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Asymmetric Hydrogenation of Ethyl Pyruvate using Layered Double Hydroxides–Supported Nano Noble Metal Catalysts

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Abstract: Layered double hydroxide (LDH)–supported nano noble metal heterogeneous catalysts are synthesized by ion exchange of K_2PtCl_6, Na_2PdCl_4 and impregnation of $RhCl_33H_2O$ followed by reduction with H_2. The LDH–Rh, Pt, and Pd catalysts are tested in the enantioselective hydrogenation of ethyl pyruvate to ethyl lactate with very good yields and enantiomeric excess's (e.e.'s) of up to 72% were obtained with Pt. The catalyst was recovered and reused for several cycles with consistent activity.

Keywords: Cinchonidine, enantioselective hydrogenation, ethyl pyruvate, ethyl lactate LDH–Pt, Rh, Pd nano particles

INTRODUCTION

Asymmetric synthesis is one of the most elegant strategies for the synthesis of drugs, agrochemicals, and fragrances/flavors. Homogeneous transition-metal complexes with chiral ligands are the most versatile and efficient catalysts.[1a,b] However, for industrial processes, heterogeneous catalysts are preferred because they can be easily separated and reused. In recent years,

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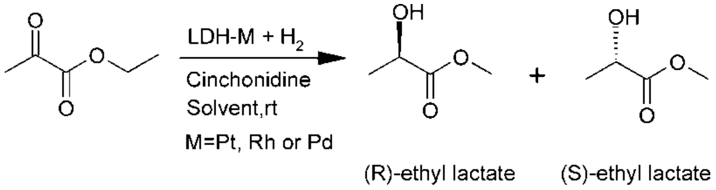
heterogeneous asymmetric catalysts are playing an important and crucial role in the development of new chemical processes.[2] Asymmetric hydrogenation of α-ketoesters was reported two decades ago by Orito et al.,[3] in which cinchona alkaloid–modified platinum was used for enantioselective hydrogenation of ethyl pyruvate to ethyl lactate. Later, Blaser et al.,[4a–d] Margitfaivi et al.,[5] Sutherland et al.,[6] Augustine et al.,[7] and Torok et al.[8] have investigated this reaction. The highest enantiomeric excess (e.e. 95–97%) was obtained under optimum reaction conditions using the supported Pt/cinchonidine systems.[4,8] As far as the properties of the supported platinum catalysts are concerned, proper platinum dispersion, the type of support material, and pore size distribution are very important. Suitable supports such as alumina, silica, and zeolites have been studied. Collier et al.[9] have investigated the enantioselective hydrogenation of ethyl pyruvate by solvent-stabilized nanoparticles of Pt and Pd prepared by metal vapor synthesis. Recently enantioselective hydrogenation of ethyl pyruvate was reported by supported Rh nanoclusters stabilized by polyvinylpyrrolidene (PVP) with cinchonidine as chiral modifier.[10] The utilization of other transition metals, such as Ru, Rh, Pd, and Ir, to replace Pt resulted in lower enantioselectivity.[9–11]

Layered double hydroxides (LDHs), a new class of basic mixed hydroxides, have recently received much attention in view of their potential usefulness as materials, anion exchangers, and more importantly as catalysts.[12] The LDHs consist of alternating cationic $M^{(II)(1-x)}M^{(III)x}(OH)_2^{x+}$ and anionic $A^{n-} \cdot ZH_2O$ layers. The positively charged layers contain edge-shared metal $M^{(II)}$ and $M^{(III)}$ hydroxide octahedral, with charges neutralized by A^{n-} anions located in the interlayer spacing or at the edges of the lamellae.

Recently we have reported LDH-supported nanopalladium catalyst for Heck, Suzuki, Sonigashira, and Stille-type coupling reactions.[13] In continuation of our work on LDHs, herein we report the catalytic performance of supported LDH–Rh, Pt, and Pd nanoparticles in the enantioselective hydrogenation of ethyl pyruvate using cinchona alkaloid as chiral modifier (Scheme 1). The effect of some reaction parameters on the enantioselectivities and catalytic activities have been studied in detail.



Scheme 1. Asymmetric hydrogenation of ethyl pyruvate.

RESULTS AND DISCUSSION

In asymmetric synthesis, the enantioselectivity is very sensitive to the solvent. Asymmetric hydrogenation of ethyl pyruvate is catalyzed by LDH–M (M = Rh, Pt or Pd)/cinchonidine system. The enantioselectivity data in Table 1 clearly indicates that among the solvents investigated, THF is the best solvent with e.e. values 72, 70, and 68 for LDH–Pt, LDH–Rh, and LDH–Pd, respectively. A similar effect was observed in the hydrogenation of ethyl pyruvate using finely dispersed oxide-supported rhodium nanoclusters with cinchonidine.[10] With LDH–Rh catalyst and cinchonidine modifier in acetic acid as solvent, complete conversion of ethyl pyruvate to ethyl lactate with 80% e.e. is observed, but the main drawback with this system is leaching of the metal from the support. All the catalysts are recyclable, and consistent activity is observed for three cycles.

During the enantioselective hydrogenation of ethyl pyruvate to ethyl lactate catalyzed by LDH–Rh, LDH–Pt, and LDH–Pd, cinchonidine not only functions as a chiral modifier that modifies ethyl pyruvate into (R)-ethyl lactate but also accelerates the reaction rate. Initially the e.e.'s increase with an increase in cinchonidine, but on further increase there is a decrease of enantioselectivity. The decrease in e.e. when the concentration of cinchonidine is high is due to the side reaction of cinchonidine during the conversion of ethyl pyruvate to ethyl lactate. Also some cinchonidine was getting hydrogenated, resulting in the decrease in enantioselectivity.[14] First the C-C double bond in the quinuclidine part of cinchonidine is hydrogenated followed by the hydrogenation of the aromatic ring, which causes a drop in enantioselectivity by decreasing the efficiency of the chiral modifier and also because of the blocking of some active sites on the surface of the metal at higher concentration of modifier.[4a]

Table 1. Effect of solvent on the enantioselective hydrogenation of ethyl pyruvate to ethyl lactate

Catalyst	Solvent	Time (h)	Conversion (%)	e.e. (%)
LDH–Pt	THF	6	100	72
	Methanol	6	100	65
	Toluene	6	100	57
LDH–Rh	THF	6	100	70
	Methanol	6	100	60
	Toluene	6	100	55
LDH–Pd	THF	6	100	68
	Methanol	6	100	50
	Toluene	6	100	45

Notes. Reaction conditions: Substrate (8.6 mmol), catalyst (50 mg), solvent (15 mL), room temp., H_2 pressure (70 bar). e.e.'s based on HPLC yields.

In summary, the LDH–Pt, LDH–Rh, and LDH–Pd catalysts developed by the simple ion exchange or impregnation technique followed by reduction are used for the asymmetric hydrogenation of ethyl pyruvate to ethyl lactate. The best result is obtained with LDH–Pt with e.e.'s up to 72%. The catalysts were reused for three cycles with consistent activity.

EXPERIMENTAL

Ethyl pyruvate was used as received from Fluka. $AlCl_3 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ were purchased from Aldrich. $RhCl_3 \cdot 3H_2O$ was purchased from Degussa Corporation, K_2PtCl_6 and Na_2PdCl_4 were purchased from Loba chemicals, and all the other chemicals were procured from local commercial sources and used as such without further purification. All the solvents procured from commercial sources were distilled before use.

General Procedure for the Preparation of LDH (Mg-Al-Cl) Support

The preparation of LDH (Mg–Al–Cl) was based on the literature procedure.[15] A mixture of $MgCl_2 \cdot 6H_2O$ (30.49 g, 0.15 mol) and $AlCl_3 \cdot 6H_2O$ (12.07 g, 0.05 mol) was dissolved in 200 ml of decarbonated and deionized water. To this aqueous solution 100 ml of sodium hydroxide (2 M) solution at 25°C was slowly added, and a further amount of 2 M NaOH solution was added to maintain a pH of 10 under nitrogen flow. The resultant suspension was stirred overnight at 70°C. The solid product was isolated by filtration, washed thoroughly with deionized water, and dried overnight at 80°C.

General Procedure for the Preparation of LDH–Pt and LDH–Pd Catalysts

LDH–Pt and LDH–Pd catalysts were prepared by the ion exchange method. K_2PtCl_6 (0.200 g, 0.4115 mmol) and Na_2PdCl_4 (0.200 g, 0.8223 mmol) were dissolved separately in 50 ml of deionized water. To these aqueous solutions, 1 g of LDH (Mg–Al–Cl) was added and stirred overnight at room temperature under a nitrogen atmosphere. The solid catalyst was filtered and washed thoroughly with 500 ml of deionized water, dried at 80°C overnight, and finally reduced with hydrogen. The platinum content in the LDH–Pt catalyst was 0.6 wt.%, and the Pd content in the LDH–Pd catalyst was 0.5 wt.% as determined by atomic absorption spectroscopy.

General Procedure for the Preparation of LDH–Rh Catalyst

$RhCl_3 \cdot 3H_2O$ (0.200 g, 0.7601 mmol) was dissolved in 50 ml of deionized water. To this aqueous solution, 1 g of LDH was added, and stirring continued at room temperature overnight under a nitrogen atmosphere. The solid catalyst was filtered and washed with 500 ml of deionized water until the catalyst was free from chloride. The catalyst was dried at 80°C overnight and finally reduced with hydrogen. The Rh content in the LDH–Rh catalyst was 0.8 wt.% as determined by atomic absorption spectroscopy.

General Procedure for the Asymmetric Hydrogenation of Ethyl Pyruvate

The hydrogenation reactions were performed in a 100 ml stainless steel autoclave at room temperature. To 1 g (8.6 mmol) of redistilled ethyl pyruvate in 15 ml of solvent, 6 mg (0.02 mmol) of the chiral modifier, cinchonidine, and 50 mg of the catalyst were added, and the reaction mixture was flushed with hydrogen gas several times before the autoclave was pressurized with hydrogen gas up to 70 bar. The stirring was continued at 1000 rpm and the progress of the reaction was monitored every hour by high-performance liquid chromatography (HPLC).

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