Catalysis Today 258 (2015) 64–69

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Rh-based catalysts supported on MCM-41-type mesoporous silica for dicyclopentadiene hydroformylation

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ARTICLE INFO

Article history:
Received 10 November 2014
Received in revised form 2 April 2015
Accepted 7 April 2015
Available online 30 April 2015

Keywords:
Dicyclopentadiene
Diformyltricyclodecanes
Hydroformylation
Mesoporous silica

ABSTRACT

Impregnation method was used in this study to prepare five different Rh based catalysts supported on MCM-type mesoporous silica materials. These catalysts were evaluated based on their performance for the hydroformylation of dicyclopentadiene (DCPD) to produce diformyltricyclodecanes (DFTD). While a selectivity of DFTD was only 8.7% using monometallic Rh/MCM-41 as catalyst, the selectivity was enhanced to 76.2% at a similar DCPD conversion using bimetallic Co–Rh/MCM-41 catalyst, even when the Co loading was very low(25 mol% relative to Rh). Extensive catalyst characterization including TPR, TPD, XRD, XPS, BET and TEM was performed to study the nature of metal modification on Rh/MCM-41. It was found that modification on the Rh/MCM-41 by Co addition could substantially enhance the selectivity towards DFTD. This improvement was likely attributed to the formation of a more reactive Rh species on the catalyst surface.

1. Introduction

With a diminishing fossil reservation and increasing demand on materials and transportation fuels, it is widely recognized that replacing fossil feedstock with renewables is a potentially promising solution. However, before the complete replacement, a more practical strategy is to better utilize the existing fossil resources. In this regard, dicyclopentadiene (DCPD), which has been widely produced as a by-product from either the C5 fraction during ethylene cracking process or light benzene fraction from the coal-coking process, is amongst those potentially usable fossil feedstock. Traditionally, applications of DCPD were limited to the synthesis of low-grade resins and additives to transportation fuels. It was reported that a series of value-added fine chemicals such as monoformyltricyclodecenes (MFTD), diformyltricyclodecanes (DFTD), tricyclodecanedimethylol (TDDMeOH) could be derived from DCPD through hydroforrmylation and its subsequent hydrogenation processing [1–4]. Several catalysis using cobalt, rhodium [5], and Co–Rh bimetallic catalysts [6–8], was reported to be capable of catalyzing the hydroformylation of DCPD. In addition, aqueous/organic biphasic catalytic system was also applied to perform the conversion of DCPD to MFTD or DFTD [9,10]. Although much progress has been achieved in homogeneous systems for DCPD hydroformylation, less success was reported regarding the heterogenization of these homogeneous catalysts. It is advantageous to develop processes based on heterogeneous catalysts where the active sites are immobilized on a porous support, contributing to its easy recovery, if comparable activity and selective could be achieved relevant to their homogeneous counterparts [11,12].

Heterogeneous Rh based catalyst has been also developed more than 20 years for the olefins hydroformylation. A multitude of organic polymers and inorganic materials such as SiO_2, Al_2O_3, MgO, ZnO, clays, active carbons and zeolites can be considered for catalyst support [13,14]. Due to the bulky size of DCPD, supports with large pore size are preferred for the desired reaction. Due to their high surface area, relatively large and tunable pore size, and facile surface functionalization properties, mesoporous silica materials are regarded as one of the most attractive catalyst supports, meanwhile, the larger pore size makes shape-selective reactions possible

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http://dx.doi.org/10.1016/j.cattod.2015.04.007
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of larger molecules like cyclic compounds [15–18]. Given the above mentioned reasons, in the current work, we chose MCM41-type mesoporous silica as the support for the hydroformylation of DCPD.

Unfortunately, catalytic activity could not be achieved for DCPD hydroformylation to form DFTD over monometallic Rh/MCM-41 catalyst, which motived us to tackle this challenge and explore a method to obtain an effective Rh based catalyst supported on the MCM-41. To achieve this goal, five types of Rh or Co–Rh bimetallic catalysts supported on MCM-type mesoporous silica materials were prepared by incipient wetness impregnation. These catalysts were evaluated based on their performance for the hydroformylation of DCPD to DFTD. The selectivity of DFTD was only 8.7% from monometallic Rh/MCM-41 catalysis. However, at a similar DCPD conversion, the selectivity was enhanced to 76.2% using the bimetallic Co–Rh/MCM-41 catalyst, even at a very low Co loading. Catalysis characterization including TPR, TPD, XRD, BET and TEM were carried out to study the nature of M modification on Rh/MCM-41. This leads to the conclusion that Co modified Rh/MCM-41 catalysts can substantially enhance the selectivity of DFTD up to more than 65% at almost complete conversion of DCPD.

2. Materials and methods

All chemicals used in the experiments were of analytical grade and were used without further purification.

2.1. Catalyst preparation

The Rh/MCM-41 was prepared using MCM-41 mesoporous silica as a support and rhodium chloride as the Rh precursor. MCM-41(10 g) was impregnated with an aqueous solution (48 ml) containing (515 mg) rhodium chloride using the incipient wetness method. After the impregnation, the samples were first dried at 393 K for 4 h, then calcined at 673 K in a quartz tube for 4 h in the air and finally reduced in a H_2 flow at 673 K for 2 h. For a nominal Rh loading of 2 wt%, the catalyst was denoted as 2% Rh/MCM-41. Similarly, the Co–Rh/MCM-41 catalysts with various Co loadings were prepared using the same method as 2% Rh/MCM-41.

2.2. Catalysts characterization

2.2.1. Porosity analysis

Porosity analysis was performed to examine the surface area, pore volume and average pore diameter of various catalysts. Adsorption/Desorption isotherm of N_2 at 76 K was obtained using an NOVA 2200e instrument. Before each measurement, the catalyst sample was degassed at 300 °C for 4 h to remove adsorbed volatile species from the catalyst surface. The isotherms were plotted with pressure and BET method was adopted to calculate the surface area, while Horwarth–Kavazoe and BJH methods were used to determine the volumes of micropore and mesopore, respectively.

2.2.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was performed with a VG ESCALAB 210 instrument equipped with an Mg anode and a multi-channel detector in order to determine the surface composition and metal speciation. Charge referencing was measured against adventitious carbon (C 1s, 285.0 eV). The surface speciation was determined from the peak areas of the corresponding lines using a Shirley-type background and empirical cross section factors for XPS.

2.2.3. Powder X-ray diffraction

X-ray diffraction (XRD) was carried out using a Siemens D/max-RB powder X-ray Diffractometer. Diffraction patterns were recorded with Cu $K\alpha$ radiation (40 mA, 40 kV) with a 2θ range of 15–70° with step increment of 0.04° and a count time of 1 s.

2.2.4. Temperature-programmed reduction

Temperature-programmed reduction (TPR) experiments were carried out on an FINESORB-3010 with a TCD detector. The catalyst (about 100 mg) was pretreated under dry air at 383 K for 1 h. The TPR profile was recorded with heating the sample from room temperature to 673 K at a ramping rate of 10 K/min under a H_2/Ar (10% v/v) flow.

2.2.5. Temperature-programmed desorption of H_2

Metal dispersion was determined by temperature-programmed desorption (TPD) of H_2 using an FINESORB-3010 analyzer with a mass detector (DM 300, AMETEK, USA). In a typical experiment, 100 mg of catalyst (dried at 383 K for 5 h before each measurement) with particle size ranging from 160 μm to 200 μm was placed in a U-shaped quartz tube. The sample was pretreated by passing hydrogen over the catalyst at a flow rate of 50 mL/min at 673 K for 1 h. The sample was then cooled to room temperature and kept in a flow of H_2 (50 mL/min) for another 1 h. Pure Ar (flow rate of 50 mL/min) was then purged over the catalyst at room temperature for additional 1 h. TPD analysis was carried out from 20 °C to 400 °C with a ramping rate of 10 °C/min with an Ar flow of 50 mL/min. The desorbed H_2 was continuously monitored by a mass spectrum ($m/z = 2$).

2.2.6. Transmission electron microscopy

The morphological properties of the catalysts were examined using a JEOL JEM-2010 instrument equipped with an energy dispersive X-ray spectroscopy (EDS) system. The JEOL JEM-1200 EXII electron microscope was operated at an accelerating voltage of 200 and 120 kV, respectively. To prepared the sample, 1 mg catalyst was dissolved in ethanol and thesolution was homogenized for 30 min by sonication. A copper grid was briefly dipped into the solution and the grid was then air dried to evaporate ethanol before measurement.

2.3. Reaction testing

Hydroformylation of DCPD was performed in a 200 mL stainless steel autoclave reactor with an inserted glass liner. Reaction temperature was controlled by using an oil bath on a digital hotplate with thermocouple, before the reaction, the catalyst was tableted, broken and mesh screened, and the size of the catalyst should be between 165 and 198 μm. In a typical experiment, the catalyst (200 mg), acetone (20 mL), triphenylphosphine (PPh_3) (0.76 mmol) and DCPD (5.0 g) were first introduced into the reactor. Then, the autoclave was purged with syngas ($CO/H_2 = 1/1$ in molar ratio) twice. The pressure was subsequently adjusted to an initial value (6 MPa) at room temperature. The reactor was heated to desired reaction temperature with a stirring rate of 650 rpm, which was found to be adequate for overcoming the diffusion limitations. An aliquot of liquid sample was taken at specified time for analysis.

After the reaction, the catalyst can be recovered by filtration. For recyclability experiment of used catalyst, another addition of PPh_3 was needed because PPh_3 was soluble in the reaction medium and cannot be easily separated after the reaction.

2.4. Reaction product analysis

The reaction effluents were analyzed using either GC–MS (Agilent 6890/5973) or GC (Shimadzu 2014) instrument equipped with a FID detector. The definitions being used in Section 3 include: the conversion of DCPD is defined as the moles of DCPD consumed divided by the moles of initial DCPD; the selectivity towards