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Immobilization of Rhodium Diphosphine Complexes on Mesoporous Al-MCM-41 Materials: Catalysts for Enantioselective Hydrogenation

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Heterogeneous chiral catalysts for the enantioselective hydrogenation of prochiral alkenes are prepared from chiral rhodium diphosphine complexes and Al-MCM-41. Impregnation of the mesoporous carrier Al-MCM-41 with the organometallic complexes in dichloromethane leads to strong and not leaching hydrogenation catalysts. The catalysts are characterized by spectroscopic methods such as FT-IR and MAS-NMR as well as thermoprogrammed desorption of ammonia, thermogravimetric analysis, and nitrogen sorption experiments. The hydrogenation of dimethylitaconate was studied as a test reaction. The immobilized catalysts showed high activity and excellent regio- and enantioselectivity. Up to 92% ee, 100% conversion, and 99% regioselectivity were observed for the hydrogenation of dimethyl (*R*)-methylsuccinate. The catalysts could be reuse d without any regeneration procedure and with no loss of catalytic acitivity. Leaching of the homogeneous complex out of the MCM-41 framework was not observed. © 2001 Academic Press

Key Words: **immobilization; rhodium; phosphine; MCM-41; asymmetric; hydrogenation.**

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1. INTRODUCTION

The immobilization of homogeneous catalyst systems is an attractive challenge because it opens access to the preparation of new, environmentally friendly means of chemical synthesis. Although homogeneous catalysts show remarkable performance for a large variety of reactions, technical problems such as separation, recovery, and recyclization of the soluble catalysts create the demand for heterogeneous catalysts with comparable performance. Often enantioselectively catalyzed reactions are exclusively performed using organometallic transition metal complexes. Various attempts toward the immobilization of organometallic complexes have been investigated previously (1) such as attaching to supporting materials by chemisorption (2, 3), immobilization by steric hindrance in zeolitic micro- or mesopores ("ship-in-the bottle" concept) (4–9), or supported liquid-phase catalysts (10). Recent reviews reveal the potential of heterogeneous chiral catalysts created by the methods mentioned (11–13).

Nanosized channels of ordered mesoporous materials related to the M41S family can be tailored to pore sizes ranging from 1.5 nm to ca. 100 nm (14). MCM-41-type molecular sieves are suitable as carriers for transition metal complexes, offering new opportunities for the encapsulation of large catalyst species and for the catalytic conversion of substrates much larger than in common zeolites (15). The application of such host/guest compounds as catalysts for oxidative reactions has been successfully tested (16–21).

Homogeneous rhodium diphosphine complexes belong to the most important catalysts in enantioselective hydrogenation reactions. We previously prepared surface-bonded rhodium phosphine complexes in Al-MCM-41. In a solution of dichloromethane, [Rh(acac)(chiraphos)] and Al-MCM-41 react to form a surface-bonded Rh-chiraphos complex due to an exchange reaction of the acetylacetonato ligand and surface oxygen of the acidic support (22). However, the occupation of the coordination sphere of the catalytic active Rh site led to the complete loss of chiral induction of this complex. Still it was our aim to immobilize such complexes without the introduction of a linker to the ligand. This method would then allow us to successfully heterogenize homogeneous catalysts without modification of their chemical structure. Recyclable catalysts have been prepared in such a manner by anchoring rhodium complexes on heteropolyacids (23).

In this paper we present new heterogeneous rhodium diphosphine catalysts and their application in the enantioselective hydrogenation of dimethylitaconate. The results indicate the localization of the complex inside the mesoporous channel system. Chiral heterogeneous rhodium diphosphine catalysts without any linker group on the complexes are prepared and successfully applied in enantioselective hydrogenation. A similar method has been published recently by R. D. Broene *et al.* (24).

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2. EXPERIMENTAL

All experiments were performed under purified inert gas by Schlenk techniques unless otherwise stated. Solvents were dried, and oxygen and moisture were removed by standard methods. Due to those facts the new systems are sometimes hard to reproduce in loading of the complex and catalytic performance. This could also be due to the properties of the Al-MCM-41 carrier materials. Due to the high air sensitivity of the organometallic complexes combined with the high surface area of the heterogeneous catalysts, the best results can be achieved only with freshly prepared materials.

Synthesis of Al-MCM-41

For the synthesis of Al-MCM-41 the quartenary ammonium surfactant $(C_{14}H_{29})N(CH_3)Br$ was added under constant stirring to a solution of tetraethylammoniumhydroxide (TEAOH) and $NaAlO_2$ at ambient temperature (14, 25). After 4 h colloidal silica (Ludox HS-40) was added dropwise over a period of 1 h, followed by vigorous stirring for 4 h. The Si/Al ratio of the gel was 40. Crystallization took place over a 7-days period at 105°C. The resulting white solid was washed with water and dried at 120°C. The template was removed by heating the material to 540°C for several hours.

Immobilization of Chiral Rhodium Diphosphine Complexes

All solvents were purified, degassed, and saturated with argon, and the preparation of the Rh complexes was carried out carefully under argon by standard Schlenk techniques. The complexes were prepared from $[CODRhCl]_2$ and 1.1 equiv of chiral diphosphine in dichloromethane as solvent. The carrier material Al-MCM-41 was then added. After the mixture was stirred for 24 h, the solid was filtered and washed thoroughly with dichloromethane until the washings remained colorless in order to remove any residual free Rh complex. After being dried in a vacuum the catalysts were Soxhlet extracted with methanol for 24 h. The absence of the homogeneous complex in the mixture was checked by ICP-AES analysis as well as by FT-IR spectroscopy. The heterogeneous catalyst has a pale yellow color similar to the color of the homogeneous complex.

Hydrogenation of Dimethylitaconate

Hydrogenation of dimethylitaconate was carried out in glass autoclaves at ambient temperature and 3 bar hydrogen pressure for 24 h. The catalyst was added to a solution of 5 mmol of olefin in 10 ml of methanol. The molar ratio of olefin to rhodium (determined by atomic absorption spectroscopy) was 1000.

Characterization

X-ray diffraction patterns of powdered samples were obtained with a Siemens D5000 diffractometer equipped with a rotating anode and Cu $K\alpha$ radiation.

Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature were measured on a Micromeritics ASAP 2010 instrument. The samples were pre-outgassed at 150°C. Pore diameter and specific pore volume were calculated according to the Barrett–Joyner–Halenda (BJH) theory. The specific surface area was obtained using the Brunauer–Emmett–Teller (BET) equation.

Chemical analysis was performed with inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Spectroflame D, Spectro Analytic Instrument).

For thermogravimetric analysis a Netzsch 209/2/E equipped with a STA 409 controller was used. The heating rate was 5°C/min, and α-Al_2O_3 was used as reference material.

The temperature-programmed desorption (TPD) of ammonia was performed at atmospheric pressure using a flow-type fixed-bed adsorber. Prior to the TPD experiments the materials were calcined at 200°C in dry nitrogen for 8 h, loaded with ammonia at 100°C, and purged with nitrogen until a stable baseline formed. The desorption was done in the temperature range 100–400°C at a heating rate of 5°C/min under nitrogen flow.

The solid-sate NMR spectra were recorded on a Bruker DSX 500 spectrometer, equipped with a 2.5-mm CP/MAS probehead. In the case of the ^{31}P-MAS NMR spectra, 5000–10,000 transients gave satisfactory signal-to-noise ratios. The samples were rotated at 20,000 Hz. The spectra were recorded at room temperature (296 K) and aqueous 85% H_3PO_4 was used as the external standard.

The reaction products were analyzed using a Siemens RGC202 gas chromatograph equipped with a 25-m Lipodex E capillary column.

3. RESULTS AND DISCUSSION

In order to get a first impression of whether the chosen carrier system would be a suitable host for the homogeneous catalysts, a computer simulation of the structures of several Rh diphosphine complexes was carried out whereby the Rh complexes were placed in a simulated tube of Al-MCM-41 (Fig. 1). The graphical illustration of CODRhDuphos fixed in Al-MCM-41 shows that the complex fits easily in a tube of 2.2 nm.

Impregnation of Al-MCM-41 with chiral rhodium diphosphine complexes leads to strong interaction of the complex in the mesoporous system of the carrier material (Fig. 2). Dichloromethane was found to be an effective solvent for the impregnation. After being stirred for 24 h the yellow solution of 0.15 mmol of [(1,5-cyclooctadiene) Rh(1, 2-bis((2*S*, 5*S*)-2,5-dimethylphospholano) benzene)]$^+$ Cl$^-$ (CODRhDuphos) complex per g of Al-MCM-41 in

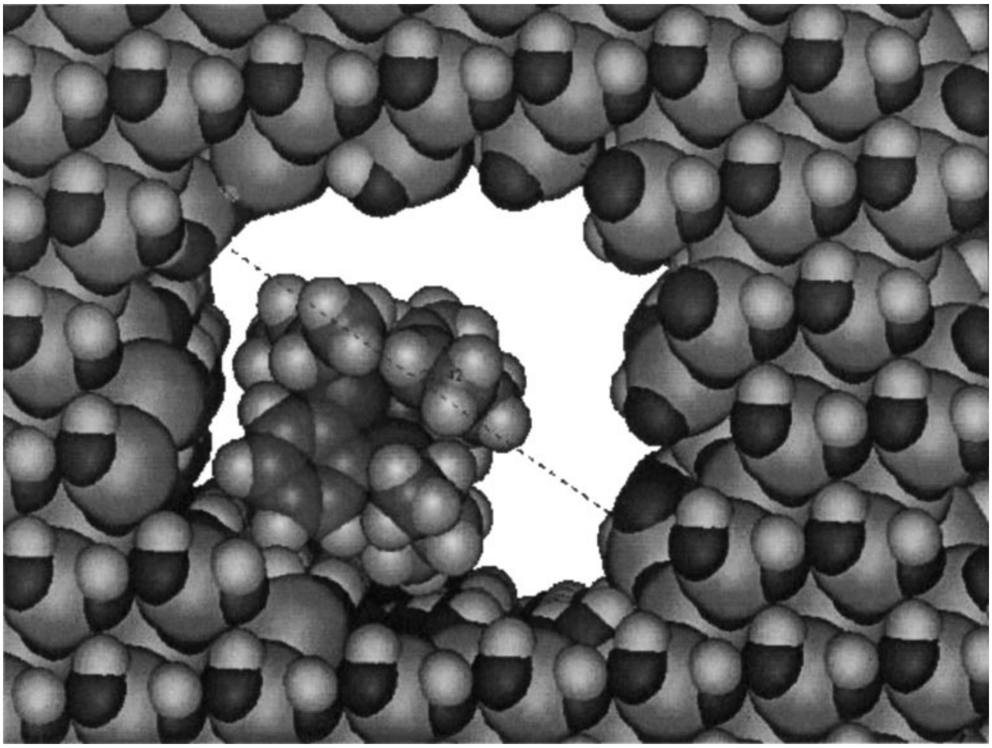

FIG. 1. Graphical illustration of CODRhDuphos fixed in Al-MCM-41.

CH_2Cl_2 solvent underwent complete decolorization. The CODRhDuphos complex is prepared by the cleavage of the CODRhchloride dimer with the diphosphine ligand Duphos. The carrier material turned yellow, indicating the homogeneous catalyst loaded onto the support. Furthermore, the FT-IR spectra of the mother liquor showed no signals corresponding to the free rhodium phosphine complex. Soxhlet extraction of the impregnated Al-MCM-41 with methanol led to a partially leaching of the complex from the carrier material. It is assumed that the organometallic complex is adsorbed on the inner and outer surfaces of the Al-MCM-41 structure. The binding energy of this adsorption varies on the different reactive sites like Brønsted and Lewis acid sites and silanol groups. Upon the extraction with methanol, which in contrast to nonpolar dichloromethane adsorbs strongly on the Al-MCM-41 surface, the organometallic complex desorbs from silanol groups due to a competitive reaction with the polar alcohol. The amount of complex immobilized on the carrier was determined by elemental analysis. Rhodium contents vary between 0.02 and 0.07 mmol per g of Al-MCM-41 depending on the amount of complex offered and on the batch of Al-MCM-41 used.

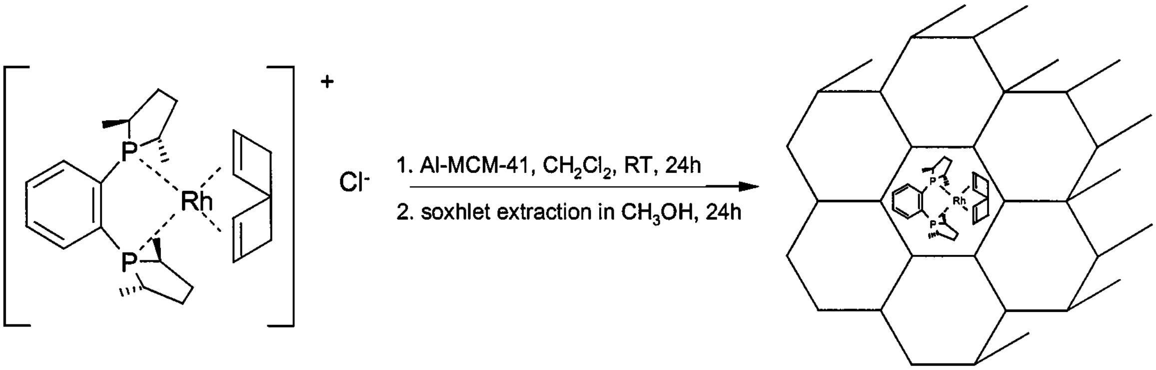

FIG. 2. Impregnation of Al-MCM-41 with rhodium diphosphine complex.

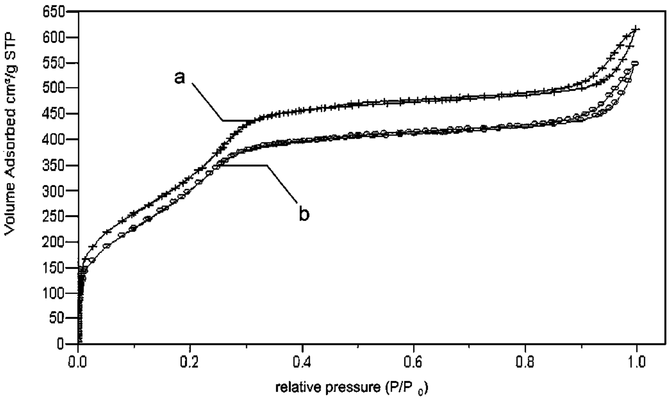

FIG. 3. N_2 adsorption and desorption isotherms of (a) Al-MCM-41 (carrier material) and (b) CODRhDuphos immobilized on Al-MCM-41.

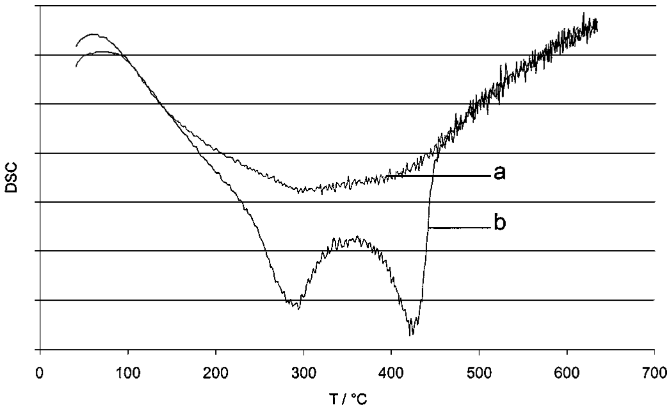

FIG. 4. DSC spectra of (a) mechanical mixture of Al-MCM-41 and CODRhDuphos and (b) CODRhDuphos immobilized on Al-MCM-41.

The X-ray diffraction pattern of the isolated yellow material shows a strong peak corresponding to the (100) reflex, indicating that the structure of the carrier material remains unchanged during the immobilization procedure.

N_2 adsorption isotherm of the supported catalyst shows a decrease of ca. 10% of mesoporous pore volume compared to the corresponding carrier material (Fig. 3 and Table 1). The BET surface was found to decrease from 1430 m^2/g in the unfunctionalized carrier material to 1250 m^2/g for the loading material with a corresponding decrease in mesopore volume from 1.25 cm^3/g to 1.07 cm^3/g (Table 1). These results indicate that the complex is deposited on the inner surface of the Al-MCM-41. The specific surface of the carrier was reduced by loading it with the complex. This is consistent with partial mesopore filling by the organometallic catalyst.

Quantitantive loading of the organometallic complex was demonstrated by thermal gravimetric analysis. Thermogravimetric and differential scanning calorimetric (DSC) measurements show that the immobilized complex is stable up to 250°C (Fig. 4). Oxidative decomposition of the fixed complex took place in two steps at 295°C and 420°C whereas a mechanical mixture of the homogeneous complex with the carrier material exhibited no distinct peaks. The loss of weight of ca. 4.5 wt% caused by the burning of the complex is consistent with the content determined by chemical analysis.

TABLE 1

Surface Areas and Pore Volumes of Al-MCM-41 (Carrier Material) and of CODRhDuphos Immobilized on Al-MCM-41

	Surface area[a] (m^2/g)	Pore volume[b] (cm^3/g)
Al-MCM-41	1430	1.25
CODRhDuphos immobilized on Al-MCM-41	1250	1.07

[a] Calculated according to the BET method.
[b] According to the BJH theory.

Temperature-programmed desorption (TPD) of ammonia shows weak acidic centers on the Al-MCM-41 carrier material. In the case of the immobilized complex the amount of desorbed ammonia decreases compared to the pure carrier material (Fig. 5). This indicates an interaction of the immobilized complex with acidic sites on the Al-MCM-41. This result is also supported by FT-IR spectroscopy.

The infrared spectra show no change of wavenumber but a decrease of intensity for the signal at ca. 3740 cm^{-1} which is assigned to the stretching vibration of terminal silanol groups (Fig. 6). The vibration bands of immobilized CODRhDuphos are similar to those in the solution of dichloromethane. However, these signals resulting from organic compounds are very weak and not characteristic enough to surely identify or resolve a structure.

In order to elucidate the chemical structure of the immobilized rhodium diphosphine complexes MAS-NMR

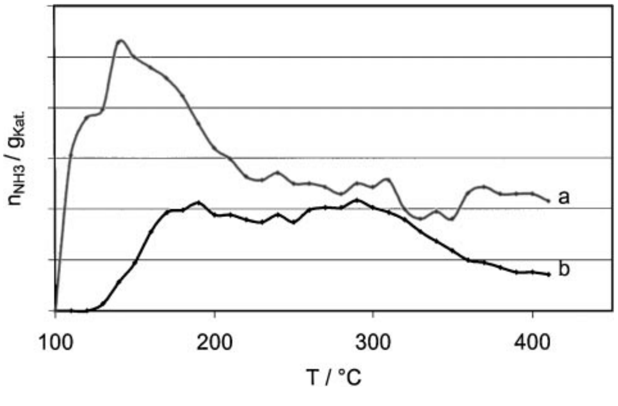

FIG. 5. Temperature-programmed desorption (TPD) of ammonia of (a) Al-MCM-41 (carrier material) and (b) CODRhDuphos immobilized on Al-MCM-41.

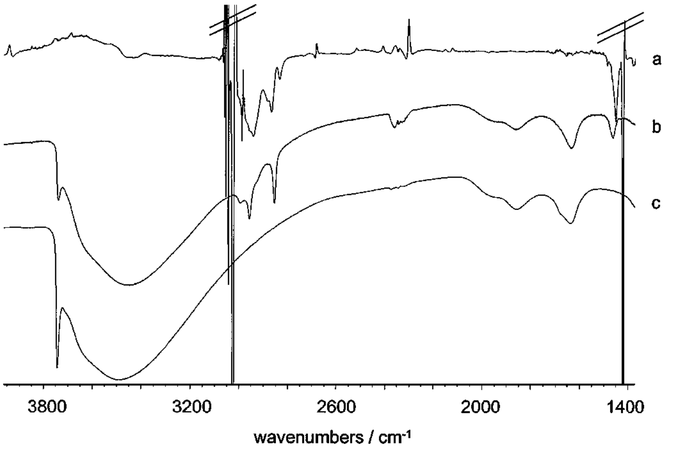

FIG. 6. IR spectra of (a) CODRhDuphos (solution in dichloromethane), (b) CODRhDuphos immobilized on Al-MCM-41 (self-supported wafer), and (c) Al-MCM-41 carrier material (self-supported wafer).

spectra of the pure Al-MCM-41 carrier, the homogeneous complexes, and the immobilized complexes have been recorded. Due to the low content of immobilized complex (4 wt%) the ^{13}C and ^{1}H resonance signals are too weak for quantitative interpretation. The pure carrier and the immobilized complexes show similar spectra for the ^{27}Al and ^{29}Si nuclei (25). This indicates that no new Al or Si species have been formed upon reaction with the rhodium complexes. It is also possible that a signal created by such a reaction is too weak to be observed in the spectra of the immobilized complexes.

^{31}P-MAS NMR spectra of the solid homogeneous CODRhDuphos complex and the same complex immobilized on Al-MCM-41 are depicted in Fig. 7. The homogeneous complex gives a strong signal at 68 ppm and two weaker ones at 78 and 90 ppm due to trace amounts of oxidic impurities. A difference in the chemical shift was observed between the solution spectrum of the homogeneous catalyst (76.3 ppm) (26) and the corresponding solid-state spectrum (68 ppm relative to external H_3PO_4). This difference could result from crystal-packing forces in the solid state which could dictate a conformational arrangement in the solid state not present in solution. The breadth of the signals prevented an accurate determination of the Rh–P coupling. The MAS NMR spectra of the immobilized CODRhDuphos complex show only one signal at 90 ppm (27). Since there is no signal of the homogeneous complex and no signal of the free phosphine ligand visible in the MAS spectra, we conclude that the phosphine ligand is completely coordinated to the rhodium. The immobilization of this rhodium-Duphos complex leads to a shift of the ^{31}P signal of 22 ppm to lower magnetic field compared

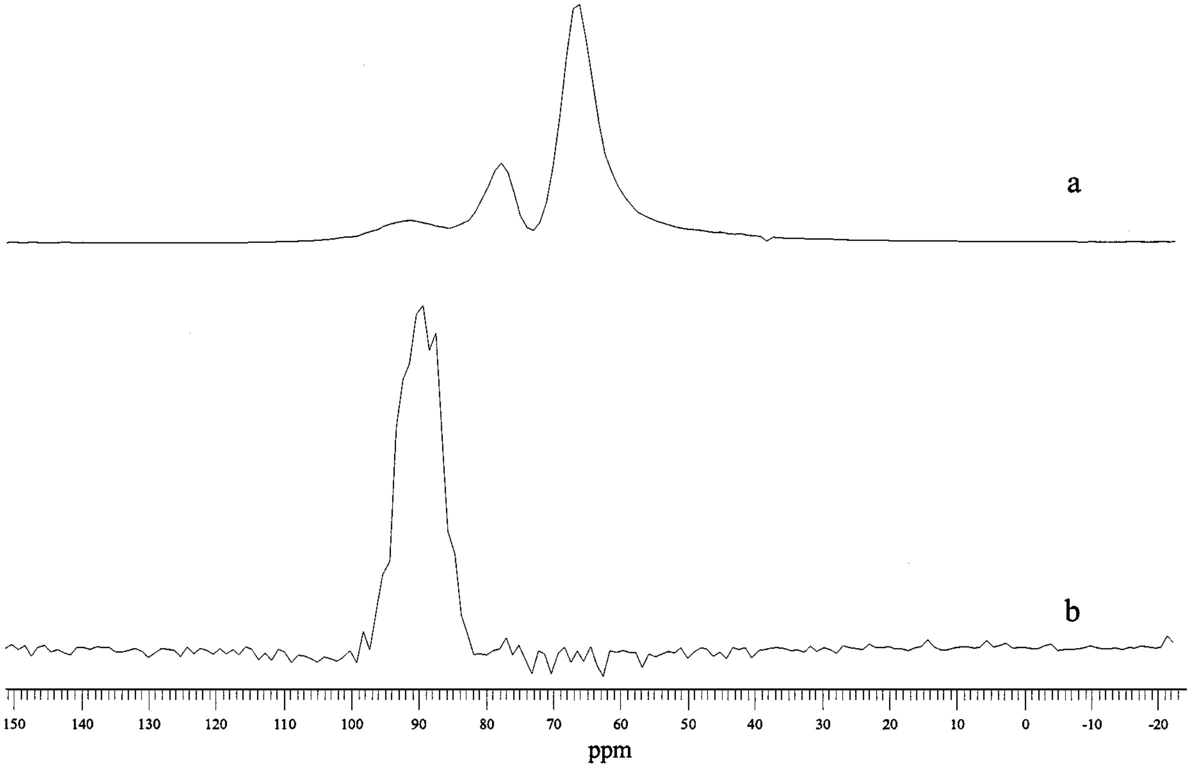

FIG. 7. ^{31}P-MAS-NMR of (a) the homogeneous CODRhDuphos complex and (b) CODRhDuphos immobilized on Al-MCM-41.

to the homogeneous complex. This shift can be attributed to an interaction of the guest complex with the surface of the Al-MCM-41 host, especially due to the interaction with a Lewis acidic center on the surface which withdraws electron density from the rhodium metal or the phosphine ligand.

Among the catalysts presented here, the rhodium complex is formed by a chiral diphosphine and a cyclooctadiene ligand. Several forces could involved in the bonding of the complex on Al-MCM-41. Electrostatic interaction of the cationic complexes occurs with the anionic framework of the Al-MCM-41 structure. A similar mechanism was reported for the immobilization of manganese complexes on Al-MCM-41 (20). Direct bridging of the rhodium to surface oxygen of the mesoporous walls has also been observed and could occur after cleavage of the diene complex during the hydrogenation reaction (22). However, no evolution of cyclooctadiene during the immobilization reaction is observed. The FT-IR spectra of the filtrate obtained after the impregnation show no excess of free cyclooctadiene.

Catalytic Tests

Several diphosphine ligands have been applied and the corresponding complexes have been tested for the immobilization. Those new catalysts are used in the enantioselective hydrogenation (Fig. 8). As a test reaction for the catalytic activity the hydrogenation of dimethylitaconate was employed. No reaction took place in the blank test when the carrier Al-MCM-41 itself was used as catalyst. The catalytic results of the immobilized rhodium complexes are depicted in Table 2. The *S*,*S*-Me-Duphos ligand reaches the best results with 92% ee at 100% conversion of dimethyl (*R*)-methylsuccinate. In this single batch reaction the substrate/rhodium ratio is 4000, resulting in a turnover number of 4000 for the immobilized Me-Duphos-rhodium complex. However, this catalysts could be recycled at least four times without any loss in activity (see Fig. 9); i.e., the TON is >16,000. The corresponding supported catalysts with *R*,*R*-Diop and *S*,*S*-Chiraphos ligands lead to enantioselectivities of 34% ee and 47% ee with lower activities. With the (+)-Norphos ligand the favored enantiomer is dimethyl (*S*)-succinate which is formed with 48% ee.

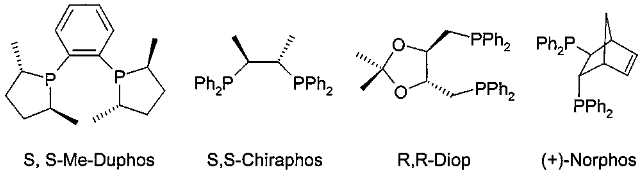

FIG. 8. Diphosphine ligands in the rhodium complexes.

TABLE 2

The Catalytic Activity and Enantioselectivity of Immobilized Rhodium Diphosphine Complexes in the Hydrogenation of Dimethylitaconate

Immobilized complex, used ligand	Conversion (%)	TON	ee (%)
S,*S*-Me-Duphos	100	>4000	92 (*R*)
R,*R*-Diop	57	2280	35 (*R*)
S,*S*-Chiraphos	8	320	47 (*R*)
(+)-Norphos	16	640	48 (*S*)

The catalyst can easily be recovered and reused without further treatment. The supported Rh-Me-Duphos catalyst was recycled four times. The conversion and the enantioselectivity of the catalyst remain at high levels after those runs (Fig. 9). After 8 to 10 consecutive runs a decrease in catalytic performance was observed. This phenomenon goes along with the formation of lumps of the catalyst. Organic deposits like polymerization products of the substrate lead to such a deactivation. However, they could not be identified by spectroscopic analysis.

In order to prove that the reaction is catalyzed heterogeneously and to exclude the possibility of leaching and homogeneous catalysis, the reaction mixture was separated from the catalyst before complete conversion occurs. This test is also known as the hot filtration test. Hydrogenation of the reaction solution following filtration after 3.5 h does not give any further reaction. After 24 h the conversion of the filtered sample remains at 14% whereas the original batch with catalyst goes to complete conversion of 100% (Fig. 10). This test proves that no homogeneous catalysis took place. ICP-AES analysis of the filtered reaction solution showed traces of rhodium, phosphorus, silicon, and aluminum. The relative amounts of this analysis correspond

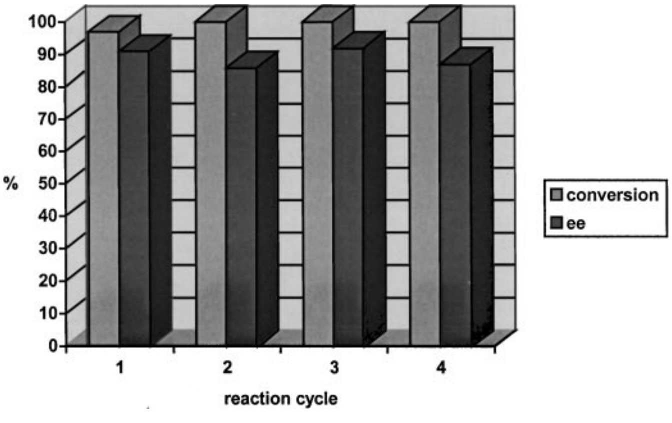

FIG. 9. The catalytic activity and enantioselectivity of immobilized CODRhDuphos complex during the recycling in the hydrogenation of dimethylitaconate.

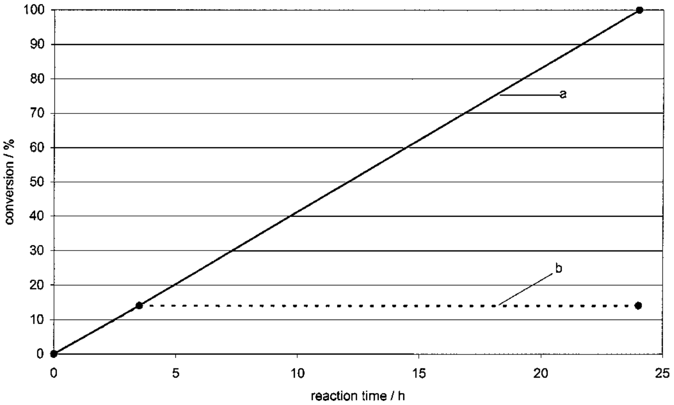

FIG. 10. Hot filtration test: (a) reaction after 24 h in the presence of immobilized CODRhDuphos; (b) reaction after catalyst has been separated after 3.5 h, the reaction does not proceed.

to the composition of the heterogeneous catalyst used. This indicates that this loss occurs by attrition of the Al-MCM-41 and not by leaching of the complex.

4. CONCLUSION

Chiral heterogeneous catalysts are prepared from chiral rhodium diphosphine complexes and Al-MCM-41. The bonding forces could be due to the ionic interaction of the cationic complex with the anionic host framework. A reduction of the weak acidic sites of Al-MCM-41 has also been observed.

These catalysts are suitable for the hydrogenation of functionalized olefins. The organometallic complexes remain stable within the mesopores of the carrier under the reaction conditions. The catalyst can be recycled by filtration or centrifugation and no leaching of the homogeneous complex was observed.

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