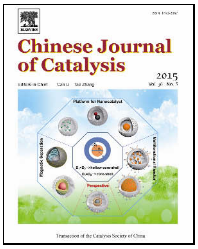
Chinese Journal of Catalysis 36 (2015) 712–720

available at www.sciencedirect.com

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



Article

Cu, Fe, or Ni doped molybdenum oxide supported on Al_2O_3 for the oxidative dehydrogenation of ethylbenzene

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ARTICLE INFO

Article history:
Received 9 January 2015
Accepted 3 February 2015
Published 20 May 2015

Keywords:
Ethylbenzene
Styrene
Molybdenum
Alumina
Dopant

ABSTRACT

Molybdenum-based catalysts supported on Al_2O_3 doped with Ni, Cu, or Fe oxide were synthesized and used in ethylbenzene dehydrogenation to produce styrene. The molybdenum oxide was supported using an unconventional route that combined the polymeric precursor method (Pechini) and wet impregnation on commercial alumina. The samples were characterized by X-ray diffraction (XRD), N_2 adsorption-desorption isotherms, temperature-programmed reduction of H_2 (H_2-TPR), and thermogravimetric (TG) analysis. XRD results showed that the added metals were well dispersed on the alumina support. The addition of the metal oxide (Ni, Cu, or Fe) of 2 wt% by wet impregnation did not affect the texture of the support. TPR results indicated a synergistic effect between the dopant and molybdenum oxide. The catalytic tests showed ethylbenzene conversion of 28%–53% and styrene selectivity of 94%–97%, indicating that the addition of the dopant improved the catalytic performance, which was related to the redox mechanism. Molybdenum oxides play a fundamental role in the oxidative dehydrogenation of ethylbenzene to styrene by its redox and acid–base properties. The sample containing Cu showed an atypical result with increasing conversion during the reaction, which was due to metal reduction. The Ni-containing solid exhibited the highest amount of carbon deposited, shown by TG analysis after the catalytic test, which explained its lower catalytic stability and selectivity.

1. Introduction

Styrene is the main product used in the manufacture of materials such as plastic, rubber, resins, and intermediates in organic synthesis. The main route for the production of styrene is the dehydrogenation of ethylbenzene in the presence of water vapor (the current industrial process) described in Eq. (1):

$$C_8H_{10}\ (g) \rightleftharpoons H_2\ (g) + C_8H_8\ (g) \qquad (1)$$

In this process, the most common catalysts used industrially are based on iron oxide (hematite) and contain various promoters such as potassium oxide, chromium, cerium, among others [1,2].

On the other hand, ethylbenzene dehydrogenation in the presence of CO_2 (Eq. (2)) has aroused considerable interest because the process with CO_2 requires less energy compared to the water vapor system.

$$C_8H_{10}\ (g) + CO_2\ (g) \rightleftharpoons C_8H_8\ (g) + CO\ (g) + H_2O\ (g) \qquad (2)$$

Furthermore, considering that CO_2 contributes to the green-

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DOI: 10.1016/S1872-2067(14)60313-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 5, May 2015

house effect, this alternative process can provide a commercial application of CO_2 as a soft oxidant [3–11].

The literature reports several methods for the synthesis and different compositions for the preparation of catalysts for the dehydrogenation of ethylbenzene in the presence of CO_2 [12–14]. Most of these studies used iron oxide (hematite) supported on Al_2O_3 or silicon. However, these materials are deactivated during the reaction, which is associated with the partial reduction of the hematite leading to the formation of magnetite. In addition, the deposition of carbon on the solid surface directly affects the conversion, selectivity, and catalyst stability [15]. Thus, finding alternatives to iron oxide that can be used under the drastic reaction conditions remains a challenge for this process [16–18]. Progress in the research of ethylbenzene dehydrogenation is mainly on the disadvantages of the commercial processes, catalyst deactivation, and environmental aspects as presented in several review articles [19–23].

Among the different materials studied, molybdenum oxide is considered promising because it gives a high activity, selectivity, and stability in this reaction [16–18]. Wong et al. [16] conducted a study of catalysts based on iron oxide and molybdenum oxide supported on MCM-41 and amorphous silica. They proposed that the interconnected defects of tubular MCM-41 provided better transport of reactant and product in the catalytic reaction, leading to better catalytic performance. In addition, molybdenum oxide exhibited catalytic activity higher than the iron oxide solids. Thus, these results demonstrated that catalysts based on molybdenum oxide could be an interesting alternative in ethylbenzene dehydrogenation.

Morán et al. [17] synthesized catalysts containing Pt, Mo, and Pt-Mo using clay as the support. These materials showed high catalytic activity in ethylbenzene dehydrogenation, which was attributed to the high thermal stability and high surface area of the support allowing a high dispersion of the metallic phase. The reduced catalysts presented higher activity than the unreduced solids.

Moronta et al. [18] studied the catalytic behavior of bimetallic catalysts containing Co and Mo supported on natural clays. These materials were tested in their reduced and unreduced form for ethylbenzene dehydrogenation. The reduced catalysts were more active than the unreduced solids. The low activity of all the catalysts was attributed to the low surface area of the support, which resulted in a low metal dispersion. It was observed that the low dispersion of the molybdenum oxide on the surface of the support was responsible for the low activity of these materials in this reaction. Hence, the development of an alternative synthesis route that optimizes the metal dispersion of Mo with a high surface area of the support is required.

In a recently published article [24], ZrO_2 was impregnated on the surface of the Al_2O_3 in order to achieve a coating without phase separation between the ZrO_2 and Al_2O_3. The X-ray diffraction (XRD) results showed that ZrO_2 can be used up to a threshold coating of 15 nm without the formation of a ZrO_2 crystalline phase. Consequently, this synthesis method is very promising for the development of catalysts with a high dispersion of the active sites.

Therefore, based on this synthesis methodology which utilizes an unconventional impregnation method combined with the polymeric precursor route, the present study shows the synthesis of catalysts containing MoO_3/Al_2O_3 using this alternative route and the influence of the addition of copper, iron, or nickel oxide on the catalytic properties for the dehydrogenation of ethylbenzene in the presence of CO_2. It is important to emphasize that catalysts containing molybdenum oxide supported on Al_2O_3 and doped with Fe, Ni, or Cu have been rarely reported in the literature for this reaction. Hence, the synthesis of new catalysts using this composition remains an interesting research topic. Furthermore, the role of molybdenum oxide in the reaction mechanism for the oxidative dehydrogenation of ethylbenzene and the influence of the dopant need to be clarified.

2. Experimental

2.1. Catalyst preparation

The sample of molybdenum oxide dispersed on Al_2O_3 was synthesized by the impregnation method. The Al_2O_3 used as support was the Degussa aeroxide particle with a surface area of 100 m^2/g (particle size estimated from isotherm data as 15 nm). However, before the impregnation process, the precursor source was prepared as a resin by the Pechini method containing Mo^{3+} ions using molybdic acid (Aldrich) [17].

The resin preparation involved the following steps. First, 26.49 g of the molybic acid solution was added to a beaker containing 200 mL of deionized water. This solution was kept under constant stirring at 80 °C for 3 h to obtain a MoO_4^{2-} suspension. Citric acid anhydride (J.T. Baker) was then added to complex the metallic ion, which gave a citric acid:Mo^{3+} complex with a metallic ion molar ratio of 3:1. The solution was kept under stirring at 80 °C for 48 h to promote the complexation process, after which 52.35 g of ethylene glycol was added and the solution was kept at 80 °C to perform the esterification and polymerization reaction.

Gravimetric analysis was carried out to determine the molybdenum oxide concentration in the resin. A quantity of resin that would result in the desired MoO_3:Al_2O_3 mass ratio was added to a beaker containing 150 mL of deionized water to coat the Al_2O_3. This system, with a viscosity similar to that of water, was stirred for 15 min and after that 1.0 g of Al_2O_3 was added. The resulting suspension was kept under constant stirring for 3 h at room temperature. It was then transferred to a round-bottomed flask, which was placed in a rotary evaporator to eliminate the water. The material obtained after evaporation of the water was calcined at 550 °C for 2 h with heating and cooling ramps of 10 °C/min. The synthesized sample has 10% by weight of molybdenum oxide on Al_2O_3. This sample was identified as 10MoAl. It is important to emphasize that the Mo^{3+} was added by an unusual way, since the molybdenum precursor (resin containing molybdenum) was added onto the Al_2O_3 support by the combination of a polymeric precursor route (Pechini) and wet impregnation on commercial Al_2O_3. This is in contrast to the normal method, which added directly an inorganic precursor as the molybdic acid onto the Al_2O_3 support.