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Journal of Molecular Catalysis A: Chemical 249 (2006) 181–190

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Organic–inorganic hybrid catalysts based on ordered porous structures for Michael reaction

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Received 11 December 2005; received in revised form 6 January 2006; accepted 9 January 2006
Available online 13 February 2006

Abstract

Two types of organic–inorganic hybrid base catalysts are prepared for the Michael reaction. Organic-functionalized molecular sieves (OFMSs), particularly “amine-immobilized porous silicates”, are designed based on a common idea of immobilizing active catalytic sites on silicate surface. Silicate-organic composite materials (SOCMs), such as “ordered porous silicate-quaternary ammonium composite materials”, are the precursors of ordered porous silicates obtained during the synthesis. The OFMSs are effective when the supports have large pore volume and/or surface area and the reaction is carried out in polar solvents ethanol and DMF. However, the activity of the OFMSs is considerably low in a non-polar solvent such as benzene. In contrast, the SOCMs are remarkably active in benzene. The organic cation-MCM-41 composite is more active than the composite of an organic cation and a microporous silicate such as zeolite beta and ZSM-12. In the SOCM catalysts, $(SiO)_3SiO^-(^+NR_4)$ moieties located at the accessible sites are considered to play some important roles. The active species are absent in the liquid phase after the reaction. The recycle of the catalyst was possible without significant loss of activity when the substrates are enough reactive.

Keywords: Michael reaction; Heterogeneous catalyst; Base catalyst; Composite material; Mesoporous silicate

1. Introduction

The past decade has seen great advances in the synthesis of new periodical mesoporous [1] and crystalline microporous materials [2]. Recently, design and preparation of organic–inorganic hybrid catalysts based on these materials are gaining great interest [3]. They are becoming important as the heterogeneous catalysts particularly for the synthesis of fine-chemicals in the liquid phase at lower temperatures. Additionally, the heterogeneous catalysis is obviously advantageous in light of the catalyst recovery and eco-benignity. There are classical examples of base-catalyzed C–C bond forming reactions such as Knoevenagel condensation [4], aldol condensation [5], and Michael addition [6], which are still useful for the production of the fine-chemicals [7]. However, solid base catalysis [8], particularly on microporous and mesoporous materials [9], is still insufficiently investigated compared to the corresponding acid catalysis. In this work, we focused on the effect of these materials on the Michael reaction (Scheme 1). Regarding the homogeneously catalyzed Michael reaction, there are quite a few examples [10,11], and even some asymmetric reactions have been successful [12–16]. However, only limited types of heterogeneous catalysts (including acid and base catalysts) have been applied to this reaction [17–21], partly because this is considered to be more “energy-demanding” reaction [22]. For the synthesis of high-silica porous silicates, quaternary ammonium cations are very often used as structure-directing agent (SDA). The silicate-organic composite materials (SOCMs for short) are obtained as precursors followed by the removal of SDA by means of calcination or extraction to give porosity. It is logical to use SDA-free materials in order to utilize their large surface area inside pores. Therefore, immobilization of organic functional groups on internal surface of porous silicates to obtain organic-functionalized molecular sieves (OFMSs as used by Jones et al. [23,24]) is a conventional and common idea for developing heterogeneous catalytic systems.

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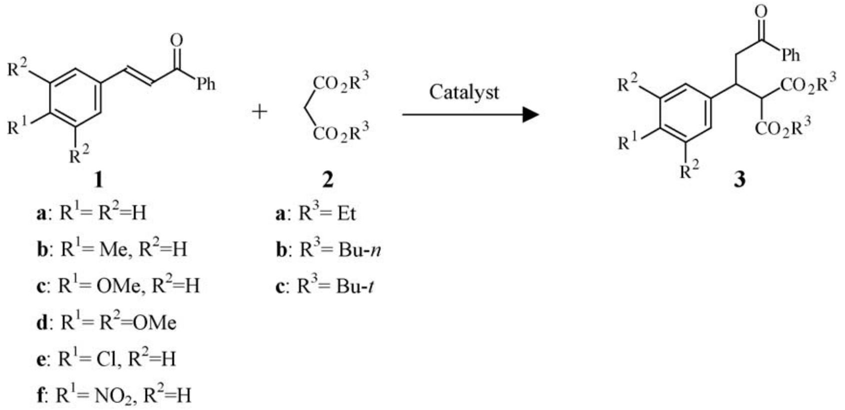
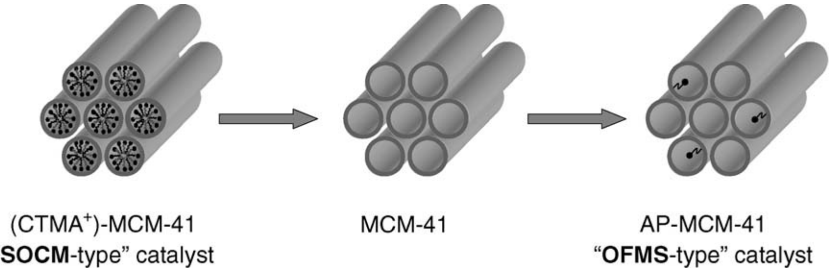
doi:10.1016/j.molcata.2006.01.015



Scheme 1.



Scheme 2.

On the other hand, no attention had been paid to the catalytic activity of as-synthesized SOCM, which is the precursor obtained during the synthesis, until we found the high catalytic activity of this non-conventional type of catalyst [25]. We have already reported the preliminary results on some C–C bond forming reactions catalyzed by the SOCM catalyst [25,26]. In this paper, we describe the detailed catalytic behavior of the non-conventional SOCM type catalysts as well as the conventional OFMS type catalysts for the Michael reaction. The SOCM and OFMS catalysts are schematically illustrated in Scheme 2.

2. Experimental

2.1. Materials

Highly dealuminated Y zeolite ($SiO_2/Al_2O_3 = 380$; HY380; Tosoh HSZ-390HUA) and dealuminated H-mordenite ($SiO_2/Al_2O_3 = 230$; HM230; Tosoh HSZ-690 HOA) were supplied from Tosoh Corporation. Organic reagents were used as received without further purification.

2.2. Measurements

X-ray diffraction (XRD) data were recorded on a Shimadzu XRD-6000 or a Rigaku RINT-2200 diffractometer using Cu Kα radiation and $\lambda = 1.5404$ Å. Elemental analyses of inorganic materials were performed using ICP (JICP-PS-1000 UV, Leeman Labs Inc.). Solution NMR spectra were obtained on a JEOL α-400 spectrometer or a JEOL JNM-AL-400 FT-NMR spectrometer. Solid NMR spectra were recorded on a Varian Inova 400 FT-NMR spectrometer. A Shimadzu DTG-50 thermogravimetric analyzer was used to carry out the thermogravimetric analysis (TGA). KBr pellet technique was used to take IR spectra of the samples on a Shimadzu FTIR 8200 PC spectrometer. Nitrogen adsorption measurements were carried out on a BELSORP 28SA gas adsorption instrument (Bel Japan). The specific surface areas (S_{BET}) and pore volumes were estimated from the N_2 adsorption isotherms at 77 K using Brunauer–Emmett–Teller (BET) equation [27] and the *t*-plot method [28], respectively. Average pore-size of mesoporous material was obtained with the N_2 adsorption branch at 77 K, using the Barrett–Joyner–Halenda (BJH) method [29]. Pore diameters of microporous materials are based on crystallographic data in the literature [30].

2.3. Synthesis of catalysts

Various high-silica molecular sieves were synthesized using organic SDA. Some of the as-synthesized samples (silicate-organic composite materials) were selected and used as SOCM catalysts. To remove the SDA inside the pore, the samples were calcined in a muffle furnace in a flow of air. Silanol-containing molecular sieves, which are suitable for the supports to prepare OFMS catalysts, were obtained by calcination of appropriate silicate-organic composite materials. Highly dealuminated zeolites such as HY380 and HM230 are also suitable supports.

2.3.1. SOCM catalyst

($CTMA^+$)-[Si]-MCM-41, (TEA^+)-[Al]-BEA, ($MTEA^+$)-[Si]-MTW denote as-synthesized pure-silica MCM-41 synthesized by using hexadecyltrimethylammonium (= cetyltrimethyl-