

Letter

Combining the advantages of homogeneous and heterogeneous catalysis: rhodium complex on functionalized MCM-41 for the hydrogenation of arenes

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Abstract

Functionalization of MCM-41 via the reaction of its surface silanols with proper agents yielded aminated and phosphinated materials, which were characterized and used to immobilize rhodium complex. These rhodium complex materials exhibited excellent performance in the hydrogenation of arenes under mild reaction conditions of 45°C and 1 atm. © 2001 Elsevier Science B.V. All rights reserved.

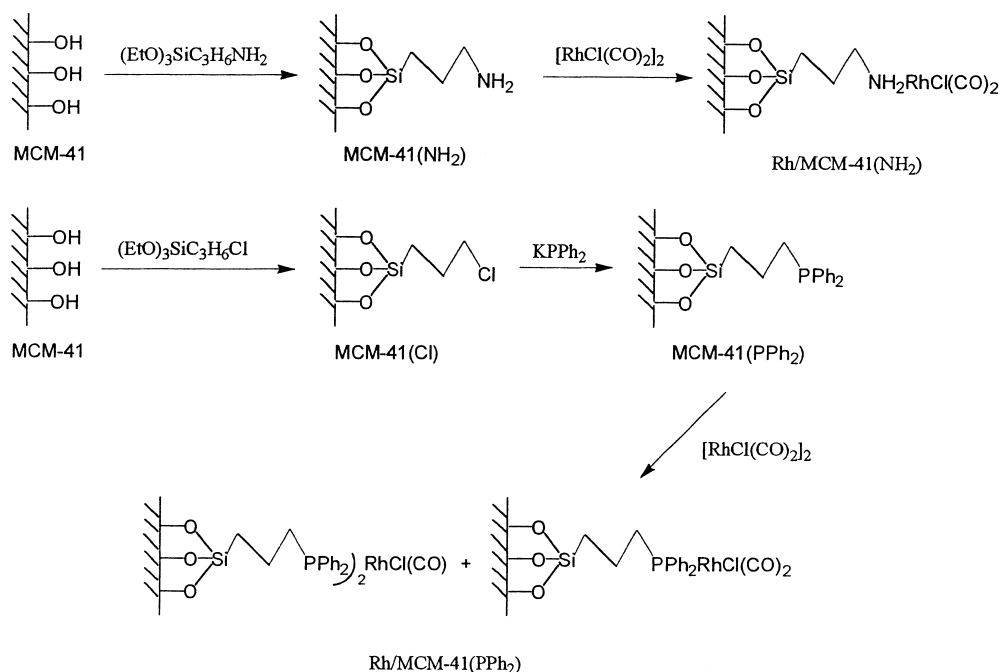
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Homogeneous transition metal complex catalysts are known to exhibit high activity and selectivity at relatively mild conditions giving few by-products, but the shortcoming of these catalysts is the obvious need for separating the catalytic species from the reaction mixtures that is usually critical for an industrial-scale process. Therefore, much attention has been focused on developing the catalysts which combine the practical advantages of conventional heterogeneous catalysts with the versatility of homogeneous transition metal ones [1]. This may be achieved by preparing a suitable transition metal complex in which one or more of ligands covalently bond to the surface of a solid support. MCM-41, a mesoporous material with a narrow pore size distribution (1.5–10 nm) and high

surface area (up to 1000 m²/g), provides great opportunities for immobilization of large catalytic species and catalytic conversion of bulky organic substrates [2]. To date, a few metal complexes on functionalized MCM-41 support have been prepared and used in organic reactions [3–10]. Continuing our efforts in synthesizing and improving the hydrothermal stability of mesoporous materials and in investigating their applications [11–14], in this study, we delineate the first immobilization of [Rh(CO)₂Cl]₂ on aminated and phosphinated MCM-41 supports, together with characterization and catalytic reactivity of these catalysts.

As shown in Scheme 1, the functionalized MCM-41 supports, MCM-41(NH₂) and MCM-41(PPh₂), were prepared from the reactions between MCM-41 and the corresponding alkoxy-silyl agents. The XRD analysis indicated that, in addition to an intense diffraction peak (100), two higher order peaks with lower intensities

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Scheme 1.

were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41. The nitrogen adsorption studies demonstrated that a significant decrease in pore size by virtue of silylation of the MCM-41 channels was observed. Additionally, upon modification the surface area and pore volume decreased obviously. These results are in good agreement with the fact that the surface modification indeed occurred inside the primary mesopores of the MCM-41.

The ligands grafted on MCM-41 support exhibited powerful complexation ability to transition metals. Treatment of MCM-41(NH₂) and MCM-41(PPh₂) with [RhCl(CO)₂]₂ in *n*-heptane produced two strongly colored materials Rh/MCM-41(NH₂) (1.6% Rh) (yellow) and Rh/MCM-41(PPh₂) (2.0% Rh) (brown), respectively (Scheme 1). It needs to note that there is no significant color change observed when the unmodified MCM-41 was directly treated with [RhCl(CO)₂]₂ under identical conditions. Thus, the change in color after immobilization is by itself a good indication that the rhodium metal is indeed coordinated by the grafted ligands. The IR spectra

of the rhodium complex functionalized materials can render additional evidence of ligand complexation. For example, the band of amino group at 1604 cm⁻¹ shifted to higher frequency (1613 cm⁻¹), while the -CH₂- deformation band at 1420 cm⁻¹ moved to low wavenumber (1411 cm⁻¹). Furthermore, the carbonyl signals provide crucial structural information concerning the surface species. Accordingly, the carbonyl peaks observed for Rh/MCM-41(NH₂) at 2090 and 2013 cm⁻¹ are attributed to geminal vibration mode of [Rh(CO)₂]. It has been documented that the reaction of [RhCl(CO)₂]₂ with nitrogen donor ligands generally leads to a splitting of the halide bridge [15]. The infrared evidence of ν(CO) is consistent with this reaction taking place with the aminated MCM-41 support. In the case of Rh/MCM-41(PPh₂), the reaction of [RhCl(CO)₂]₂ with the grafted phosphine ligands was found to be more complicated; the infrared spectrum of this sample exhibited an intense peak at 2003 cm⁻¹ with a smaller peak at 2081 cm⁻¹, suggesting the presence of at least two distinct types of surface species. We infer that two typical reactions occurred between [RhCl(CO)₂]₂ and the phosphines:

Table 1
Hydrogenation of arenes over Rh/MCM-41(NH₂) and Rh/MCM-41(PPh₂) catalysts^a

Substrate	TO ^b for Rh/MCM-41(NH ₂) mol H ₂ (mol Rh) ⁻¹	TO ^b for Rh/MCM-41(PPh ₂) mol H ₂ (mol Rh) ⁻¹	Product ^c
Benzene	130 (22 h)	288 (20 h)	Cyclohexane
Toluene	121 (19 h)	278 (17 h)	Methylcyclohexane
<i>p</i> -Xylene	42 (45 h)	63 (21 h)	1,4-Dimethylcyclohexane
Mesitylene	37 (66 h)	34 (46 h)	1,3,5-Trimethylcyclohexane

^a Reaction conditions: 100 mg of catalyst; 2.0 ml of substrate; 10 ml of ethanol solvent; 45°C and 1 atm of hydrogen.

^b Turnover number corresponds to the reaction time in parentheses.

^c The products were identified by GC.

substitution of a carbonyl as well as splitting of the halide bridge. It should be noted that both rhodium complex functionalized samples are essentially stable; IR spectra showed no apparent change in their carbonyl bands during several weeks of storage in air at room temperature.

The rhodium complex functionalized materials, Rh/MCM-41(NH₂) and Rh/MCM-41(PPh₂), were employed as catalysts in the hydrogenation of arenes under the conditions of 45°C and 1 atm. The rates of hydrogenation reactions in the presence of the catalysts were determined and calculated by following the rate of hydrogen uptake. The reaction results are given in Table 1. It can be seen that the Rh/MCM-41(PPh₂) catalyst is much more active than the Rh/MCM-41(NH₂) catalyst towards all substrates. The hydrogenation of arenes leads to the quantitative formation of corresponding cyclohexane derivatives: no GC or NMR evidence was found for the presence of hydrogenolyzed, cracked or partially reduced products. An increasing number of methyl substituents on the aromatic nucleus in the series of reactants studied (i.e. toluene, *p*-xylene and mesitylene) leads to a decrease of the catalytic turnover number. Additionally,

several hours (ca. 5 h) were in general needed to activate the two catalysts to reach their best performance level. During the activation period, the color change from yellow to light brown (Rh/MCM-41(NH₂)) or from brown to deep brown (Rh/MCM-41(PPh₂)) was evidently observed. The durability of the two catalysts was tested for four successive hydrogenations of toluene in the following way. After a catalytic run, the solid catalyst particles were collected by filtration and then used as a catalyst in the next cycle of hydrogenation. As shown in Table 2, both catalysts exhibited higher activity in the second cycle than in the first. After the second run, the activity gradually decreased, but it was still comparable to that in the first cycle. Since the catalysts could lose catalytically active species into the organic phase, the toluene hydrogenation reaction was attempted in the absence of the catalysts, using the filtrate at conditions identical to those above; no further hydrogen assumption was observed. To the same filtered solution, cyclohexene, a more active substrate, was added and the hydrogenation reaction was performed in a Parr reactor under the conditions of 10 atm and 80°C; gas chromatography analysis revealed that there was no

Table 2
Durability of Rh/MCM-41(NH₂) and Rh/MCM-41(PPh₂) in the hydrogenation of toluene^a

Reaction cycle	TO ^b for Rh/MCM-41(NH ₂) mol H ₂ (mol Rh) ⁻¹	TO ^b for Rh/MCM-41(PPh ₂) mol H ₂ (mol Rh) ⁻¹
1st	121 (19 h)	278 (17 h)
2nd	145 (19 h)	306 (17 h)
3rd	118 (19 h)	264 (17 h)
4th	109 (19 h)	246 (17 h)

^a Reaction conditions are given in footnote a of Table 1.

^b Turnover number corresponds to the reaction time in parentheses.

hydrogenation reaction product detected. These results unambiguously show that catalytically active rhodium species is not leached from the solid catalyst phase under hydrogenation conditions.

After the catalysts were used for the hydrogenation of toluene for 24 h, IR analysis showed that all $\nu(\text{CO})$ bands almost disappeared. This phenomenon is in good agreement with the presence of induction period for both catalysts: several hours are required to convert the rhodium complexes to active species with high catalytic performance in the hydrogenation reactions. It should be noted, however, that the bands corresponding to the grafted amine and phosphine ligands were still clearly recorded. Additionally, elemental analysis by ICP revealed that no rhodium species was detected from the filtrate. These results indicate that both the rhodium–amine and the rhodium–phosphine complexes on MCM-41 support appear to essentially retain their structures even after extended use.

Catalytic hydrogenation reactions must in general operate under pressurized hydrogen atmosphere (≥ 10 atm), particularly for the substrates of arenes [16]. Only a few homogeneous catalysts were found to be active using one atmosphere of hydrogen, but their activities were quite low [17]. In this experiment, both catalysts, Rh/MCM-41(NH_2) and Rh/MCM-41(PPh_2), exhibited excellent performance in the hydrogenation of arenes under mild reaction conditions (45°C and 1 atm). We deduce that such performance can be rationalized by noting that (1) all rhodium centers are molecularly dispersed on the surface of the functionalized MCM-41 support, (2) as a catalytic site, each active rhodium center would be in principle effective, (3) the unique high surface area and big pore size of the MCM-41 support present maximum access to reactant molecules. Investigation on a comparison of these catalysts with Rh/functionalized SiO_2 in the hydrogenation of arenes

(including several bulky substrates) as well as studies on the oxidative state of rhodium and the state of ligands of rhodium complex on MCM-41 support during the hydrogenation reactions are currently in progress.

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References

- [1] F.T. Hartley, Supported Metal Complexes, Reidel, Dordrecht, 1985.
- [2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [3] C. Hubber, K. Moller, T. Bein, *Chem. Commun.* (1994) 2619.
- [4] R. Burch, N. Cruise, D. Gleeson, S.T. Tsang, *Chem. Commun.* (1996) 951.
- [5] P. Sutra, D. Brunel, *Chem. Commun.* (1996) 2485.
- [6] C.J. Liu, S.G. Li, W.Q. Pang, C.M. Che, *Chem. Commun.* (1997) 65.
- [7] S. Ernst, M. Selle, *Micropor. Mesopor. Mater.* 27 (1999) 355.
- [8] N. Bellocq, S. Abramson, M. Lasperas, D. Brunel, P. Moreau, *Tetrahedron: Asymm.* 10 (1999) 3229.
- [9] S.G. Shyu, S.W. Cheng, D.L. Tzou, *Chem. Commun.* (1999) 2337.
- [10] J.M. Thomas, T. Maschmeyer, B.F.G. Johnson, D.S. Shepard, *J. Mol. Catal. A: Chem.* 141 (1999) 139.
- [11] S. Kawi, M.W. Lai, *Chem. Commun.* (1998) 1407.
- [12] S.C. Shen, S. Kawi, *J. Phys. Chem. B* 103 (1999) 8870.
- [13] G.J. Li, S. Kawi, *Sens. Actuators B: Chem.* 59 (1999) 1.
- [14] A.M. Liu, K. Hidajat, S. Kawi, *Chem. Commun.* (2000) 1145.
- [15] L.D. Rollman, *Inorg. Chim. Acta* 6 (1972) 137.
- [16] E.G. Fidalgo, L. Plasseraud, G.S. Fink, *J. Mol. Catal. A: Chem.* 132 (1998) 5.
- [17] J. Blum, I. Amer, A. Zoran, Y. Sasson, *Tetrahedron Lett.* 24 (1983) 4139.