Applied Catalysis A: General 429–430 (2012) 85–91

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Preparation of amine-immobilized solid base catalysts by plasma polymerization of 1,2-diaminocyclohexane

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ARTICLE INFO

Article history:
Received 26 July 2011
Received in revised form 5 April 2012
Accepted 7 April 2012
Available online 14 April 2012

Keywords:
Plasma polymerization
1,2-Diaminocyclohexane
Amine-immobilized
Solid base catalysts

ABSTRACT

Thin films were deposited onto silica–alumina powders by plasma polymerization of 1,2-diaminocyclohexane to prepare amine-immobilized solid base catalysts. The existence of amine moieties in the films was confirmed by solid-state ^{13}C NMR, FT/IR, and XPS analyses. The silica–alumina powders deposited with the films showed strong base catalytic activity when evaluated based on the adsorption/desorption pattern of acidic gases (NO_2 and CO_2) and the conversion of benzaldehyde in Knoevenagel condensation reaction between benzaldehyde and ethylcynoacetate. Adsorbed acidic gases still remained even at 400 °C due to strong chemisorptions. When the plasma polymerization was carried out by a two-step process, the conversion was as high as 91.2% and adhesion of the films could be improved. The conversion was 82.0% even after the repeated use for 3 times when the films were deposited by the two-step process.

1. Introduction

Base catalysts are widely used for the formation of C–C bonds in organic synthetic reactions such as Aldol, Claisen, and Knoevenagel condensation reactions. These condensation reactions have commercially been carried out using a large amount of metal hydroxides and alkoxides or organic amines as a base catalyst. However, the use of metal hydroxides and alkoxides has some drawbacks due to the production of salt wastes. The salt wastes are highly corrosive and reaction products have to be separated from the wastes and purified through several complicated steps. Soluble organic amines are also industrially used for base-catalyzed reactions but it is very difficult to separate reaction products from the used catalysts.

Heterogeneous base catalysts were proposed as an alternative to the homogeneous base catalysts for easy work-up and recycling. Traditional heterogeneous base catalysts are limited to metal oxides (MgO, CaO) or supported alkaline metals on alumina [1–9]. Their application as a base catalyst, however, is limited because they are rapidly deactivated by water and CO_2 [10]. Several organic amine-immobilized porous solids were developed to compensate for the defect of metal oxides [11–13]. The use of organic amine-immobilized base catalysts has an advantage in that organic amine moieties act as active sites and solid supports make it easy to separate and recycle. The organic amine-immobilized catalysts can be prepared by various methods [11,14–18]. However, conventional methods for the immobilization of organic amines onto solid supports require several separation and refining steps in addition to the complicated synthetic steps. Recently, development of an alternative environmentally safe process becomes one of the key challenges of chemical reactions. Thus, simplification of the immobilization step by an environmentally friendly process is required.

The aim of this work is to investigate a novel approach for the preparation of an organic amine-immobilized solid base catalyst by means of plasma polymerization. The plasma process is well known as an efficient process to functionalize the surface of a solid substrate by depositing a highly cross-linked pinhole-free polymeric thin film without changing its bulk properties [18–26]. Deposited films by plasma polymerization process are known to show good chemical, thermal, and mechanical stabilities with good adhesion to various substrates. Particularly, plasma polymerization of an amine precursor results in the deposition of highly cross-linked thin plasma-polymer film onto a substrate which contains primary, secondary, and tertiary amine moieties in the backbone. Therefore, this method is highly attractive for the preparation of an organic amine-immobilized solid base catalyst since it does not require the separation step are not required and is environmentally friendly process [27].

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http://dx.doi.org/10.1016/j.apcata.2012.04.012