Improved Palladium and Nickel Catalysts Heterogenised on Oxidic Supports (Silica, MCM-41, ITQ-2, ITQ-6)

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Abstract: Two series of solid catalysts in which a chiral palladium or nickel complex with Schiff bases as ligands have been immobilized on ordered mesoporous silica supports (MCM-41), delaminated ITQ-2, ITQ-6 zeolites and amorphous silica have been prepared. Hydrogenation of alkenes and imines was studied with the homogeneous as well as with the counterpart heterogenized catalysts. The high accessibility introduced by the structure of the supports allows the preparation of highly efficient immobilized catalysts with TOFs of 1,000,000 h^{-1}. A moderate acidity in the support increases the catalytic activity considerably, and the easy recoverable immobilized catalysts can duplicate the activity of the homogeneous analogues. No deactivation of the catalysts was observed after repeated recycling.

Keywords: chiral Schiff bases; hydrogenation; immobilized; nickel; palladium

Introduction

The development of efficient catalytic asymmetric reactions is one of the most challenging tasks in current synthetic chemistry, much effort having been devoted to the creation of new chiral N-ligands and their metal complexes for evaluation in advanced asymmetric catalysis.[1] Condensation between an amine and an aldehyde, forming what is called a Schiff base, was one of the earliest reported reactions in chemistry.[2] Schiff bases are an important class of ligands in coordination chemistry and have studied extensively[3] as they are selective and sensitive toward various metal ions. Jacobsen and Katsuki developed tetradentate salen ligands, now one of the most intensely studied classes of chiral Schiff bases, able to coordinate easily to a wide variety of metals. Chiral salen-containing complexes are now used as catalysts for a variety of enantioselective reactions such as oxidation, aziridination, cyclopropanation, Diels–Alder cyclisation, hydrogenation, etc.[4]

We are focusing on new chiral Schiff base ligands containing pyrrolidinamino functionalities in place of one phenolic group on salen ligands. The syntheses of the palladium and nickel(II) complexes are reported. The method we have developed should allow the easy synthesis of a wide variety of chiral Shiff base ligands. The iminophenoxy ligands were designed to coordinate with Pd(II) and Ni(II), and the additional amino group could be varied in order to improve the activities of the complexes in catalytic hydrogenation reactions of alkenes and imines.

Remarkable developments in homogeneous catalysis have taken place over the past two decades.[5] Unfortunately the recovery of the precious metals and expensive ligands from the reaction medium is often not feasible. For this reason, there have been many approaches to "heterogenising" homogeneous catalysts by attaching well defined molecular species to polymeric supports.[6] Despite the development of some very effective supported systems,[7] a general strategy for mimicking solution behaviour is yet to be developed. Reactions on supports are generally slower and less predictable than their solution counterparts, commonly requiring excesses of reagents, higher temperatures and longer reaction times.[8]

The discovery of mesoporous molecular sieves has provided new possibilities in catalysis.[9] These mesoporous materials have unique structures characterised by high surface areas, large pores, and high long-range order; properties that make them ideal catalyst supports. MCM-41 type silicates have been used as supports for a variety of metals and metal complexes.[10] Recently a new type of high surface area materials called delaminated zeolites has been proposed as an alternative to the known material.[11] Delaminated zeolites possess a high thermal/hydrothermal stability and acidity as in

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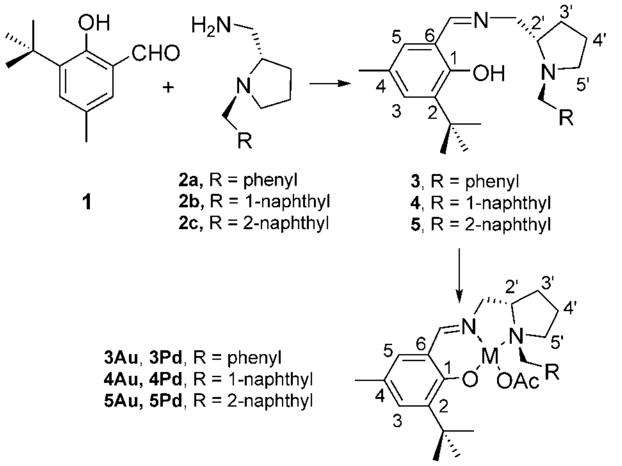
zeolites, and a very high external/internal surface area ratio as in amorphous materials. The characteristics named above make these delaminated zeolites a very promising material as catalysts, fillers, and supports for any type of active species. Our approach to the preparation of Pd and Ni complexes – both homogeneous and supported on mesoporous solids – involves the use of chiral Schiff base ligands as shown in Schemes 1 and 2. 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,[12] even if they require relatively high H_2 pressures ($\sim$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 [N,N,O]-Pd and -Ni complexes are active catalysts for hydrogenation of alkenes and imines at 4 bar H_2 pressure. Moreover by properly choosing the support it is possible to achieve a twofold increase in activity with respect to the homogeneous counterpart, by means of a cooperative effect of the support that may stabilise the charged reaction transition state.

Results and Discussion

Synthesis of Homogeneous Catalysts (Reference Systems)

All soluble ligands relevant for this work have been obtained in high yields as described previously.[13] The synthesis is shown in Scheme 1.



Scheme 1. Synthesis of soluble ligands and homogeneous complexes.

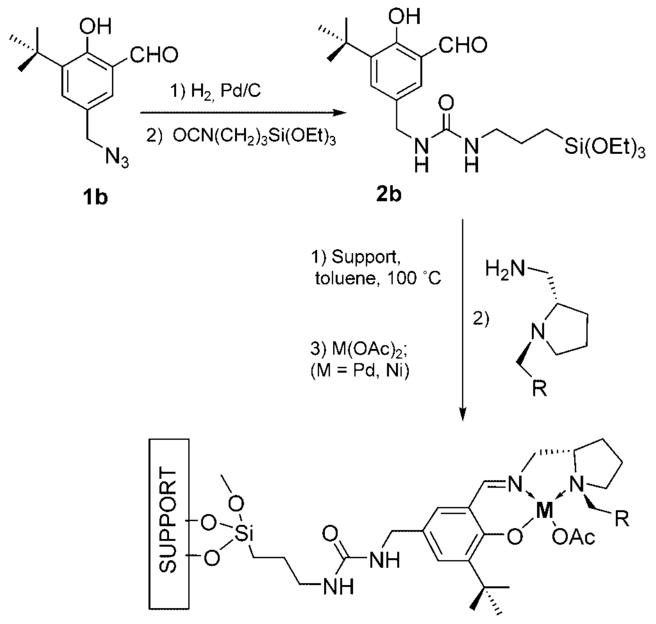
Preparation of Immobilized Ligands and Complexes

In the last years we have developed a modular system combining functionalised ligands with different supports and linkers in order to have a systematic access to a variety of immobilised chiral catalysts.[7f–h,14] We have applied here this methodology (Scheme 2) to immobilise Schiff base ligands on a mesoporous silica support, selected to encompass a wide range of topologies, 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 with hexagonal symmetry with regular monodirectional channels of 3.5 nm in diameter. On the other hand, ITQ-6 and ITQ-2 delaminated zeolites present both short- and long-range order, together with a very large, well structured external surface in which the silanol groups act as grafting centres. 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 $\sim 0.8 \times 0.8$ nm dimensions, while in the case of the ITQ-6 these "cups" are less deep ($\sim$0.3 nm). In a previous work and by a molecular dynamics study, we have shown that there is a minimum of potential energy in the void space of the "cups" in the ITQ-2, in which the molecules that can fit 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", one can envisage a structural model analogous to that presented by Breslow et al.[15] for cyclodextrins, in which the grafted complex site is located at the border of the cyclodextrin "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 is adsorbed in the cavity of the delaminated zeolite and reacts 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, and consequently an increase in the rate of the reaction should occur.

All solids were functionalised in the same manner according to the procedure shown in Scheme 2. Supported precursors, **2-(support)**, were obtained by refluxing a mixture of the precursor **2** and the respective support, in toluene, for 16 hours. These anchored aldehydes reacted with an equimolar amount of (*S*)-(*N*-benzyl-2-pyrrolidinyl)methylamine, (*S*)-[1-(1-naphthylmethyl)-2-pyrrolidinyl]methylamine or (*S*)-[1-(2-naphthylmethyl)-2-pyrrolidinyl]methylamine to afford the supported chiral Schiff ligands, **3–5-(support)**, as fine powdered solids. These materials were characterised by microanalysis, FT IR and ^{13}C NMR. In the ^{13}C NMR spectra, the C–OH carbon signal appears at $\delta = \sim 153$ ppm, and the imine carbon signals appear at $\delta = 165–166$ ppm.

Table 1. Textural characteristics of the solid supports.

Support (Pure Silica)	BET Surface Area ($m^2 \cdot g^{-1}$)	Micropore Surface (t-plot $m^2 \cdot g^{-1}$)	External (or Mesoporous) Surface Area ($m^2 \cdot g^{-1}$)
Silica	750		
MCM-41	1030	0	1030
ITQ-2	830	130	700
ITQ-6	618	10	608



R = phenyl: **3M-(Sil, MCM-41, ITQ-2, ITQ-6)**
R = 1-naphthyl: **4M-(Sil, MCM-41, ITQ-2, ITQ-6)**
R = 2-naphthyl: **5M-(Sil, MCM-41, ITQ-2, ITQ-6)**

Scheme 2. Synthesis of heterogenised ligands and complexes.

Synthesis and Characterisation of Heterogenised Complexes

The heterogenised ligands reacted with palladium(II) or nickel(II) acetate to furnish the corresponding anchored Pd and Ni complexes that were used for catalytic hydrogenation. The catalytic activities of the anchored complexes were also compared to those of the homogeneous ones (**3–5Pd** and **3-5Ni**) that were synthesised starting from **3–5** as shown in Scheme 1.

The catalysts prepared in this way presented metal loadings of 0.1–0.30 mmol metal/g support as determined by atomic absorption analysis. The solids were characterised by FTIR, DFTR and ^{13}C NMR spectroscopy.

Infrared and Electronic Spectra

Peaks due to the support dominate the spectra. These include the O–H vibration in the range 3700–3300 cm^{-1}.

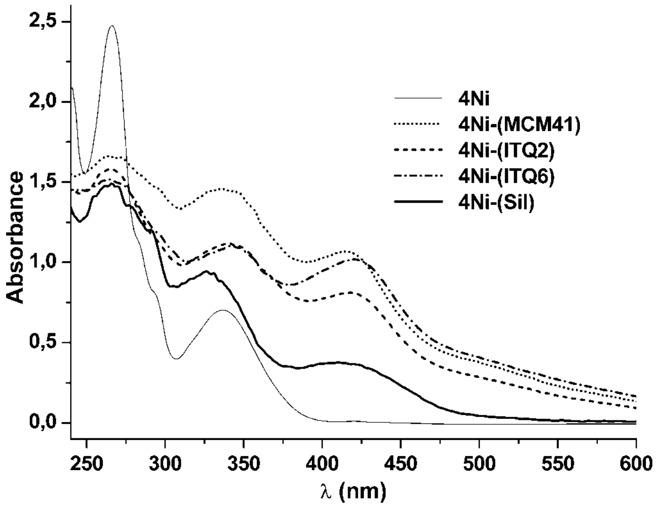


Figure 1. Diffuse reflectance spectra of soluble and heterogenised complexes.

Some of the bands characteristic of the complexes could, however, could be distinguished. Major zeolite framework bands appeared around 1140, 1040, 960, 785 and 740 cm^{-1}. FTIR spectra are characteristic for the binding of imine nitrogen. The 1600 cm^{-1} frequencies may be assigned to C=C and azomethine C=N vibrations, shifted to lower wavenumbers (relative to the free ligands) due to N-coordination of the imine.[16] The IR spectra also shows strong bands at 1290 and ~ 1500 cm^{-1} assigned to the symmetric and asymmetric ν(COO) vibrations, respectively, in agreement with those expected for monocoordinate acetate ligands.[17] New bands in the 500–600 cm^{-1} region are ascribed to ν(M–O).

The chiral Schiff base $M^{II}(OAc)$ complexes immobilised on supports have been characterised by diffuse reflectance UV spectroscopy and the typical UV-VIS spectra are given in Figure 1. The DFTR spectra for all complexes were obtained in the 200–800 nm range. The complexes show several band maxima in the UV region agreeing with the assignment of the bands as intraligand π→π*, n→π* transitions in the aromatic ring, azomethine group and charge-transfer transition.[18] The bands in the 400–450 nm region correspond to *d-d* transitions expected for planar complexes[19] and MLCT bands. The diffuse reflectance spectra of M(ligand) complexes are almost identical before and after heterogenisation process, indicating that the complexes maintain their geometry and their electronic surroundings even after heterogenisation without significant distortion.

NMR Spectra

Diamagnetic palladium and nickel complexes have been characterised by ^{13}C NMR spectroscopy. In all cases, the spectra show the simultaneous occurrence of two set of signals which are attributable on the one hand to the substituted benzaldimine entity and on the other hand to the aliphatic part of the ligand. The ^{13}C NMR spectra showed the signals assigned to the C=N carbon shifted to high field and C1 at δ ~162 shifted downfield confirming that metallation had occurred.

Catalytic Hydrogenation

The availability of the structurally well defined Ni(II) and Pd(II) complexes enables us to explore the possibilities of these complexes in hydrogenation reactions. The hydrogenation of simple alkenes (cyclohexene, cyclooctene), diethyl itaconate, diethyl 2-benzylidenesuccinate, diethyl 2-naphthylidenesuccinate and imines such as *anti-N*-benzyl-(1-phenylethylidene)imine or 5-phenyl-3,4-dihydro-2*H*-pyrrole (Figure 2) with Pd and Ni complexes were carried out under standard conditions (EtOH as the solvent, 4 atm hydrogen pressure, 40 °C). The hydrogenation was carried out to explore the possibilities of recovering the catalysts, the influence of the nature of the support, and for a comparison of the activity and stability of supported catalysts with their homogeneous counterpart. Tables 2–6 summarise the catalytic results obtained when homogeneous Schiff base complexes were immobilised on different supports.

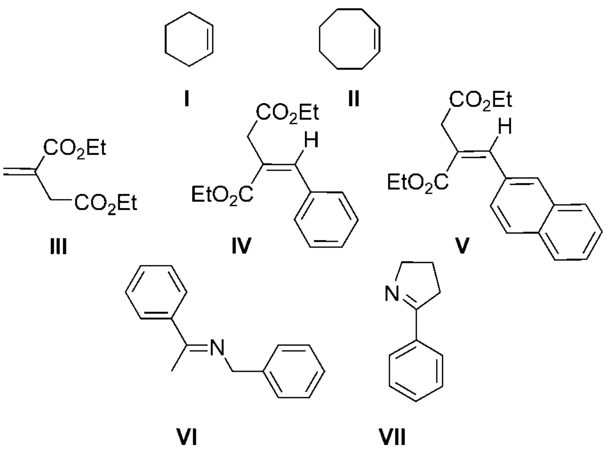


Figure 2. Tested models for the hydrogenation reactions.

The results show that the homogeneous Pd and Ni systems lead to quantitative conversion of olefins under the hydrogenation conditions. In the present study, the order of reactivity may be explained on the basis of the steric factors. There were no significant differences in the electronic natures of the complexes.

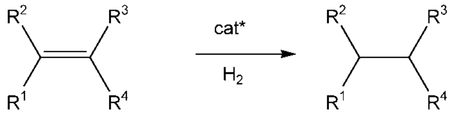
As Tables 2 and 3 show, the heterogenised catalysts had, in general, higher activities than the homogeneous counterpart (Figure 3). If we compare the heteroge-

Table 3. Turnover rates for the catalytic hydrogenation of **II** with catalysts derived from ligands **4,5**.

	4Pd	**4Ni**	**5Pd**	**5Ni**
Homo	842760	964320	684000	961920
MCM-41	901080	1013640	846720	999120
ITQ-2	930480	1033200	907440	1033680
ITQ-6	947280	1075800	947400	1047960
Silica	882960	986400	758880	945960

TOF: h^{-1}; conditions: 4 atm, 40 °C; S/C ratio 100000: 1.

Table 2. Turnover rates for the catalytic hydrogenation of alkenes with catalysts derived from ligand **3**.



	Pd	Ni	Pd	Ni	Pd	Ni	Pd	Ni	Pd	Ni
	I		**II**[a]		**III**		**IV**		**V**	
Homo	4040	4020	20500	21800	3360	2400	640	220	153	117
MCM-41	4200	4620	18600	19500	4980	4650	900	670	187	307
ITQ-2	5700	6000	22500	22805	5220	6000	943	630	280	420
ITQ-6	5220	5340	15000	25500[b]	4860	5520	810	530	207	226
Silica	4260	3120	13500	12300	4680	3360	809	450	200	149

TOF: h^{-1}; conditions: 4 atm, 40 °C, S/C ratio 1000: 1.

[a] S/C ratio 10000: 1.

[b] S/C ratio 100000: 1; TOF: 128500 h^{-1}.

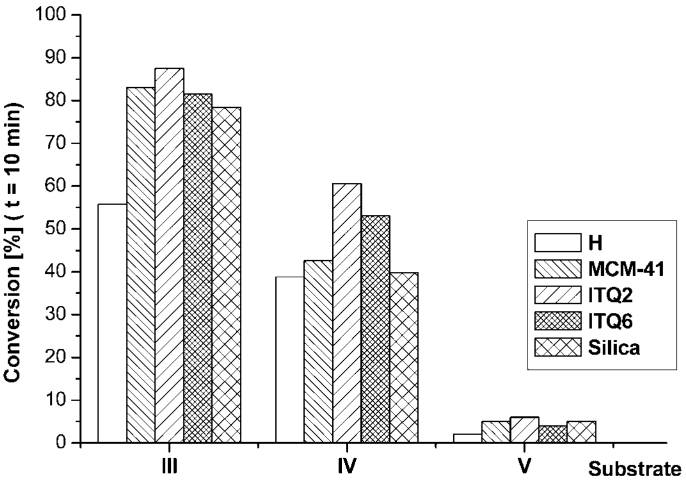


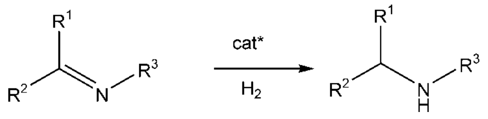
Figure 3. Comparison of the catalytic activities of homogeneous and heterogenised **3Pd** on the hydrogenation reaction of olefins.

nised catalysts we can observe that the activity of the ITQ-2 complex is higher. Depending on the studied substrate the TOFs are about 2 to 3 times higher than those observed on the silica supported or homogeneous catalyst. These results indicate that either the support or the metal complexes have a considerable effect on the catalytic process, because of the stability of the active metallic species formed. The fact that the heterogenised catalysts have higher reaction rates is one of the expected advantages of using heterogenised catalysts and is in good agreement with our former results.[4b] In different systems we have observed higher reaction rates on heterogenised samples. The explanation could be that in the homogeneous condition the reaction rate is decreased by the poor solubility of these complexes in most organic solvents and by self-degradation. If we eliminate these factors by heterogenising the complex we can expect a higher reaction rate. The site isolation effect which works on the heterogenised condition may also be an explanation for the higher rate, since the complex is in a molecularly dispersed form and because of this, is not subject to self-degradation. After prolonged storage (3–6 months) at room temperature our heterogenised catalysts showed the same features as the freshly prepared catalysts in the standard hydrogenation reaction.

It was recently reported that Ir-xyliphos complexes are very active and enantioselective catalysts for the hydrogenation of imines.[20] However, when they were supported on silica the authors found that the activity of the heterogenised analogues 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 immobilised systems were susceptible to deactivation. In their excellent work, Pugin et al.[20] show that the decrease in activity and catalyst life of their imine hydrogenation homogeneous catalyst upon heterogenisation 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 20,000 h^{-1}) and productivity (TON up to 195,000) of the silica bound catalyst; these values are much higher than previously reported on diphosphine Rh (2000 h^{-1}) or Ru (400 h^{-1}).[7,21]

From the above work it appeared to us that mesostructured solids and – well structured – all accessible delaminated zeolites could be suitable supports for immobilising 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 (acidity) of the catalyst surface, could introduce an additional benefit from the point of view of increasing reactant concentration at the surface, and/or stabilising reaction transition states. Thus, for investigating these factors, we have selected two model imines [*anti-N*-benzyl-(1-phenylethylidene)imine, **VI**, 5-phenyl-3,4-dihydro-2*H*-pyrrole, **VII**].

Table 4. Turnover rates for the catalytic hydrogenation of imines.



	3Pd **VI**[a]	3Ni	3Pd **VII**[a]	3Ni	4Pd **VI**[b]	4Ni	5Pd **VI**[b]	5Ni
Homo	3240	4800	167	93	337500	410940	309240	461520
MCM-41	5520	4860	500	440	603240	623520	322560	476160
ITQ-2	5640	5700	560	533	402840	447720	375000	620960
ITQ-6	4860	5640	517	513	676320	600480	428520	620000
Silica	3900	4440	160	153	294000	416640	285660	361440

[a] TOF: h^{-1}; conditions: 4 atm, 40 °C, S/C ratio 1000:1.
[b] S/C ratio 100000:1

For carrying out the hydrogenation reaction, we have used our less conventional imine hydrogenation catalysts based on Ni and Pd Schiff bases that can be economically attractive with respect to those based on Rh, Ru or Ir. The reaction conditions chosen were also milder ($P \leq 10$ bar) than those reported before.

The results presented in Table 4 show that the Pd and Ni complexes described here are very active in the homogeneous phase with TOF of $\sim 10^6\ h^{-1}$. 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 complex and not to any metal formed by decomposition of the complex in the reaction media. In order to do this, the methodology used was as described in the literature.[22] 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 filtered. The filter did not show traces of bulk metal (microscope, 100 × magnification). Another problem that can mask the results may come from the unperceived presence of colloidal metal in "homogeneous" catalysts. Such colloidal particles can be catalytically active, and may be responsible for all of 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, or to show that any bulk metal that is precipitated is catalytically inactive. Then, we have made a test using colloidal nickel as catalyst for the hydrogenation of imine **VI** and no reaction was observed after 3 h. Another consideration that supports the view that the solutions are homogeneous is the reproducibility of the reactions.

It appears from the experiments described above that Ni- and Pd-salen complexes are stable under the reaction conditions and are very active for imine hydrogenation. When they were supported on amorphous silica, the TOF did not decrease but remained practically the same as that in the homogeneous phase. Interestingly, the activity of the catalyst increased when supported on the mesoporous molecular sieve MCM-41. The increase in activity is even higher in the case of the delaminated zeolitic ITQ-2 material whose surface is formed by cups in which the reactant will be concentrated by adsorption.[11] In this case, the activity when grafted on ITQ-2 is almost double that for the unsupported homogeneous catalyst.

In order to check for the presence of metal clusters supported on the solid matrix, we have characterised the solid before and after reaction. As can be deduced from IR, ^{13}C NMR and UV-VIS spectra, the nature of supported species is the same and the most important signals appear in the same position after reaction. Also, high resolution TEM does not show changes before and after reaction.

In a previous paper, Pugin et al. have shown that acetic acid increases the reaction rate for the hydrogenation reaction in the homogeneous phase. The reason for this was claimed to be caused by the stabilisation of the transition state by the H^+ in the reaction media. 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 reaction rate, we should increase still further the rate of the reaction by introducing some acidity on the support. To do this, we have prepared MCM-41 and ITQ-2 containing a tetrahedrally coordinated framework of Al. By doing this, Brönsted acidity has developed on the catalyst as can be seen by IR spectroscopy of adsorbed pyridine. Indeed, after pyridine adsorption and desorption at 150 °C in vacuum, an IR band at 1545 cm^{-1} develops that is due to pyridinium ions formed by pyridine protonation on the surface Brönsted acid sites of the carrier.

Table 5. Influence of the acidity of the supports on the activity in hydrogenation.[a]

Catalyst	Si/Al	**III**	**IV**	**V**
3Pd-(MCM-41)	∞	4980	900	187
3Pd-(MCM-41)	15	9091	4285	300
3Pd-(MCM-41)	50	6000	1896	290
3Pd-(ITQ-2)	∞	5220	943	280
3Pd-(ITQ-2)	20	9450	4850	291

[a] TOF: h^{-1}; conditions: 4 atm, 40 °C; S/C ratio: 1000:1.

Table 6. Influence of the Sn on the activity in hydrogenation.[a]

Catalyst	Sn[b]	**III**	**IV**	**V**
3Pd-(MCM-41)	–	4980	900	187
3Pd-(MCM-41)	grafted	4912	1182	188
3Pd-(MCM-41)	synthesis	4236	618	193

[a] TOF: h^{-1}; conditions: 4 atm, 40 °C; S/C ratio: 1000:1.
[b] 10–12% SnO_2.

When the hydrogenation was performed with Pd- and Ni-salen complexes grafted on the acidic MCM-41 (Si/Al = 15, 50) and ITQ-2 (Si/Al = 20) an increase in the reaction rate is observed (Table 5) with respect to the catalysts with non-acidic 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, TOF as high as $9 \cdot 10^3\ h^{-1}$ can be obtained for the hydrogenation of diethyl succinates.

On the other hand, Sn has been widely investigated as a selectivity promoter for the hydrogenation of C=C double bonds, C=O aldehydic or ketonic groups;[23] for this reason, we aimed to investigate the effect of Lewis acidic Sn(IV) centres on the catalytic behaviour of Pd in the hydrogenation of **III**, **IV** and **V** (Table 6). We have prepared two series of Sn-MCM-41 supports, one of then with the tin centres introduced during the

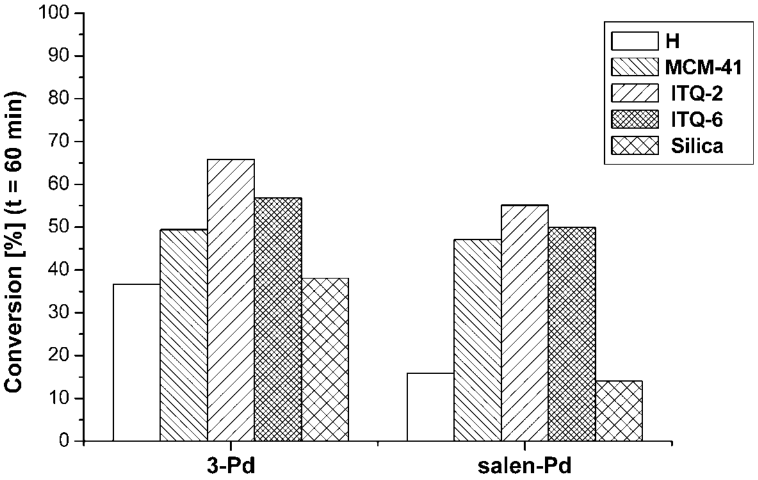
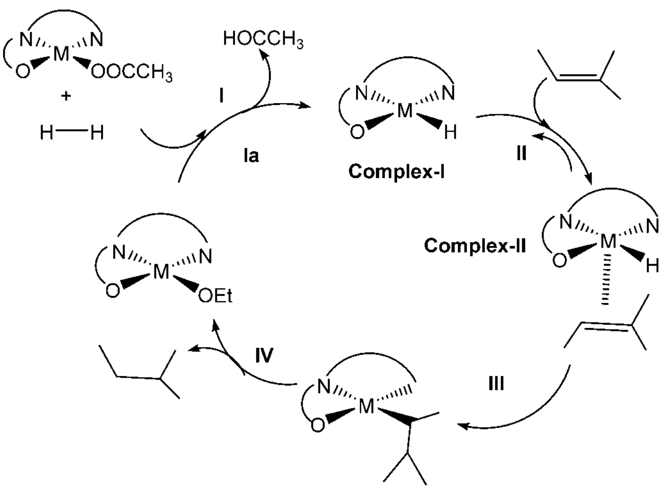


Figure 4. Comparison of the catalytic activities of 3Pd and salen-Pd on the hydrogenation of imine **VII**.

MCM-41 synthesis (Sn_{synth}-MCM-41), and other in which the Sn has been incorporated to MCM-41 in a post-synthesis treatment by a grafting procedure (Sn_{graft}-MCM-41). Table 6 shows that these Sn systems do not improve the catalytic performance of 3Pd-(MCM-41) catalyst and produce a lower activity.

There is, however, one aspect that we have not achieved with these catalysts and that is high enantioselectivity. Indeed, the Pd and Ni catalysts, despite their very high activity, give enantioselectivities in the order of 10–15%. We believe that the low enantioselectivity of the complexes for hydrogenation of prochiral substrates 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 centre by only one face is not sufficiently favoured in this case.



Scheme 3. Proposed reaction pathway for the hydrogenation reactions with Pd and Ni(II) complexes.

Comparison of Title Catalysts with Salen Complexes

The performance of catalysts described in the present work has been compared with that showed by soluble and heterogenised Pd and Ni complexes derived from the related salen ligand {salen = (*R*,*R*)-*N*′,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine}.[24] The result is displayed in Figure 4.

Under the conditions described in the experimental section, the Pd catalysts derived from ligand **3** display higher activity than those derived from salen ligand. One has to conclude that the our simpler chiral Schiff base ligands containing pyrrolidinylamino functionalities in place of one phenolic group on salen ligands improve the catalytic properties of salen-derived catalysts.

The accumulated evidence concerning the mechanisms of homogeneously catalysed hydrogenation indicates that three principal modes of hydrogen activation are suitable: oxidative addition, and homolytic or heterolytic hydrogen cleavage. In the case of these Pd and Ni complexes, heterolytic cleavage is preferred to give a hydride intermediate which involves charge separation without any oxidation of the metal. Heterolytic cleavage of hydrogen by Pd complexes has been proposed before[25] and is supported from our experiments using more polar and protonic acid media which produce a significant increase of reaction rate, probably favouring charge separation in the step of formation of the intermediate (Table 5).

On the basis of the experimental results a reaction pathway based on heterolytic hydrogen cleavage (different from the oxidative addition of H_2, generally accepted for Rh and Ir complexes) is proposed in Scheme 3. The catalyst adds hydrogen to give **Complex-I** which is formed between the catalyst and hydrogen, involving hydride ion transfer to the palladium replacing acetate ion, leaving acetic acid. In the second equilibrium step

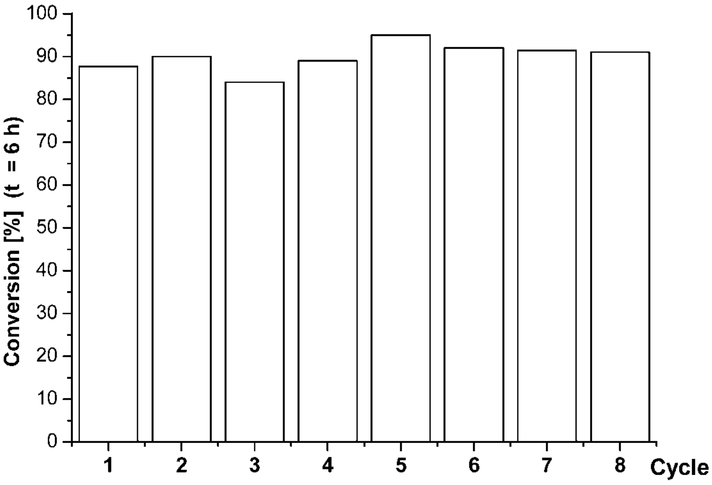


Figure 5. Recycling of **3Pd-(MCM-41)** in the hydrogenation of diethyl 2-benzylidenesuccinate.

the 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.

Recycling of Heterogenised Catalysts

The major advantage of the use of heterogenised metal complexes as catalysts for this reaction is the ease with which they can be recovered as stable species from the reaction mixture by simple filtration and reused. We have carried out the heterogeneous asymmetric hydrogenation of olefins until completion, filtered and washed the heterogenised catalyst, then added fresh substrate, and solvent without further addition of catalyst, for several consecutive experiments and have found that both yield and activity are retained (Figure 5). After each experiment a portion of supported catalyst was analysed to determine the concentration of metal still present in the support. Filtrate has been used in a new reaction and was not found to catalyse hydrogenation.

Conclusion

In conclusion, we have shown that it is possible to boost the activity of a transition metal complex 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 reaction is higher than with the homogeneous counterpart or when grafted on amorphous silica.

An additional boost in activity is achieved with these supported salen complexes by changing the polarity (acidity) of the catalyst, as a consequence of the stabilisation 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 for other more enantioselective transition metal complexes is opened.

Experimental Section

General Remarks

All preparations of metal complexes were carried out under dinitrogen by conventional Schlenk tube techniques. Solvents were carefully degassed before use. The silylating agent $OCN(CH_2)Si(OEt_3)$, was obtained from ABCR. C, H and N analysis were carried out by the analytical department of the Institute of Materials Science (C.S.I.C.) with a Perkin-Elmer 240C apparatus. Metal contents were analysed by atomic absorption using a Perkin Elmer Analyst 300 atomic absorption apparatus and plasma ICP Perkin Elmer 40. IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) in KBr pellets; ^1H NMR, ^{13}C NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers. Chemical shifts are referred to tetramethylsilane (internal standard). High resolution ^{13}C MAS or CP/MAS NMR 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 μs, 90^0 pulse width, 2 ms contact time and 5–10 recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle ($54^0 44'$) was 4 KHz.[26] Optical rotation values were measured at the sodium D line (589 nm) with a Perkin Elmer 241 MC polarimeter. Gas chromatographic analysis was performed using a Hewlett-Packard 5890 II with a flame ionisation detector in a cross-linked methylsilicone column.

The inorganic supports for anchoring were silica gel [Merck silica, average pore diameter 40 Å], purely siliceous MCM-41,[9] and delaminated zeolites ITQ-2 and ITQ-6.[11] In addition, Al-containing MCM-41 (Si/Al: 15, 50), Al-containing ITQ-2 (Si/Al: 20) and Sn-containing MCM-41 (~10–12% Sn) were used as supports for loading the complex.

Synthesis of Ligands

The soluble ligands 3–5 have been synthesised in high yields as described previously,[13] and the heterogenised ligands were obtained as described below.

General Heterogenisation of Hydroxyaldehyde

Typically, to a suspension of silica or the corresponding mesoporous solids MCM-41, ITQ-2 or ITQ-6 (2 g) in toluene (25 mL), stirred at room temperature for 30 minutes, a solution of 2 mmol of the aldehyde **2** 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 vacuum for 24 hours to afford the anchored precursors **precursor-(support) [2-Sil, 2-MCM-41, 2-ITQ-2, 2-ITQ-6]**. The loadings are based on the percent of nitrogen obtained from the elemental analysis data.

2-(Sil): anal. found: C 12.3, H 2.17, N 1.8%; (0.63 mmol/g); IR (KBr): ν = 3478 (NH), 1642, 1564 cm^{-1} (C–O, C=C); UV-VIS: λ = 243, 298, 410 nm; ^{13}C NMR (solid): δ = 196.35 (*C*HO), 159.0 (NH*C*ONH), 130.18 [*C*-C(CH_3)$_3$], 120.15 (*C*-CHO), 42.83 (NH*C*H$_2$Ph), 27.54 [C(*C*H$_3$)$_3$], 20.50 (CH$_2$*C*H$_2$CH$_2$–), 17.53 (*C*H$_3$CH$_2$O–), 5.04 (*C*H$_2$Si–).

2-(MCM-41): anal. found: C 13.4, H 2.8, N 1.5%; (0.55 mmol/g); IR (KBr): ν = 3421 (NH), 1642, 1564 cm^{-1} (CO, C=C); UV-VIS: λ = 360, 425 nm. ^{13}C NMR (solid): δ = 199.29 (*C*HO), 160.58 (NH*C*ONH), 147.84 (*C*OH), 138.13 (*C*-CHNH-), 130.98 (*C*H$_{arom}$), 120.18 (*C*-CHO), 57.45 (CH$_3$*C*H$_2$O–), 54.29 (NH*C*H$_2$Ph), 42.04 (NH*C*H$_2$CH$_2$–), 27.60 [C(*C*H$_3$)$_3$], 18.99 (*C*H$_3$CH$_2$O–), 9.64 (*C*H$_2$Si–).

2-(ITQ-2): anal. found: C 12.9, H 2.2, N 1.4%; (0.50 mmol/g); IR (KBr): ν = 3414 (NH), 1640, 1557 cm^{-1} (CO, C=C); UV-VIS: λ 0 223, 260, 340 nm. ^{13}C NMR (solid): δ = 198.53 (*C*HO), 158.74 (NH*C*ONH), 150.00 (*C*OH), 138.35 (*C*-CHNH–), 132.53 (*C*H$_{arom}$), 120.39 (*C*-CHO), 58.03 (CH$_3$*C*H$_2$O–), 53.90 (NH*C*H$_2$Ph), 41.53 (NH*C*H$_2$CH$_2$–), 28.42 [C(*C*H$_3$)$_3$], 17.02 (*C*H$_3$CH$_2$O–), 9.74 (*C*H$_2$Si–).

2-(ITQ-6): anal. found: C 8.7, H 1.4, N 1.1%; (0.38 mmol/g); IR (KBr): ν = 3415 (NH), 1640, 1555 cm^{-1} (CO, C=C); UV-VIS: λ = 215, 258, 334 nm; ^{13}C NMR (solid): δ = 197.56 (*C*HO), 159.95 (NH*C*ONH), 146.84 (*C*OH), 138.84 (*C*-CHNH–), 132.04 (*C*H$_{arom}$), 119.91 (*C*-CHO), 57.79 (CH$_3$*C*H$_2$O), 52.45 (NH*C*H$_2$Ph), 41.77 (NH*C*H$_2$CH$_2$–), 27.70 [C(*C*H$_3$)$_3$], 15.81 (*C*H$_3$CH$_2$O), 10.22 (*C*H$_2$Si–).

2-(MCM-41, Si/Al ≈ 15): anal. found: C 36.2, H 3.3, N 1.4%; (0.47 mmol/g); IR (KBr): ν = 3407 (NH), 1639, 1512 cm^{-1} (CO, C=C); UV-VIS: λ = 349, 264, 223 nm; ^{13}C NMR (solid): δ = 199.00 (*C*HO), 161.02 (NH*C*ONH), 147.41 (*C*OH), 137.83 (*C*-CHNH–), 131.26 (*C*H$_{arom}$), 120.03 (*C*-CHO), 57.31 (CH$_3$*C*H$_2$O–), 54.05 (NH*C*H$_2$Ph), 42.00 (NH*C*H$_2$CH$_2$–), 27.43 [C(*C*H$_3$)$_3$], 19.12 (*C*H$_3$CH$_2$O–), 9.58 (*C*H$_2$Si–).

2-(MCM-41, Si/Al ≈ 50): anal. found: C 28.1, H 5.3, N 2.7%; (0.96 mmol/g); IR (KBr): ν = 3408 (NH), 1642, 1563 cm^{-1} (CO, C=C); UV-VIS: λ = 353, 266, 226, 203 nm; ^{13}C NMR (solid): δ = 198.95 (*C*HO), 160.13 (NH*C*ONH), 148.23 (*C*OH), 137.95 (*C*-CHNH–), 131.00 (*C*H$_{arom}$), 120.12 (*C*-CHO), 57.33 (CH$_3$*C*H$_2$O–), 54.00 (NH*C*H$_2$Ph), 42.00 (NH*C*H$_2$CH$_2$–), 27.20 [C(*C*H$_3$)$_3$], 19.00 (*C*H$_3$CH$_2$O–), 9.10 (*C*H$_2$Si–).

2-(ITQ-2, Si/Al ≈ 20): anal. found: C 13.7, H 2.5, N 1.6%; (0.56 mmol/g); IR (KBr): ν = 3422 (NH), 1642, 1565 cm^{-1} (CO, C=C); UV-VIS: λ = 346, 265, 223 nm; ^{13}C NMR (solid): δ = 198.23 (*C*HO), 158.60 (NH*C*ONH), 150.75 (*C*OH), 138.54 (*C*-CHNH–), 132.50 (*C*H$_{arom}$), 120.08 (*C*-CHO), 58.00 (CH$_3$*C*H$_2$O–), 53.92 (NH*C*H$_2$Ph), 41.50 (NH*C*H$_2$CH$_2$–), 28.43 [C(*C*H$_3$)$_3$], 17.00 (*C*H$_3$CH$_2$O–), 9.24 (*C*H$_2$Si–).

2-(MCM-41, Sn$_{synth}$): anal. found: C 20.3, H 3.1, N 3.3%; (1.2 mmol/g); IR (KBr): ν = 3394 (NH), 1644, 1565 cm^{-1} (CO, C=C); UV-VIS: λ = 432, 343, 265, 224 nm.

2-(MCM-41, Sn$_{graft}$): anal. found: C 17.6, H 2.6, N 2.5%; (0.9 mmol/g); IR (KBr): ν = 3428 (NH), 1640, 1566 cm^{-1} (CO, C=C); UV-VIS: λ = 426, 347, 267, 227 nm. ^{13}C NMR (solid): δ = 198.65 (*C*HO), 160.32 (NH*C*ONH), 147.75 (*C*OH), 138.00 (*C*-CHNH–), 131.04 (*C*H$_{arom}$), 120.43 (*C*-CHO), 57.00 (CH$_3$*C*H$_2$O–), 54.32 (NH*C*H$_2$Ph), 41.86 (NH*C*H$_2$CH$_2$–), 27.22 [C(*C*H$_3$)$_3$], 19.05 (*C*H$_3$CH$_2$O–), 9.21 (*C*H$_2$Si–).

Synthesis of Heterogenised Terdentate Ligands

Typically, a stirred slurry of 1 mmol of the corresponding anchored hydroxyaldehyde **2-(Sil, MCM-41, ITQ-2, ITQ-6)** was prepared in ethanol (10 mL) under argon at room temperature. After 10 min, 125 mg (1.1 mmol) of the amine were added and stirred for 16 hours. 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 ligands: **ligand-(support)**.

3-(Sil): anal. found: C 17.1, H 2.7, N 2.8%; (0.60 mmol/g); IR (KBr): ν = 1628, 1564 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 227, 268, 350, 430 nm; ^{13}C NMR (solid): δ = 165.39 (*C*H=N), 159.81 (NH*C*ONH), 156.04 (*C*-OH), 137.60 (*C6*, *C*$_{arom}$, *C4*, *C2*), 128.26 (*C*$_{arom}$, *C3*, *C5*), 64.80 (*C2′*, CH=N*C*H$_2$), 60.19 (*C*H$_2$Ph), 56.79 (*C5′*), 43.33 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 34.35 [*C*(CH$_3$)$_3$], 26.70 [C(*C*H$_3$)$_3$, *C3′*], 21.97 (*C*H$_2$CH$_2$Si, *C4′*), 10.20 (*C*H$_2$Si).

3-(MCM-41): anal. found: C 16.3, H 3.0, N 2.5%; (0.44 mmol/g); IR (KBr): ν = 1630, 1557 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 224, 264, 347, 419 nm; ^{13}C NMR (solid): δ = 166.60 (*C*H=N), 160.53 (NH*C*ONH), 153.62 (*C*-OH), 136.99 (*C6*, *C*$_{arom}$, *C4*, *C2*), 128.74 (*C*$_{arom}$, *C3*, *C5*), 66.50 (*C2′*, CH=N*C*H$_2$), 58.98 (*C*H$_2$Ph), 53.64 (*C5′*), 42.48 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 28.40 [C(*C*H$_3$)$_3$, *C3′*], 22.09 (CH$_2$*C*H$_2$Si, *C4′*), 8.02 (*C*H$_2$Si).

3-(ITQ-2): anal. found: C 15.4, H 2.4, N 2.2%; (0.41 mmol/g); IR (KBr): ν = 1628, 1557 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 226 262, 332, 423; ^{13}C NMR (solid): δ = 166.96 (*C*H=N), 160.41 (NH*C*ONH), 152.28 (*C*-OH), 137.72 (*C6*, *C*$_{arom}$, *C4*, *C2*), 128.62 (*C*$_{arom}$, *C3*, *C5*), 65.04 (*C2′*, CH=N*C*H$_2$), 58.86 (*C*H$_2$Ph), 54.12 (*C5′*), 43.20 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 36.29 [*C*(CH$_3$)$_3$], 25.74 [C(*C*H$_3$)$_3$, *C3′*], 23.06 (CH$_2$*C*H$_2$CH$_2$Si, *C4′*), 11.54 (*C*H$_2$Si).

3-(ITQ-6): anal. found: C 11.6, H 1.8, N 1.7%; (0.31 mmol/g); IR (KBr): ν = 1628, 1564 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 219, 262, 329, 414 nm; ^{13}C NMR (solid): δ = 166.24 (*C*H=N), 159.20 (NH*C*ONH, *C*OH), 136.87 (*C6*, *C*$_{arom}$, *C4*, *C2*), 128.02 (*C*$_{arom}$, *C3*, *C5*), 63.71 (*C2′*, CH=N*C*H$_2$), 53.88 (*C5′*), 43.69 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 35.08 [*C*(CH$_3$)$_3$], 29.98 [C(*C*H$_3$)$_3$, *C3′*], 23.06 (CH$_2$*C*H$_2$CH$_2$Si, *C4′*), 12.26 (*C*H$_2$Si).

3-(MCM-41, Si/Al ≈ 15): anal. found: C 17.4, H 2.4, N 2.7%; (0.5 mmol/g); IR (KBr): ν = 1630 cm^{-1} (C=N); UV-VIS: λ = 420, 337, 264, 223 nm.

3-(MCM-41, Si/Al ≈ 50): anal. found: C 25.9, H 2.9, N 5.1%; (0.9 mmol/g); IR (KBr): ν = 1634 cm^{-1} (C=N); UV-VIS: λ = 404, 332, 262, 226 nm.

3-(ITQ-2, Si/Al ≈ 20): anal. found: C 17.8, H 2.6, N 2.9%; (0.5 mmol/g); IR (KBr): ν = 1631 cm^{-1} (C=N); UV-VIS: λ = 411, 332, 265, 227 nm.

3-(MCM-41, Sn$_{synth}$): anal. found: C 21.4, H 3.0, N: 3.5%; (0.6 mmol/g); IR (KBr): ν = 1638 cm^{-1} (C=N); UV-VIS: λ = 429, 338, 266, 228 nm.

3-(MCM-41, Sn$_{graft}$): anal. found: C 19.0, H 3.1, N 3.1%; (0.5 mmol/g); IR (KBr): ν = 1634 cm^{-1} (C=N); UV-VIS: λ = 431, 335, 264, 228 nm; ^{13}C NMR (solid): δ = 165.70 (*C*H=N), 160.21 (NH*C*ONH), 154.04 (*C*-OH), 137.32 (*C6*, *C*$_{arom}$, *C4*, *C*2), 128.50 (*C*$_{arom}$, *C*3, *C*5), 66.65 (*C*2′, CH=N*C*H$_2$), 59.14 (*C*H$_2$Ph), 53.75 (*C*5′), 42.52 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 28.35 [C(*C*H$_3$)$_3$, *C*3′], 22.00 (CH$_2$*C*H$_2$Si, *C*4′), 8.00 (*C*H$_2$Si).

4-(Sil): anal. found: C 20.5, H 3.1, N 3.1%; (0.55 mmol/g); IR (KBr): ν = 1640–1600 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 415, 327, 266 nm; ^{13}C NMR (solid): δ = 169.45 (NH*C*ONH), 156.21 (*C*H=N), 129.76–120.00 (*C*$_{arom}$), 62.43–61.00 (*C*2′, CH=NC*H*$_2$), 59.11 (*C*5′), 58.87 (*C*H$_{2\text{-naphthyl}}$), 43.04 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 30.23 [*C*(CH$_3$)$_3$], 27.83 (*C*3′), 25.07 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 22.32 (*C*H$_3$), 10.84 (*C*H$_2$Si).

4-(MCM-41): anal. found: C 20.3, H 2.9, N 3.1%; (0.56 mmol/g); IR (KBr, cm^{-1}): ν = 1634–1599 (C=N, C=O, C=C); UV-VIS: λ = 423, 337, 266, 222; ^{13}C NMR (solid): δ = 169.65 (NH*C*ONH), 156.32 (*C*H=N), 129.80–120.00 (*C*$_{arom}$), 62.50–61.00 (*C*2′, CH=NC*H*$_2$), 59.00 (*C*5′), 58.75 (*C*H$_{2\text{-naphthyl}}$), 43.00 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 30.20 [*C*(CH$_3$)$_3$], 27.80 (*C*3′), 25.00 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 22.06 (*C*H$_3$), 10.45 (*C*H$_2$Si).

4-(ITQ-2): anal. found: C 19.4, H 3.0, N 2.6%; (0.45 mmol/g); IR (KBr): ν = 1638–1602 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 427, 336, 265, 221 nm; ^{13}C NMR (solid): δ = 170.23 (NH*C*ONH), 157.01 (*C*H=N), 130.00–120.00 (*C*$_{arom}$), 62.50–60.80 (*C*2′, CH=NC*H*$_2$), 59.00 (*C*5′), 58.56 (*C*H$_{2\text{-naphthyl}}$), 43.00 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 30.00 [*C*(CH$_3$)$_3$], 28.03 (*C*3′), 25.00 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 22.72 (*C*H$_3$), 10.65 (*C*H$_2$Si).

4-(ITQ-6): anal. found: C 20.2, H 2.7, N 2.9%; (0.51 mmol/g); IR (KBr): ν = 1636–1600 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 432, 336, 264, 221 nm; ^{13}C NMR (solid): δ = 169.67 (NH*C*ONH), 156.02 (*C*H=N), 130.00–120.00 (*C*$_{arom}$), 63.00–61.00 (*C*2′, CH=N*C*H$_2$), 59.04 (*C*5′), 58.93 (*C*H$_{2\text{-naphthyl}}$), 43.00–42.87 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 30.41 [*C*(CH$_3$)$_3$], 27.92 (*C*3′), 25.00 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 22.30 (*C*H$_3$), 10.92 (*C*H$_2$Si).

5-(Sil): anal. found: C 20.8, H 3.1, N 3.1%; (0.56 mmol/g); IR (KBr): ν = 1638–1590 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 426 nm; ^{13}C NMR (solid): δ = 160.01 (*C*H=N), 141.0–118.50 (*C*$_{arom}$), 62.85 (*C*2′), 60.13 (CH=N*C*H$_2$), 59.52 (*C*H$_{2\text{-naphthyl}}$), 54.15 (*C*5′), 43.63–42.07 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 33.14 [*C*(CH$_3$)$_3$], 29.97 [C(*C*H$_3$)$_3$], 25.45 (*C*3′); 23.54 (*C*H$_3$), 20.36 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 9.63 (**C**H$_2$Si).

5-(MCM-41): anal. found: C 27.2, H 5.2, N 3.3%; (0.59 mmol/g); IR (KBr): ν = 1638–1600 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 415, 334, 270 nm; ^{13}C NMR (solid): δ = 159.81 (*C*H=N), 140.70–118.41 (C$_{arom}$), 62.72 (*C*2′), 60.23 (CH=N*C*H$_2$), 59.42 (*C*H$_{2\text{-naphthyl}}$), 54.25 (*C*5′); 43.51–42.19 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 33.00 [*C*(CH$_3$)$_3$], 29.88 [C(*C*H$_3$)$_3$], 25.38 (*C*3′), 23.50 (*C*H$_3$), 20.32 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 9.44 (*C*H$_2$Si).

5-(ITQ-2): anal. found: C 33.7, H 5.5, N 4.7%; (0.83 mmol/g); IR (KBr): ν = 1638–1598 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 427, 336, 265, 221 nm; ^{13}C NMR (solid): δ = 159.86 (*C*H=N), 140.90–118.20 (C$_{arom}$), 62.81 (*C*2′), 60.03 (CH=N*C*H$_2$), 59.22 (*C*H$_{2\text{-naphthyl}}$), 54.15 (*C*5′), 43.50–42.20 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 33.00 [*C*(CH$_3$)$_3$], 29.85 [C(*C*H$_3$)$_3$], 25.33 (*C*3′), 23.61 (*C*H$_3$), 20.26 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 9.53 (*C*H$_2$Si).

5-(ITQ-6): anal. found: C 23.1, H 3.6, N 3.2%; (0.56 mmol/g); IR (KBr): ν = 1636–1595 cm^{-1} (C=N, C=O, C=C); UV-VIS: λ = 432, 336, 264, 221 nm; ^{13}C NMR (solid): δ = 159.85 (*C*H=N), 141.00–118.40 (*C*$_{arom}$), 62.77 (*C*2′), 60.19 (CH=N*C*H$_2$), 59.46 (*C*H$_{2\text{-naphthyl}}$), 54.15 (*C*5′), 43.50–42.00 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 33.08 [*C*(CH$_3$)$_3$], 29.90 [C(*C*H$_3$)$_3$], 25.31 (*C*3′), 23.58 (*C*H$_3$), 20.35 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 9.41 (*C*H$_2$Si).

Synthesis of Metal Complexes

The homogeneous chiral complexes[13] were also synthesised and used as catalysts to compare the catalytic activities and to evaluate the relations between the structural features of ligands and activity. Heterogenised complexes were synthesised following the general method. To a suspension of heterogenised ligand in toluene (20 mL) at room temperature was added an ethanolic solution of Pd(OAc)$_2$ or Ni(OAc)$_2$ (0.5 mmol/15 mL). The resulting mixture was stirred under reflux for 12 h, cooled to room temperature and filtered. The solid was washed several times with ethanol, dried and filtered to afford the respective heterogenised complexes, **complex-(support)**, in almost quantitative yields.

3Pd-(Sil): anal. found: C 15.3, H 1.8, N 2.2, Pd 5.8%; (0.54 mmol/g); IR (KBr): ν = 1627–1564 (C=N, C=O, C=C), 558 cm^{-1} (Pd-O); UV-VIS: λ = 411 nm; ^{13}C NMR (solid): δ = 180.74 (OO*C*CH$_3$), 169.09 (NH*C*ONH), 161.69 (*C*-O-Pd), 156.35 (*C*H=N), 128.68 (*C*$_{arom}$, *C*5, *C*3), 121.16 (*C*6), 65.71 (CH=N*C*H$_2$, *C*2′), 61.34 (*C*H$_2$Ph), 56.49 (*C*5′), 42.05 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 33.68 [*C*(CH$_3$)$_3$], 28.22 [C(*C*H$_3$)$_3$, *C*3′], 20.33 (OOC*C*H$_3$, *C*4′, CH$_2$*C*H$_2$CH$_2$Si), 7.84 (*C*H$_2$Si).

3Pd-(MCM-41): anal. found: C 15.0, H 2.0, N 2.2, Pd 2.9%; (0.27 mmol/g); IR (KBr: ν = 1632–1558 (C=N, C=O, C=C), 562 cm^{-1} (Pd-O); UV-VIS: λ = 225, 352, 410 nm; ^{13}C NMR (solid): δ = 180.40 (OO*C*CH$_3$), 160.07 (NH*C*ONH, *C*-O-Pd), 155.30 (*C*H=N), 137.61 (*C*2), 128.70 (*C*$_{arom}$, *C*5, *C*3), 120.00 (*C*6), 70.60 (CH=N*C*H$_2$, *C*2′), 63.21 (*C*H$_2$Ph), 58.64 (*C*5′), 42.97 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 34.50 [*C*(CH$_3$)$_3$], 28.20 [C(*C*H$_3$)$_3$, *C*3′], 23.34 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 16.66 (OOC*C*H$_3$), 11.23 (*C*H$_2$Si).

3Pd-(ITQ-2): anal. found: C 13.4, H 1.4, N 1.9, Pd 3.3%; (0.31 mmol/g); IR (KBr): ν = 1630–1562 (C=N, C=O, C=C), 560 cm^{-1} (Pd-O); UV-VIS: λ = 225, 258, 289, 335, 412 nm; ^{13}C NMR (solid): δ = 186.92 (OO*C*CH$_3$), 169.09 (NH*C*ONH, *C*-O-Pd), 158.65 (*C*H=N), 137.78 (*C*2), 126.14 (*C*$_{arom}$, *C*5, *C*3), 119.22 (*C*6), 65.23 (CH=N*C*H$_2$, *C*2′), 62.56 (*C*H$_2$Ph), 57.83 (*C*5′), 46.66 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 34.04 [*C*(CH$_3$)$_3$], 28.95 [C(*C*H$_3$)$_3$, *C*3′], 24.09 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 17.30 (OOC*C*H$_3$), 12.45 (*C*H$_2$Si).

3Pd-(ITQ-6): anal. found: C 9.8, H 0.9, N 1.4, Pd 2.7%; (0.25 mmol/g); IR (KBr): ν = 1630–1564 (C=N, C=O, C=C), 534 cm^{-1} (Pd-O); UV-VIS: λ = 229, 257, 285, 338, 410 nm; ^{13}C NMR (solid): δ = 185.23 (OO*C*CH$_3$), 164.23 (NH*C*ONH), 160.23 (*C*-O-Pd), 156.23 (*C*H=N), 137.90 (*C*2), 127.83 (*C*$_{arom}$, *C*5, *C*3), 120.07 (*C*6), 65.35 (CH=N*C*H$_2$, *C*2′), 62.31 (*C*H$_2$Ph), 56.98 (*C*5′), 48.97 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 34.65 [*C*(CH$_3$)$_3$], 29.55 [C(*C*H$_3$)$_3$, *C*3′], 23.61 (*C*4′, CH$_2$*C*H$_2$CH$_2$Si), 19.12 (OOC*C*H$_3$), 9.41 (*C*H$_2$Si).

3Pd-(MCM-41, Si/Al ≈ 15): anal. found: C 15.7, H 2.0, N 2.5, Pd: 4.3%; (0.4 mmol/g); IR (KBr): ν = 1630 (CO), 1564(C=N), 454 cm^{-1} (Pd-O); UV-VIS: λ = 408, 343, 289, 255, 229 nm.

3Pd-(MCM-41, Si/Al ≈ 50): anal. found: C: 18.9; H: 3.6; N: 2.5; Pd: 4.4%; (0.4 mmol/g); IR (KBr): ν = 1626 (CO), 1555 (C=N), 442 cm^{-1} (Pd-O); UV-VIS: λ = 405, 344, 289, 254, 230 nm.

3Pd-(ITQ-2, Si/Al ≈ 20): anal. found: C 16.6, H 2.4, N 2.7, Pd 5.1%; (0.5 mmol/g); IR (KBr): ν = 1621 (CO), 1557

(C=N), 450 cm^{-1} (Pd-O); UV-VIS: λ = 407, 350, 285, 237; ^{13}C NMR (solid): δ = 187.00 (OO*C*CH$_3$), 169.00 (NH*C*ONH, *C*-O-Pd), 158.76 (*C*H=N), 137.82 (*C2*), 126.04 (*C*$_{arom}$, *C5*, *C3*), 119.19 (*C6*), 65.27 (CH=N*C*H$_2$, *C2′*), 62.59 (*C*H$_2$Ph), 57.80 (*C5′*), 46.70 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 34.00 [*C*(CH$_3$)$_3$], 29.00 [C(*C*H$_3$)$_3$, *C3′*], 24.05 (*C4′*, CH$_2$*C*H$_2$CH$_2$Si), 17.26 (OOC*C*H$_3$), 12.41 (*C*H$_2$Si).

3Pd-(MCM-41, Sn$_{synth}$): anal. found: C 22.7, H 2.7, N 2.7, Pd 6.9%; (0.6 mmol/g); IR (KBr): ν = 1628 (CO), 1560 (C=N), 450 cm^{-1} (Pd-O); UV-VIS: λ = 417, 343, 261, 225 nm.

3Pd-(MCM-41, Sn$_{graft}$): anal. found: C 31.9, H 5.9, N 5.5, Pd 1.3%; (0.1 mmol/g); IR (KBr): ν = 1636 (CO), 1564 (C=N), 450 cm^{-1} (Pd-O); UV-VIS: λ = 422, 342, 264, 220 nm.

3Ni-(Sil): anal. found: C 15.6, H 2.2, N 2.5, Ni 10.1%; (0.45 mmol/g); IR (KBr): ν = 1618–1564 (C=N, C=O, C=C), 571 cm^{-1} (Ni-O); UV-VIS: λ = 265, 330, 412 nm; ^{13}C NMR (solid): δ = 182.40 (OO*C*CH$_3$), 174.14 (NH*C*ONH, *C*-O-Pd), 158.61 (*C*H=N), 140.66 (*C2*), 128.04 (*C*$_{arom}$, *C5*, *C3*), 79.02 (CH=N*C*H$_2$, *C2′*), 60.09 (*C*H$_2$Ph, *C5′*), 42.86 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 28.06 [C(*C*H$_3$)$_3$), *C3′*], 23.21 (*C4′*, CH$_2$CH$_2$*C*H$_2$Si, OOC*C*H$_3$), 11.97 (*C*H$_2$Si).

3Ni-(MCM-41): anal. found: C 16.4, H 2.1, N 2.6, Ni 6.4%; (0.36 mmol/g); IR (KBr): ν = 1630–1567 (C=N, C=O, C=C), 568 cm^{-1} (Ni-O); UV-VIS: λ = 234, 268, 338, 414 nm; ^{13}C NMR (solid): δ = 198.94 (OO*C*CH$_3$), 160.23 (NH*C*ONH, *C*-O-Pd), 152.47 (*C*H=N), 136.69 (*C2*), 128.56 (*C*$_{arom}$, *C5*, *C3*), 120.31 (C6), 73.60 (CH=N*C*H$_2$, *C2′*), 63.53 (*C*H$_2$Ph), 58.67 (*C5′*), 40.47 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 34.29 [*C*(CH$_3$)$_3$], 27.73 [C(*C*H$_3$)$_3$, *C3′*], 22.27 (*C4′*, CH$_2$CH$_2$*C*H$_2$Si, OOC*C*H$_3$), 15.36 (*C*H$_2$Si).

3Ni-(MCM-41, Si/Al ≈ 15): anal. found: C 14.7, H 1.1, N 2.0, Ni 3.2%; (0.18 mmol/g); IR (KBr): ν = 1632 (CO), 1568 (C=N), 457 cm^{-1} (Ni-O); UV-VIS: λ = 495, 412, 339, 266 nm.

3Ni-(ITQ-2): anal. found: C 14.0, H 1.1, N 2.0, Ni 1.4%; (0.20 mmol/g); IR (KBr): ν = 1628–1557 (C=N, C=O, C=C), 557 cm^{-1} (Ni-O); UV-VIS: λ = 236, 263, 390 nm: ^{13}C NMR (solid): δ = 184.82 (OO*C*CH$_3$), 174.14 (NH*C*ONH, *C*-O-Pd), 158.86 (*C*H=N), 128.56 (*C*$_{arom}$, *C5*, *C3*), 118.58 (*C6*), 59.61 (*C*H$_2$Ph, *C5′*), 42.86 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 34.61 [*C*(CH$_3$)$_3$], 29.03 [C(*C*H$_3$)$_3$, *C3′*], 23.45 (*C4′*, CH$_2$CH$_2$*C*H$_2$Si, OOC*C*H$_3$), 10.83 (*C*H$_2$Si).

3Ni-(ITQ-6): anal. found: C 9.1, H 1.1, N 1.3, Ni 0.9%; (0.13 mmol/g); IR (KBr): ν = 1621–1554 (C=N, C=O, C=C), 592 cm^{-1} (Ni-O); UV-VIS: λ = 260, 328, 415 nm; ^{13}C NMR (solid): δ = 190.89 (OO*C*CH$_3$), 165.34 (NH*C*ONH, *C*-O-Pd), 159.60 (*C*H=N), 127.31 (*C*$_{arom}$, *C5*, *C3*), 118.34 (*C6*), 76.59 (CH=N*C*H$_2$, *C2′*), 62.28 (*C*H$_2$Ph), 44.08 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 24.42 (*C4′*, CH$_2$CH$_2$*C*H$_2$Si, OOC*C*H$_3$), 8.41 (*C*H$_2$Si).

4Pd-(Sil): anal. found: C 19.5, H 3.0, N 3.0, Pd 4.9%; (0.46 mmol/g), IR (KBr): ν = 1638–1572 (C=N, C=O, C=C), 557 cm$_{-1}$ (Pd-O); UV-VIS: λ = 206, 221, 424 nm; ^{13}C NMR (solid): δ = 180.03 (OO*C*CH$_3$), 169.09 (NH*C*ONH), 160.69 (*C*-O-Pd), 159.35 (*C*H=N), 128.68–120.16 (*C*$_{arom}$), 65.45–63.00 (*C2′*, CH=N*CH$_2$*), 60.11 (*C5′*), 59.05 (*C*H$_{2\text{-naphthyl}}$), 44.05 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 30.68 [*C*(CH$_3$)$_3$], 28.67 (*C3′*), 25.14 (*C4′*, CH$_2$*C*H$_2$CH$_2$Si), 22.16 (*C*H$_3$), 20.76 (OCO*C*H$_3$), 7.84 (*C*H$_2$Si).

4Pd-(MCM-41): anal. found: C 13.2, H 1.6, N 1.5, Pd 4.2%; (0.39 mmol/g); IR (KBr): ν = 1634–1564 (C=N, C=O, C=C), 571 cm^{-1} (Pd-O); UV-VIS: λ = 223, 268, 410 nm; ^{13}C NMR (solid): δ = 180.00 (OO*C*CH$_3$), 169.14 (NH*C*ONH), 160.64 (*C*-O-Pd), 159.33 (*C*H=N), 128.80–120.00 (*C*$_{arom}$), 65.50–63.00 (*C2′*, CH=N*CH$_2$*), 60.15 (*C5′*), 59.00 (*C*H$_{2\text{-naphthyl}}$), 44.08 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 30.63 [*C*(CH$_3$)$_3$], 28.69 (*C3′*), 25.18 (*C4′*, CH$_2$*C*H$_2$CH$_2$Si), 22.06 (*C*H$_3$), 20.79 (OCO*C*H$_3$), 7.76 (*C*H$_2$Si).

4Pd-(ITQ-2): anal. found: C 18.0, H 2.9, N, 2.6, Pd 3.4%; (0.32 mmol/g); IR (KBr): ν = 1638–1566 (C=N, C=O, C=C), 594 cm^{-1} (Pd-O); UV-VIS: λ = 221, 264, 287, 341, 419 nm; ^{13}C NMR (solid): δ = 179.12 (OO*C*CH$_3$), 169.29–160.09 (NH*C*ONH, *C*-O-Pd), 159.67 (*C*H=N), 130.00–120.0 (*C*$_{arom}$), 62.25, 61.90 (*C2′*, CH=N*CH$_2$*), 59.81, 58.60 (*C5′*; (*C*H$_{2\text{-naphthyl}}$), 44.00 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 30.86 [*C*(CH$_3$)$_3$], 29.17, 23.14, 22.06, 20.04 (*C3′*, *C4′*, *C*H$_3$, CH$_2$CH$_2$CH$_2$Si, OCO*C*H$_3$), 7.76 (*C*H$_2$Si).

4Pd-(ITQ-6): anal. found: C 19.6, H 2.8, N 2.9, Pd 4.7%; (0.44 mmol/g); IR (KBr): ν = 1637–1564 (C=N, C=O, C=C), 592 cm^{-1} (Pd-O); UV-VIS: λ = 224, 260, 291, 342, 417 nm; ^{13}C NMR (solid): δ = 180.00 (OO*C*CH$_3$), 169.00 (NH*C*ONH), 160.74 (*C*-O-Pd), 159.41 (*C*H=N), 128.70–120.00 (*C*$_{arom}$), 65.50–63.00 (*C2′*, CH=N*CH$_2$*), 60.09 (*C5′*), 59.00 (*C*H$_{2\text{-naphthyl}}$); 44.13–44.01 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 30.70 [*C*(CH$_3$)$_3$], 28.65 (*C3′*), 25.12 (*C4′*, CH$_2$*C*H$_2$CH$_2$Si), 22.19 (*C*H$_3$), 20.71 (OCO*C*H$_3$), 7.79 (*C*H$_2$Si).

4Ni-(Sil): anal. found: C 19.8, H 3.6, N 3.0, Ni 1.3%; (0.22 mmol/g); IR (KBr): ν = 1642–1572 (C=N, C=O, C=C), 557 cm^{-1} (Ni-O); UV-VIS: λ = 214, 261, 359, 421 nm; ^{13}C NMR (solid): δ = 179.16 (O*C*OCH$_3$), 162.60 (*C*-O-Ni), 162.24 (*C*H=N), 141.50–120.00 (*C*$_{arom}$), 62.39 (*C2′*), 61.81 (CH=N*C*H$_2$), 57.00 (*C*H$_{2\text{-naphthyl}}$), 54.20 (*C5′*), 44.00 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH)), 35.36 [*C*(CH$_3$)$_3$], 30.00 [C(*C*H$_3$)$_3$], 29.63 (*C3′*), 28.19 (*C*H$_3$), 25.00 (*C4′*), 20.82 (CH$_2$*C*H$_2$CH$_2$Si, OCO*C*H$_3$), 7.73 (*C*H$_2$Si).

4Ni-(MCM-41): anal. found: C 16.5, H 2.8, N 2.5, Ni 1.0%; (0.16 mmol/g); IR (KBr): ν = 1643–1570 (C=N, C=O, C=C), 557 cm^{-1} (Ni-O); UV-VIS: λ = 219, 266, 338, 414 nm; ^{13}C NMR (solid): δ = 178.75 (O*C*OCH$_3$), 162.61 (*C*-O-Ni), 162.20 (*C*H=N), 141.50–120.13 (*C*$_{arom}$), 62.37 (*C2′*), 61.70 (CH=N*C*H$_2$), 57.06 (*C*H$_{2\text{-naphthyl}}$), 54.18 (*C5′*), 44.00 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 35.32 [*C*(CH$_3$)$_3$], 30.09 [C(*C*H$_3$)$_3$], 29.60 (*C3′*), 28.11 (*C*H$_3$), 24.85 (*C4′*), 20.79 (CH$_2$*C*H$_2$CH$_2$Si, OCO*C*H$_3$), 7.76 (*C*H$_2$Si).

4Ni-(ITQ-2): anal. found: C 18.3, H 2.8, N 2.5, Ni 0.9%; (0.16 mmol/g); IR (KBr): ν = 1638–1562 (C=N, C=O, C=C), 554 cm^{-1} (Ni-O); UV-VIS: λ = 209, 223,266, 340, 418 nm.

4Ni-(ITQ-6): found: C 20.1, H 2.5, N 2.7, Ni 1.7%; (0.29 mmol/g); IR (KBr): ν = 1636–1566 (C=N, C=O, C=C), 592 cm^{-1} (Pd-O); UV-VIS: λ = 224 264, 341, 421 nm.

5Pd-(Sil): anal. found: C 17.6, H 3.0, N 2.7, Pd 5.9%; (0.56 mmol/g); IR (KBr): ν = 1646–1572 (C=N, C=O, C=C), 571 cm^{-1} (Pd-O); UV-VIS: λ = 218, 270, 360 nm.

5Pd-(MCM-41): anal. found: C 19.7, H 3.0, N 2.9, Pd 5.4%; (0.51 mmol/g); IR (KBr): ν = 1630–1566 (C=N, C=O, C=C), 564 cm – 1 (Pd-O); UV-VIS: λ = 205, 222, 314, 412 nm.

5Pd-(ITQ-2): anal. found: C 18.1, H 2.5, N 2.6, Pd 7.7%; (0.72 mmol/g); IR (KBr): ν = 1636–1560 (C=N, C=O, C=C), 557 cm^{-1} (Pd-O); UV-VIS: λ = 223, 262, 343, 408 nm; ^{13}C NMR (solid): δ = 176.23 (O*C*OCH$_3$), 160.92 (*C*-O-Pd), 157.81 (*C*H=N), 138.70–117.91 (C$_{arom}$), 63.62 (*C2′*), 61.23 (CH=N*C*H$_2$), 59.98 (*C*H$_{2\text{-naphthyl}}$), 56.85 (*C5′*), 44.21–43.89 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH), 33.39 [*C*(CH$_3$)$_3$], 28.88 [C(*C*H$_3$)$_3$], 27.38 (*C3′*), 25.50 (*C*H$_3$), 21.78 (*C4′*, CH$_2$*C*H$_2$CH$_2$Si), 18.34 (OCO*C*H$_3$), 7.64 (*C*H$_2$Si).

5Pd-(ITQ-6): anal. found: C 18.0, H 2.3, N 2.8, Pd 11.0%; (0.80 mmol/g); IR (KBr): ν = 1628–1564 (C=N, C=O, C=C), 571 cm^{-1} (Pd-O); UV-VIS: λ = 218, 270, 360 nm.

5Ni-(Sil): anal. found: C 20.5, H 3.0, N 3.0, Ni 2.0%; (0.34 mmol/g); IR (KBr): ν = 1622–1574 (C=N, C=O, C=C), 550 cm^{-1} (Ni-O); UV-VIS: λ = 212, 264, 341, 422 nm.

5Ni-(MCM-41): anal. found: C 21.8, H 3.9, N 3.0, Ni 1.8%; (0.30 mmol/g); IR (KBr): ν = 1620–1568 (C=N, C=O, C=C), 557 cm^{-1} (Ni-O); UV-VIS: λ = 216, 265, 336, 414 nm.

5Ni-(ITQ-2): anal. found: C 18.9, H 2.8, N 2.5, Ni 1.2%; (0.19 mmol/g); IR (KBr): ν = 1634–1564 (C=N, C=O, C=C), 552 cm^{-1} (Ni-O); UV-VIS: λ = 221, 267, 337, 418 nm.

5Ni-(ITQ-6): anal. found: C 22.7, H 2.50, N 2.9, Ni 1.9%; (0.32 mmol/g); IR (KBr): ν = 1620–1566 (C=N, C=O, C=C), 592 cm^{-1} (Ni-O); UV-VIS: λ = 224, 266, 340, 424 nm; ^{13}C NMR (solid): δ = 163.50 (*C*-O-Ni), 163.25 (*C*H=N), 142.63–121.14 (C_{arom}), 64.10 (*C2′*), 63.07 (CHN=*C*H$_2$), 61.23 ($CH_{2\text{-naphthyl}}$), 58.56 (*C5′*); 44.43–42.89 (*C*H$_2$*C*H$_2$*C*H$_2$Si, *C*CH$_2$NH), 32.32 [*C*(CH$_3$)$_3$], 30.63 [C(*C*H$_3$)$_3$], 29.39 (*C3′*), 25.97 (*C*H$_3$), 24.45 (*C4′*), 21.79 (CH$_2$*C*H$_2$CH$_2$Si, OCO*C*H$_3$), 7.65 (*C*H$_2$Si).

Catalytic Experiments

The catalytic properties, in hydrogenation reactions, of the Pd and Ni complexes were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 mL capacity at 40 °C temperature, 4 atm dihydrogen pressure and 1/1000, 1/10000 or 1/1000000 metal/substrate molar ratio. The evolution of the reaction and optical purity (ee) of hydrogenated product were monitored by gas chromatography with a chiral glass capillary column {mixture of methyl silicone (OV-1701) and methylsilicone-heptakis-[2,3-dipentyl-6-(*tert*-butyldimethylsilyl)]-β-cyclodextrin as stationary phase}.[27]

Recovery and Recycling of Catalysts

At the end of the hydrogenation process, the mixture of reaction was filtered; the residue of zeolite-containing catalyst was washed with CH$_2$Cl$_2$ to completely remove the remains of products and/or reactants and used again.

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