located at the border of the cyclodextrine cup. In our case, the metal complex will be located at the border of the inorganic silicate cups. Then, one may expect that the reactant adsorbed in the cup of the delaminated zeolite will react there with the catalyst located at the border. If this model is correct, we should expect an increase in the concentration of reactants close to the catalytic active site, with the corresponding increase in reaction rate.
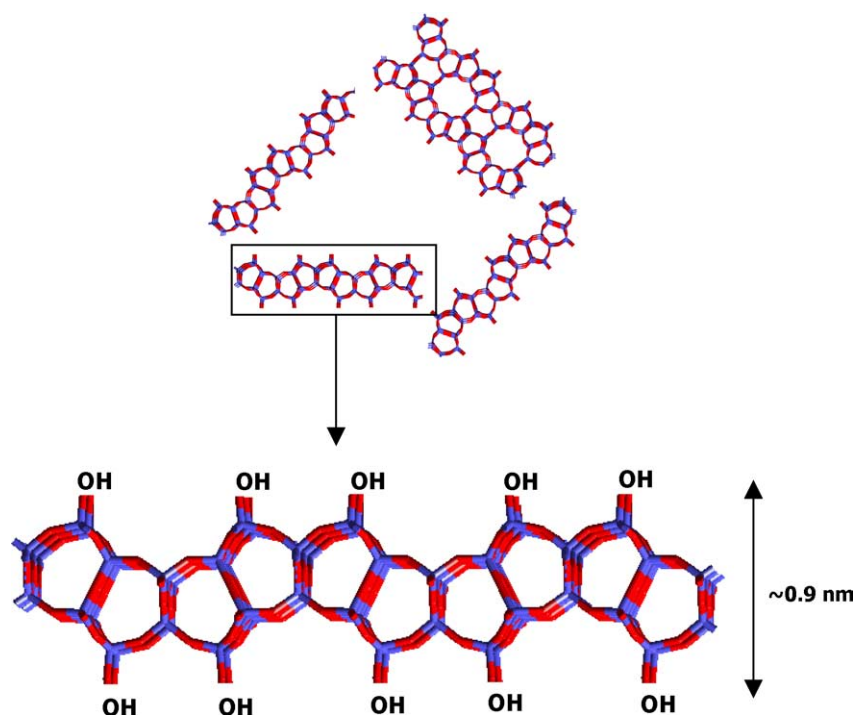

Fig. 1. Structure of ITQ-6, as an ideal single layer of a delaminated ferrierite zeolite.
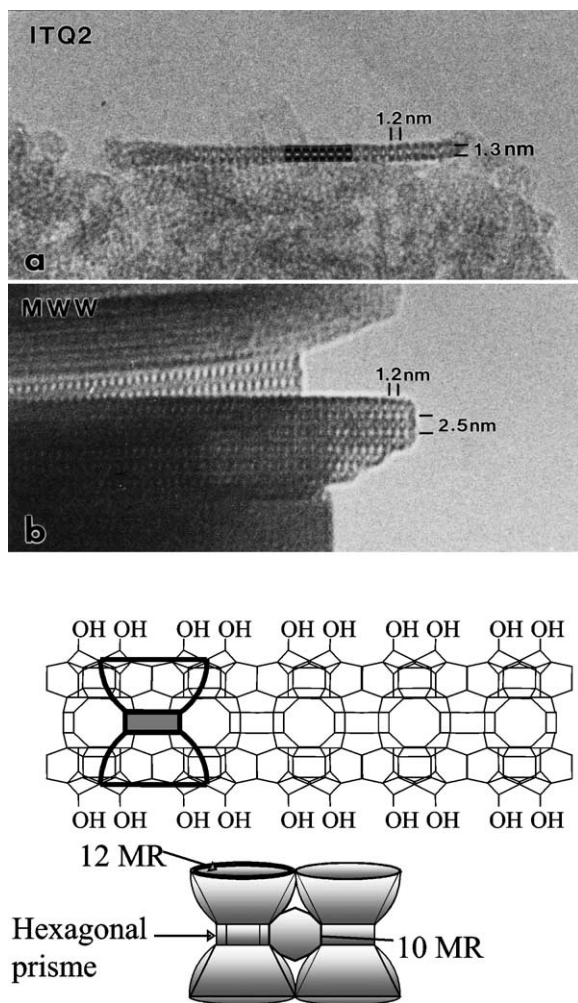
Fig. 2. Structure of ITQ-2, as an ideal single layer of a MWW zeolite structure.

It was recently reported that Ir–xyliphos complexes are very active and enantioselective catalysts for the hydrogenation of imines [15]. However, when they were supported on silica the authors found that the activity of the heterogenized analogs was lower by a factor of 2 to 5. Moreover, they observed that the polystyrene-bound complexes were much less active and, in contrast with the homogeneous complexes, the immobilized systems were susceptible to deactivation. In their excellent work, Pugin et al. [15a] show that the decrease in activity and catalyst life of their imine hydrogenation homogeneous catalyst upon heterogenization was probably due to limited mass transport in the pores and to the proximity of the Ir complexes. in any case and by working at 80 bars and 25–30 °C in the presence of acetic acid, Pugin et al. obtained an unprecedented high activity (TOF up to 20×10^3 h^{-1}) and productivity (TON up to 195×10^3) of the silica-bound catalyst, that are much higher than previously reported on diphosphine Rh (2×10^3 h^{-1}) or Ru (4×10^2 h^{-1}) [1,16].

From the above work it appeared to us that mesostructured solids, and well-structured all-accessible delaminated

zeolites could be suitable supports for immobilizing homogeneous imine hydrogenation catalysts, since they could avoid the mass-transfer limitations of the previously reported support. Moreover, the fact that we could control, up to a certain point, the polarity and acidity of the catalyst surface could introduce an additional benefit from the point of view of increasing reactant concentration at the surface, and/or stabilizing reaction transition states. Thus, for investigating these factors, we have selected two model imines (*anti*-N-benzyl-(1-phenylethylidene)imine, **I**, and 5-phenyl-3,4-dihydro-2*H*-pyrrole, **II**):
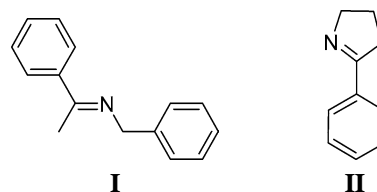
For carrying out the hydrogenation reaction, we have prepared less conventional imine hydrogenation catalysts based on Ni and Pd salen that can be economically attractive with respect to those based on Rh, Ru, or Ir. The reaction conditions chosen were also milder ($P \leqslant 10$ bar) than those reported before.

The results presented in Table 3, for the complexes derived from ligand **4b**, show that the Pd and Ni complexes described here are very active in the homogeneous phase with TOF of $\sim 10^5$ h^{-1}. On the other hand, the activity of catalysts **4a** was much lower and consequently further work will be only done with catalysts **4b**. This value is much higher than those reported before for Ir, Rh, and Ru complexes. We have checked that the catalytic activity observed is due to the organometallic complex and not to any metal formed by decomposition of the complex in the reaction media. In order to do this, we have followed the methodology reported in [17]. The presence of bulk metal was eliminated as follows: the reaction mixtures were passed through a micropore filter, the reactor was washed with ethanol, and the washings were filtered. The filter did not show traces of bulk metal (microscope, 100× magnification). Another problem that can mask the results may come from the unnoticed presence of colloidal metal in "homogeneous" catalysts. Such colloidal particles can be catalytically active and may be re-

Table 3

Hydrogenation of imines catalyzed by homogeneous and heterogenized Ni– and Pd–salen complexes[a] derived from ligand **4b**

Catalyst	Imine **I**		Imine **II**	
	Pd	Ni	Pd	Ni
Homo	110	118	75	83
MCM-41	143	176.2	94	102
ITQ-2	150	180	122	135
ITQ-6	148	150	115	128
Silica	120	140	70	80

[a] TOF, h^{-1} × 10^3; conditions, 4–5 atm., 40 °C. S/C molar ratio, 100000/1.

sponsible for the observed catalytic activity, since they may or may not be subsequently precipitated. It is not sufficient, therefore, to verify merely that the solutions are clear, nor to show that any bulk metal that is precipitated is catalytically inactive. We have performed an additional test using colloidal nickel as catalyst for the hydrogenation of imine **I**, and no reaction was observed after 3 h. Furthermore, there is another consideration that supports the view that the solutions are homogeneous and this is the reproducibility of the reactions.

It appears from the experiments described above, that Ni and Pd salen complexes are stable under reaction conditions and are very active for imine hydrogenation. When they were supported on amorphous silica, the TOF did not decrease but remains practically the same as that in the homogeneous phase. Interestingly, the activity of the catalyst increases when supported on the mesoporous molecular sieve MCM-41. The increase in activity is even higher in the case of the delaminated zeolitic materials whose surface is formed by accessible cups in which the reactant will be concentrated by adsorption [9]. In this case, the activity when grafted on ITQ-2 is almost double that of the unsupported homogeneous catalyst. The results show the benefit of the high surface area, accessibility, and adsorption properties of MCM-41, ITQ-2, and ITQ-6. Furthermore these structured materials allow modifications of the surface that can further enhance the catalytic performance of the hybrid organic–inorganic catalysts.

In a previous paper, Pugin et al. have shown that acetic acid increases the reaction rate for the hydrogenation of imines in the homogeneous phase. The reason for this was claimed to be caused by the stabilization of the transition state by the H^+ in the reaction media, as can be seen from Scheme 2. If this is true, and since we have claimed an important role of the adsorption characteristics of the mesoporous and delaminated zeolite supports on the catalytic activity, we should further increase the reaction rate by introducing some acidity on the support. To do this, we have prepared MCM-41 and ITQ-2 containing tetrahedrally coordinated framework Al. By doing this, Brønsted acidity has been developed on the catalyst as can be seen by IR spectroscopy of adsorbed pyridine (Fig. 3). Indeed, after pyridine adsorption and desorption at 150 °C in
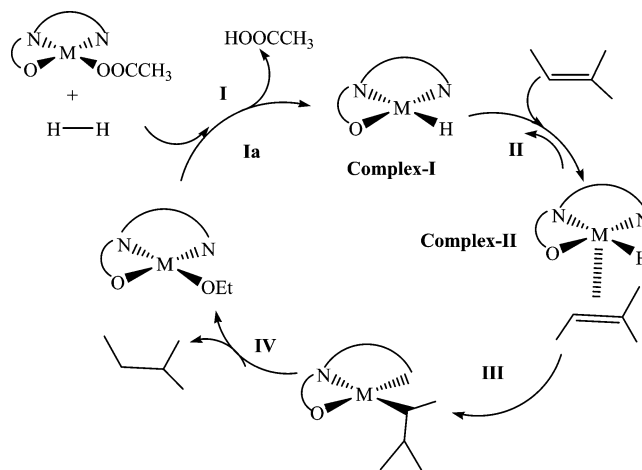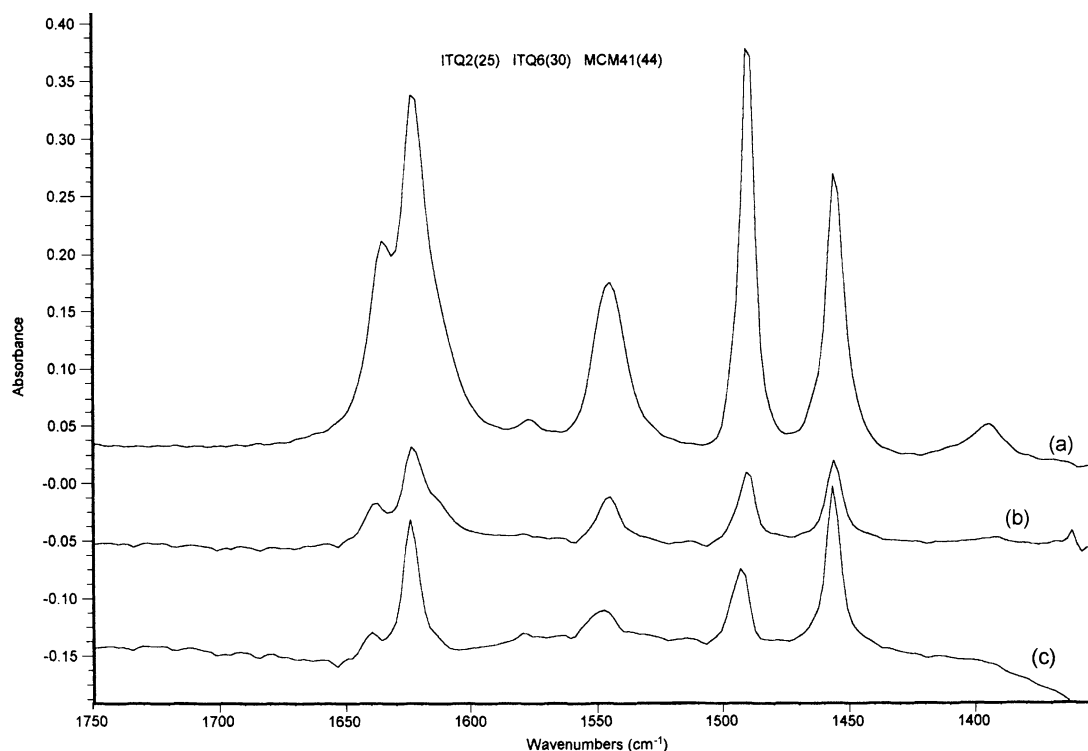

Scheme 2

Fig. 3. IR spectroscopy of pyridine adsorbed on acid ITQ-2 (a), ITQ-6 (b), and MCM-41 (c).

Table 4
Influence of the acidity of the supports on the activity of catalysts **4bNi** in hydrogenation of imines[a]

Catalyst	Si/Al	Imine **I**	Imine **II**
MCM-41	∞	176	102
MCM-41	93	228	124
ITQ-2	∞	180	135
ITQ-2	25	211	164
ITQ-6	∞	150	128
ITQ-6	30	194	156

[a] TOF: $h^{-1} \times 10^{-3}$; conditions: 4–5 atm., 40 °C. S/C molar ratio, 100000/1.

vacuum, an IR band at 1545 cm^{-1} develops that is due to the formation of pyridinium ions formed by pyridine protonation on the surface Brønsted acid sites of the carrier.

When hydrogenation of the imines was performed with Pd and Ni salen complexes grafted on the acidic MCM-41, ITQ-2, and ITQ-6 an increase in the reaction rate is observed (Table 4) with respect to the catalysts with nonacidic supports. At this point, it is worth noting that by grafting on an acidic delaminated zeolite with well-structured cups at the surface in which the substrate is adsorbed and concentrated, TOFs as high as 2×10^5 h^{-1} can be obtained for the hydrogenation of imines. Contrary to what was observed with Ir–xyliphos, the stability of the catalyst toward recycling is good, and no decrease in activity was observed after four times reuse.

On the basis of these experimental results a reaction pathway based on the heterolytic hydrogen cleavage (different from the oxidative addition of H_2, generally accepted for Rh and Ir complexes) is proposed in Scheme 2. The catalyst adds hydrogen to give **complex I** which is formed between the catalyst and the hydrogen, involving hydride ion transfer to the palladium replacing acetate ion, leaving acetic acid. In the second equilibrium step alkene forms a π-complex, i.e., **complex II** with the palladium and simultaneous hydride ion transfer taking place from palladium to alkene. The last step involves transfer of a proton to the substrate, leading to the separation of the hydrogenated product from the catalyst; thus a stable catalyst is regenerated.

There is, however, an aspect that we have not achieved with these catalysts and this is high enantioselectivity. Indeed, the salen Pd and Ni catalysts, despite their very high activity, give enantioselectivities in the order of 10–15%. These are far away from the up to 80% obtained with Ir–xyliphos. We believe that the low enantioselectivity of the salen complexes for hydrogenation of imines can be due to the planarity of the metal complex. The intermediate species also presents a square-planar structure and the approximation of the substrate to the catalytic center by only one face is not favored enough in this case.

4. Conclusions

We have shown that it is possible to boost the activity of an organometallic catalyst by using an adequate support. We have seen that by using mesostructured silicates and delaminated zeolites as carriers, both with very high surface areas and accessibility to reactants, together with high adsorption capacity, the activity of the grafted Pd and Ni salen complex for the hydrogenation of imines is higher than with the homogeneous counterpart or when grafted on amorphous silica.

An additional boost in activity is achieved with those supported salen complexes by changing the acidity of the support, as a consequence of the stabilization of the reaction transition state.

The stability of the catalysts was excellent and no deactivation was observed.

With the Pd and Ni salen catalysts the enantioselectivity was low, but the possibility of using these supports with different transition metal complexes for other enantioselective reactions is open.

Acknowledgments

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