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ScienceDirect

Catalysis Today 121 (2007) 130–139

CATALYSIS TODAY

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Enantioselective hydrogenation over immobilized rhodium diphosphine complexes on mesostructured materials

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Abstract

New heterogeneous chiral catalysts were prepared from rhodium diphosphine complexes [Rh(P–P)COD]Cl ((P–P) = diphosphine ligand and COD = cyclooctadiene), and Al–MCM-41, Al–MCM-48, and Al–SBA-15, respectively. Impregnation of the mesoporous Al–MCM-41, Al–MCM-48, and Al–SBA-15 with the organometallic complexes in dichloromethane led to strongly bonded hydrogenation catalysts. The catalysts were characterised with XRD, FT-IR and MAS-NMR, as well as thermoprogrammed desorption of ammonia, thermogravimetric analysis, and nitrogen sorption experiments. The hydrogenation of dimethyl itaconate, methyl α-acetamidoacrylate, and methyl α-acetamidocinnamate were studied as test reactions. The immobilized catalysts showed high activities and excellent chemo- and enantioselectivities. Up to 98% e.e., >99% conversion and 99% selectivity were observed in the case of studied prochiral olefins. The catalysts could be reused without a loss of catalytic activity. Leaching of the homogeneous complex out of the mesoporous framework was not observed.

Keywords: Immobilization; Rhodium; Diphosphine; Al–MCM-41; Al–MCM-48; Al–SBA-15; Asymmetric; Hydrogenation

1. Introduction

Chiral synthesis has received much attention because of the rapid growth of the pharmaceutical and agrochemical market in the last decades [1–3]. For economic, environmental, and social reasons, the trend towards the application of optically active compounds is undoubtedly increasing. Among the various methods for selective production of single enantiomers, asymmetric catalysis is the most attractive method from the atom economic point of view [4,5]. Homogeneous asymmetric catalysis has made tremendous progress over the last decades and is well recognized in this field. This fact has also been expressed by dedicating the Nobel Prize Award for chemistry in 2001 to Noyori, Sharpless and Knowles [6].

Transition metal catalyzed reactions are among the most efficient routes to obtain compounds with high enantiomeric purities. Especially hydrogenations are of particular industrial relevance because of the high efficiencies that can be obtained with a relatively small environmental impact [5]. Among others, complexes of rhodium, ruthenium, and more recently iridium, have been used successfully for catalytic asymmetric hydrogenations of prochiral olefins [4,7,8]. The use of an iridium complex as hydrogenation catalyst in the critical synthesis step for the preparation of grass herbicide ‘‘Metolachlor’’ shows that the use of these catalysts is not limited to the laboratory scale [9].

Rhodium based complexes have long been investigated in asymmetric hydrogenations, achieving high reaction rates and excellent enantioselectivities under optimized reaction conditions [10,11]. Among these ligands, chiral diphosphines are known to perform excellent results in this type of reaction for more than 30 years [12,13]. However, homogeneous asymmetric catalysts are not used to their full extent, which for a large part is due to problems in separation and recycling of the expensive chiral catalysts. Although these problems can be ignored on a small lab scale, they are of a decisive importance for the economical and technological viability of a large scale production. Furthermore, even if the activity and selectivity of homogeneous catalysts is exceptionally high, toxicological and environmental problems should also be taken into account.

Since the late 1970s, many approaches have been published by academic and industrial researchers to ‘‘heterogenize’’,

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0920-5861/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.cattod.2006.11.023

"immobilize" or "anchor" homogeneous catalysts on solid supports [14–16]. Many excellent reviews have emerged in recent years, which describe in detail the synthesis and use of polymer-supported catalysts [17,18] and catalysts on inorganic carriers [19–21], or both [22–24]. However, the catalytic properties of these immobilized catalysts have shown an enormous variation and in many cases were significantly below those of the homogeneous analogues. Since the reasons for these differences in performance are usually not understood, it is still of interest to test different immobilization methods and supports in order to get a systematic picture of positive and negative effects.

Mesoporous molecular sieves have received much attention in the field of catalysis, especially for their use as supports. Ion exchange, catalytic and adsorptive properties of molecular sieve materials are based on the existence of acid sites which arise from the presence of accessible hydroxyl groups associated with tetrahedral framework aluminum in a silica framework. Our research was focused on the use of M41S and SBA-15 type materials as carriers, which are characterized by a well defined pore structure and high surface area, offering new opportunities for the immobilization of large homogeneous catalyst species without any modification of their chemical structure [25–29]. MCM-48 has been investigated to a lesser extent even though it should be more applicable as a catalyst or adsorbent due to its three-dimensional pore architecture. The recently discovered pure silica phase, designed SBA-15, has long range order, large monodispersed mesopores (up to 50 nm) and thicker walls (typically between 3 and 9 nm) which make it more thermally and hydrothermally stable than the M41S type materials. Unfortunately, as the pure silica SBA-15 is synthesized in strong acid media (2 M HCl solution), incorporation of framework aluminum into SBA-15 by direct synthesis seems to be impossible because most aluminum sources dissolve in strong acids. Previous studies have shown that aluminum can be effectively incorporated into siliceous SBA-15 via various post synthesis procedures, e.g. by grafting aluminum onto SBA-15 wall surfaces with anhydrous $AlCl_3$ or aluminum isopropoxide in nonaqueous solutions, or sodium aluminate in aqueous solutions followed by calcination [30,31].

Herein, we present a very straightforward way for the immobilization of rhodium diphosphine complexes. This heterogenization is based on an ionic interaction between the negatively charged Al–M41S or Al–SBA-15 framework and the cationic rhodium of the organometallic complex. Furthermore, activity of the obtained catalysts in the enantioselective hydrogenation of different prochiral olefins was investigated.

2. Experimental

It is well known that Rh-complexes containing diphosphines are very sensitive to moisture and oxygen. Phosphines can be easily oxidized under such conditions, and then loose their catalytic activity. Considering these reasons, all the experiments involving diphosphines, rhodium diphosphine complexes and immobilized complexes were carried out in argon filled Mbraun LabStar glovebox or using standard Schlenk-type techniques. In order to remove all adsorbed water molecules, the solid supports were calcined overnight at 300 °C prior to the immobilization of organometallic complexes. Moreover, all used solvents were dried and degassed using well-known standard methods.

2.1. Preparation of the mesostructured materials

Al–MCM-41 was prepared according to a slightly altered method reported by van Hooff [32]. In a 250 mL PE flask, 10.5 g tetraethylammonium hydroxide (TEAOH, 40 wt.%, aqueous), 0.21 g $NaAlO_2$ and 50 g H_2O were mixed together and stirred at room temperature for 1 h, followed by the addition of 10 g tetradecyltrimethylammonium bromide. The resulting mixture was stirred for 4 h. Then, 15.23 g Ludox-HS 40 were added dropwise over a period of 1 h, followed by vigorous stirring at ambient temperature for 4 h. The crystallisation took place at 105 °C for 6 days. After the third and fifth day, pH was adjusted at 10.2 using CH_3COOH (10 wt.%, aqueous). After crystallisation, the solid phase was recovered by filtration and well washed with water. The white material was dried at 120 °C overnight, followed by calcination in static air at 540 °C for 6 h (heating rate 1 °C/min).

Al–MCM-48 was prepared as follows: in a 500 mL PE flask, TEAOH (40 wt.%, aqueous), $NaAlO_2$ and water were stirred at room temperature for 1 h, followed by the addition of cetyltrimethylammonium bromide. Then, Ludox HS-40 was added dropwise over a period of 1 h, followed by vigorous stirring for 4 h. The molar composition of the gel was as follows: Si/Al = 40, TEAOH/Si = 0.3, surfactant/Si = 0.45 and water/Si = 60. The crystallization was performed at 120 °C for 8 days using a Teflon lined autoclave. After the second, fourth and sixth day, pH was adjusted at 10.8 using CH_3COOH (10 wt.%, aqueous). The final solid reaction product was extracted from the autoclave, filtered, washed with distilled water and dried at 120 °C overnight. Finally, the solid was calcined at 540 °C for 6 h (heating rate 1 °C/min).

For SBA-15 synthesis, 20 g of amphiphilic triblock copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (average molecular weight 5800, Aldrich), was dispersed in 150 g of water and 600 g of 2 M HCl solution while stirring, followed by the addition of 42 g of tetraethyl orthosilicate to the homogeneous solution with stirring. This gel mixture was continuously stirred at 40 °C for 6 h, and finally crystallized in a Teflon-lined autoclave at 90 °C for 3 days. After crystallization the solid product was filtered, washed with deionized water, and dried in air at room temperature. The material was calcined in static air at 550 °C for 24 h to decompose the triblock copolymer and obtain a white powder (SBA-15) [27]. This white powder is used as the parent material to produce aluminum-containing material denoted as Al–SBA-15.

Silica SBA-15 (10 g, 166.5 mmol Si) was dispersed in 250 mL of dry hexane containing 0.85 g (4.1 mmol Al) aluminum isopropoxide. The resulting suspension was stirred at room temperature for 24 h, and afterwards the powder was filtered, washed with dry hexane, and dried at 120 °C in air. This solid Al–SBA-15 was then calcined in static air at 550 °C for 6 h (heating rate 1 °C/min) [30].