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Magnetically separable Pt catalyst for asymmetric hydrogenation

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ABSTRACT

A magnetic Pt/SiO_2/Fe_3O_4 catalyst consisting of chirally modified platinum supported on silica coated magnetite nanoparticles was prepared using an easy synthetic route and successfully applied for the enantioselective hydrogenation of various activated ketones. The magnetic catalyst modified with cinchonidine showed a catalytic performance (activity, enantioselectivity) in the asymmetric hydrogenation of various activated ketones in toluene comparable to the best known Pt/alumina catalyst used for these reactions. The novel catalyst can be easily separated from the reaction solution by applying an external magnetic field and recycled several times with almost complete retention of activity and enantioselectivity.

1. Introduction

Catalyst separation and recycling are essential steps in catalytic technology and frequently affect the overall process economy. A possible solution to facilitate this step is the use of solid catalysts with magnetic properties which can be efficiently separated from the reaction medium applying an external magnetic field [1–6]. In particular magnetic particles in the nanometer range are superparamagnetic and have therefore exceptional properties, suitable both for catalytic reactions in solution and for magnetic recovery. On the one hand, superparamagnetic particles are intrinsically non-magnetic above the so-called blocking temperature and have therefore no tendency to aggregate in solution allowing optimal mixing conditions for catalytic reactions. On the other hand, these nanoparticles are readily magnetized by an external magnetic field which favors their separation from the reaction solution. The approach of using magnetically recoverable catalysts has been recently followed by supporting a metal catalyst on a magnetic support, for example in decarboxylative coupling [7], olefin epoxidation [8], and hydrogenation reactions [9–11]. In the field of asymmetric hydrogenation reactions, to the best of our knowledge, the only example of magnetic separation is the immobilization of a homogeneous asymmetric ruthenium catalyst on magnetic nanoparticles [12]. In this approach the precious catalyst, which is active in the hydrogenation of aromatic ketones, was chemically bound to magnetic SiO_2/Fe_3O_4 nanoparticles, and thus separated and reused after the reaction.

The present investigation deals with a different approach to asymmetric hydrogenation [13–17]: the well known technique of chiral surface modification by means of cinchona alkaloids is coupled with the use of a magnetic support thus obtaining a truly heterogeneous rather than an immobilized homogeneous-type catalyst. We prepared and structurally characterized a magnetic chirally modified Pt catalyst for the enantioselective hydrogenation of activated ketones and compared its catalytic behavior with that of one of the best known commercial Pt/alumina catalysts applied for this kind of reactions. The recyclability of the novel catalyst was tested by performing several magnetic separations and reactions without further activation of the catalyst.

2. Experimental

2.1. Materials

For the preparation of the catalyst ferric chloride hexahydrate (>99%) and ferrous chloride tetrahydrate (>99%) purchased from Aldrich were used. Sodium silicate powder was purchased from Fisher Scientific AG and platinum (II) acetylacetonate from ABCR. Cinchonidine (CD, ⩾98%) was purchased from Fluka and acetic acid (99.8%) from Acros Organics. Toluene from Fluka (⩾99.7%) was dried over molecular sieve 4A. The substrates α,α,α-trifluoroacetophenone (Fluka, ⩾98%), ethyl pyruvate (Acros Organics, ⩾98%), ketopantolactone (DSM Nutritional Products AG) and

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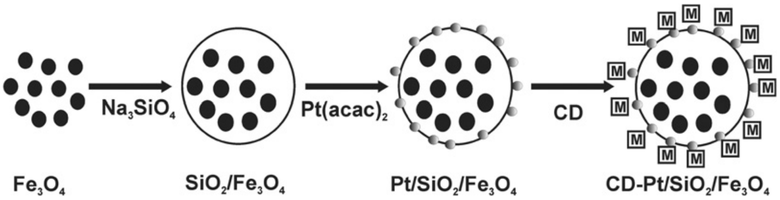

Fig. 1. Preparation of the magnetic, chirally modified Pt/SiO$_2$/Fe$_3$O$_4$ (M represents cinchonidine).

methylbenzoylformate (Acros Organics, 99%) were used without further purification.

2.2. Catalyst preparation

The magnetite nanoparticles were prepared by coprecipitation according to the synthesis reported by Liu et al. [18]: 11.67 g of $FeCl_3 \cdot 6H_2O$ and 4.3 g $FeCl_2 \cdot 4H_2O$ were dissolved in 200 ml of distilled water. The solution was stirred under constant nitrogen gas flow and heated up at 85 °C. Subsequently 15 ml of 25% $NH_3 \cdot H_2O$ were added to the solution which immediately became dark brown indicating the formation of the magnetite particles. The solution was stirred for further 30 min at 85 °C under inert atmosphere. After cooling down to room temperature the magnetic nanoparticles were separated from the water solution. 47.50 g of sodium silicate were dissolved in 400 ml of distilled water and the pH was adjusted to pH = 12–13 using hydrochloric acid. Since the solution was not completely clear the non-dissolved sodium silicate was filtered off. The magnetic particles were added to the silicate solution which was stirred mechanically and heated to 80 °C. The pH of the solution was slowly adjusted to pH = 6–7 by adding dropwise under stirring a solution of 37% HCl dissolved in the same volume of water. The silica coated magnetic nanoparticles were filtered off and the coating procedure was repeated. The Pt/SiO$_2$/Fe$_3$O$_4$ catalyst was prepared by incipient wetting impregnation. 9.4 g of the silica coated magnetite particles were dried in air at 80 °C for 4 h. 1.02 g of platinum (II) acetylacetonate was dissolved in the minimum quantity of toluene necessary for dissolution. The solution was added dropwise to the dried silica coated magnetic nanoparticles under vigorous stirring until the solid had a sticky appearance. Then the solid was dried in air at 100 °C. The procedure was repeated several times. At the end the solid was dried at 100 °C over night and then calcined at 400 °C for approximately 2 h. The solid was then pressed in pellets which were crushed and sieved to obtain particles with a size between 100 µm and 200 µm. The catalyst preparation route is schematically shown in Fig. 1.

A commercial 5 wt% Pt/alumina catalyst (Engelhard 4759) served as a reference for the catalytic tests. Characteristic properties of this catalyst which has been frequently applied in the enantioselective hydrogenation over cinchona-modified platinum have been specified in Refs. [19,20].

2.3. Catalyst characterization

The nitrogen adsorption isotherm of the magnetic catalyst was measured at 77 K with a Micromeritics ASAP 2000 apparatus after degassing the sample at 80 °C in vacuum for 2 h. The multipoint BET specific surface area was obtained in the p/p_0 range of 0.05–0.3.

The XRD pattern of the samples were recorded with a Siemens D5000 powder X-ray diffractometer using Cu $K\alpha$ radiation in the range of $15^\circ < 2\theta < 65^\circ$ and a step size of 0.01°.

The platinum content was determined using a SpectrAA Varian atomic absorption spectrometer after dissolving the supported platinum in aqua regia. Atomic absorption was also applied to determine potential leaching of iron into solution during hydrogenation.

The magnetic measurements were performed with a superconducting quantum interference device (SQUID MPMS-XL) at room temperature and 5 K.

For transmission electron microscopy (TEM), the catalyst material was dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid (Okenshoji Co. Ltd.). The microscope (Tecnai 30F FEI with a field emission cathode, operated at 300 kV) was also equipped with a high angle annular dark-field (HAADF) detector for scanning transmission electron microscopy showing the metal particles with bright contrast (Z contrast). For qualitative analysis, the electron beam was set to selected areas in the scanning transmission electron microscopy (STEM) images and the signal was measured by energy dispersive X-ray spectroscopy (EDXS; detector: EDAX).

Attenuated total reflection–infrared spectroscopy measurements were performed with a home-build stainless steel batch reactor cell equipped with a mechanical stirrer and possessing a ZnSe crystal window at the bottom used as internal reflection element. The cell, which was kept at a constant temperature of 298 K with a thermostat, was mounted on the optical bench of a FT-IR spectrometer (Bruker Optics Equinox 55) equipped with a MCT detector cooled with liquid nitrogen. The ATR-IR spectra were recorded by averaging 100 scans at a resolution of 4 cm^{-1}.

2.4. Hydrogenation reactions

For the enantioselective hydrogenation the catalyst was treated at 250 °C under nitrogen flow for 30 min, followed by reduction at 250 °C in H$_2$ flow for 2 h and cooling down to room temperature in H$_2$ flow. The commercial Pt/Al$_2$O$_3$ catalyst was activated with a standard procedure [19]: heating at 400 °C under N$_2$ flow for 30 min, reduction at the same temperature under H$_2$ flow for 1 h and then cooling to RT in H$_2$. For the reaction at 11 bar, 42 mg of catalyst, 5 ml of toluene, 2 mg of cinchonidine (CD) and 1.85 mM of substrate were stirred at 1000 rpm in a parallel pressure reactor system Endeavor^{TM} with eight mechanically stirred reactors. For recycling the catalyst was magnetically separated and washed twice with toluene and the reaction was repeated under the same conditions as described above. The enantiomeric excess is expressed as $\text{ee}\ (\%) = [|(R-S)|/(R+S)] \cdot 100$ and the error in ee values is calculated as standard deviation of four distinct measurements and corresponds to $\sigma_{\text{ee}} = (1\text{–}3)\%$. The products were identified by GC on a Thermo Finnigan Trace 2000 using a CP-Chirasil-Dex CB capillary column and a FID detector. The high pressure reaction was performed under the same conditions but at 100 bar and in a stainless steel batch reactor equipped with a glass liner.

For conversion and recycling measurements 13 mg of catalyst, 2 mg of CD and 3.7 mM of substrate ketopantolactone (KPL, dihydro-4,4-dimethyl-2,3-furandione) were used. The error bars in this case are calculated as the difference in the values of two distinct measurements.