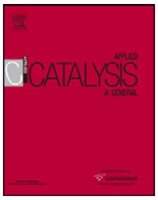
Applied Catalysis A: General 390 (2010) 225–234

Contents lists available at ScienceDirect

Applied Catalysis A: General

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



Ethylbenzene dehydrogenation over binary FeO_x–MeO_y/Mg(Al)O catalysts derived from hydrotalcites

Rabindran J. Balasamy[a], Alam Khurshid[a], Ali A.S. Al-Ali[a], Luqman A. Atanda[a], Kunimasa Sagata[b], Makiko Asamoto[b], Hidenori Yahiro[b], Kiyoshi Nomura[c], Tsuneji Sano[d], Katsuomi Takehira[a,d,*], Sulaiman S. Al-Khattaf[a,**]

[a] *KAUST Center in Development, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*
[b] *Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan*
[c] *School of Engineering, University of Tokyo, Hongo 7-3-1, Bunkyoku, Tokyo 113-8656, Japan*
[d] *Department of Applied Chemistry, Graduate School of Engineering, Kagamiyama, 1-4-1, Hiroshima University, Higashi-Hiroshima 739-8527, Japan*

ARTICLE INFO

Article history:
Received 27 August 2010
Received in revised form 12 October 2010
Accepted 15 October 2010
Available online 23 October 2010

Keywords:
Ethylbenzene dehydrogenation
Styrene
FeO_x–MeO_y/Mg(Al)O catalyst
Hydrotalcite

ABSTRACT

A series of FeO_x–MeO_y/Mg(Al)O catalysts were prepared from hydrotalcite-like compounds as precursors and were tested in the ethylbenzene dehydrogenation to styrene in He atmosphere at 550 °C. The hydrotalcite-like precursors of the metal compositions of $Mg_3Fe_{0.25}Me_{0.25}Al_{0.5}$ (*Me* = Cu, Zn, Cr, Mn, Fe, Co and Ni) were coprecipitated from the nitrates of metal components and calcined to mixed oxides at 550 °C. After the calcination, the mixed oxides showed high surface area of 150–200 $m^2\,g_{cat}{}^{-1}$, and were mainly composed of (Mg*Me*)(Fe^{3+}Al)O periclase in the bulk, whereas the surface was enriched by (Mg*Me*)(Fe^{3+}Al)$_2O_4$ pinel. Among the *Me* species tested, Co^{2+} was the most effective, followed by Ni^{2+}. Co^{2+} addition increased the activity of original FeO_x/Mg(Al)O catalyst, whereas Ni^{2+} increased the activity at the beginning of reaction, but deactivated the catalyst during the reaction. The other metals formed isolated MeO_x species in the catalyst, resulting in a decrease in the activity compared to the original FeO_x/Mg(Al)O catalyst. The active Fe species exists as metastable Fe^{3+} on the FeO_x/Mg(Al)O catalyst. By the addition of Co^{2+}, the reduction–oxidation between Fe^{3+} and Fe^{2+} was facilitated and, moreover, the active Fe^{3+} species was stabilized. It is likely that the dehydrogenation proceeds on the active Fe^{3+} species via its reduction–oxidation assisted by Co^{2+}.

1. Introduction

Styrene, an important basic chemical as a raw material for polymers, is produced commercially by the dehydrogenation of ethylbenzene using an Fe–K oxide catalyst in the presence of a large excess amount of superheated steam at 600–700 °C, just below the temperature where the thermal cracking becomes significant [1]. Potassium enhances the activity of iron oxide by an order of magnitude [2] and reduces the formation of carbonaceous surface deposits or coke that deactivates the catalysts [2,3]. Muhler et al. [4–6] studied on the catalyst structure under reaction conditions and found evidence for the existence of $KFeO_2$, which was in situ identified as the active phase for ethylbenzene dehydrogenation also by Lundin et al. [7] and Coulter et al. [8]. Benzene and toluene as by-products may be formed at different sites [2,8,9].

Steam is used not only to provide the thermodynamic driving force of the reaction, due to its endothermic character, but also to reduce the partial pressure of substrates, thus shifting the chemical equilibrium to higher styrene conversion [10]. Moreover, steam assists the surface formation of active $KFeO_2$ species [5], reduces the formation of coke and keeps the catalyst clean and active [11]. However, it must be noticed that steam is used in an important molar excess with respect to ethylbenzene (6–13:1); the amount of energy spent is very high (1.5×10^6 kcal/styrene tonne) [12].

The commercial Fe–K oxide catalyst has some disadvantages: (i) The active Fe^{3+} oxidation state is unstable; hematite (α-Fe_2O_3) or $KFeO_2$ is preferred for styrene production, but tends to be reduced to lower oxides and even to elemental iron, both of which catalyze coke formation and dealkylation [13]. (ii) The catalysts have low surface area. (iii) They are deactivated with time, being susceptible to poisoning by halides and residual organic chloride impurities [1]. The most serious deactivation is caused by the migration and loss of potassium promoter [4,14,15].

---

* Corresponding author. Permanent address: Hiroshima University, Higashi-Hiroshima 739-8527, Japan. Tel.: +966 3 860 1429; fax: +966 3 860 4234.
** Corresponding author. Tel.: +966 3 860 1429; fax: +966 3 860 4234.
E-mail addresses: takehira@hiroshima-u.ac.jp (K. Takehira), skhattaf@kfupm.edu.sa (S.S. Al-Khattaf).

0926-860X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2010.10.017

The search for new catalyst systems which have high surface areas and can stabilize the active state of iron, in the absence of potassium and steam, is much needed. Aluminum was proved to be an excellent promoter, preventing sintering in iron-oxide catalysts [16]. MgO had especially good characteristics as an additive to a K-promoted iron oxide catalyst among a series of alkaline earth oxides [17]. Mg^{2+} ions possess a small ionic radii leading to a high electrostatic potential due to the stable valence state, resulting in an effective suppression of Fe sintering due to the reduction of Fe^{2+} to Fe^0.

The starting materials can also significantly affect the catalytic performance. There has been for the past years an increased interest in using hydrotalcite-like compounds as precursors for mixed oxide catalysts in various reactions as reviewed by Cavani et al. [18]. The hydrotalcite-derived catalysts have high thermal stability and good metal dispersion, which has been attributed to the particular structure of the hydrotalcite through a homogeneous distribution of the metallic cations in the brucite-type sheets. FeO_x/Mg(Al)O [19], FeO_x/Mg(Zn,Al)O [20], and FeO_x/Zn(Al)O [21] catalysts derived from hydrotalcites were tested in the dehydrogenation of ethylbenzene under a CO_2 atmosphere. The activity losses over the FeO_x/Mg(Al)O catalysts with time-on-stream were completely restored by oxygen pulses [19]. The FeO_x/Mg(Zn,Al)O catalysts afforded the highest ethylbenzene conversion of 53.8% and a styrene selectivity of 96.7% at 500 °C [20]. The FeO_x/Zn(Al)O catalysts were effective and gave an areal rate of 4.15 mmol min^{-1} m^{-2} although the surface area was as low as 22.1 m^2 $g_{cat}{}^{-1}$ [21]. The authors previously reported that behaviors of FeO_x/Mg(Al)O catalysts derived from hydrotalcite-precursors are completely different from those reported in the preceding papers [19–21]; no favorable effect of either the additions of CO_2 and O_2 or the oxidation pretreatment of the catalyst on the activity was observed, whereas the reduction pre-treatment afforded the catalyst with higher activity as well as higher stability [22].

In the present paper, we report the effect of the addition of second metal component on the activity of FeO_x/Mg(Al)O catalysts in the dehydrogenation of ethylbenzene in a He atmosphere.

2. Experimental

2.1. FeO_x/Mg(Al)O-based catalysts preparation

The Mg–Al(Fe) hydrotalcite-like compound as a precursor of FeO_x/Mg(Al)O catalyst was synthesized using a co-precipitation of metal nitrates, following the method by Miyata and Okada [23] after minor modifications. Metal composition was fixed at $Mg_3Fe_{0.5}Al_{0.5}$ based on the preceding paper [22]. An aqueous solution containing the nitrates of Mg^{2+}, Fe^{3+} and Al^{3+} (ca. 0.05 mol in total/200 ml) was added slowly with vigorous stirring into an aqueous solution of sodium carbonate (0.04 mol/400 ml). To test the effect of the second metal component, a half molar amount of Fe^{3+} was replaced by Cu^{2+}, Zn^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+} or Ni^{2+} in the FeO_x/Mg(Al)O; the catalysts were prepared by adding each metal nitrate in the mixed solution of the nitrates of Mg^{2+}, Fe^{3+} and Al^{3+}. In all cases, the pH of the solution was adjusted at 10.0 by dropping a 1 M aqueous solution of sodium hydroxide, leading to a precipitation of heavy slurry. After the solution was aged at 60 °C for 24 h, the precipitates were filtrated, washed with de-ionized water (1000 ml), dried in air at 100 °C for 4 h, and calcined at 550 °C for 12 h in a muffle furnace in a static air atmosphere. To test the effect of calcination temperature, the precipitates were also calcined at 650, 750 and 850 °C, respectively, for 12 h. Metal composition was fixed at $Mg_3Fe_{0.25}\mathit{Me}_{0.25}Al_{0.5}$ in all catalysts. The concentration of Na^{2+} in the catalysts after the calcination was confirmed to be below 10 ppm by atomic absorption. As a control, FeO_x/MgO (Mg_3Fe_1) and FeO_x/Al_2O_3 (Fe_1Al_1) catalysts were prepared by co-precipitation of the nitrates in the same way. Also as a control, a commercial Fe–K oxide catalyst, Styromax®-4, supplied from Sud-Chemie Catalysts Japan, Inc. was used.

2.2. Characterizations of catalysts

The catalyst precursors and the catalysts were characterized by atomic absorption (AA), powder X-ray diffraction (XRD), transmission Mössbauer spectrometry (Mössbauer), thermogravimetric-differential thermal analysis (TG–DTA), nitrogen adsorption–desorption (N_2 absorption–desorption), temperature-programmed reduction (H_2-TPR) and X-ray photoelectron spectroscopy (XPS) methods.

AA measurements were carried out with a Perkin Elmer AAnalyst 100 using a mixed gas of acetylene–N_2O–air.

XRD was recorded on a Mac Science MX18XHF-SRA powder diffractometer with monochromatized Cu Kα radiation (λ = 0.154 nm) at 40 kV and 30 mA. The diffraction pattern was identified through comparison with those included in the JCPDS (Joint Committee of Powder Diffraction Standards) database and literatures.

Mössbauer spectra of pelletized powder samples were recorded at room temperature, using a constant acceleration mode (Topologic System Co.) of a radiation source with about 40 MBq 57Co(Cr) and a YAP scintillation counter. Doppler velocity was calibrated with reference to α-Fe.

TG–DTA of the catalyst was performed under an inert atmosphere of N_2 (20 ml min^{-1}) with a TA Instrument SDT Q 600 using 50 mg of sample at a rate of 10 °C min^{-1}.

N_2 adsorption–desorption isotherms at −196 °C were measured using a conventional volumetric apparatus (Bel Japan, BELSORP Mini). Before adsorption measurements, samples (ca. 0.1 g) were heated at 400 °C for 10 h under nitrogen flow. Surface areas and pore diameters were calculated by the Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) [24] method, respectively.

H_2-TPR of the calcined catalysts was carried out by flowing 5 vol.% H_2/N_2 (30 cm^3 min^{-1}) in the temperature range of 100–900 °C. The sample temperature increased with a rate of 10 °C min^{-1} and the amount of H_2 consumed was monitored by a thermal conductivity detector of a gas chromatograph (Shimadzu, GC-8AIT) [25].

XPS measurements were performed on a Perkin Elmer 1600E spectrometer using Mg Kα radiation as excitation source. In charge-up correction, the calibration of binding energy (BE) of the spectra was referenced to the C 1s electron bond energy corresponding to graphitic carbon at 284.5 eV. In addition, relative atomic sensitivity factors (ASFs) were used to determine practically more accurate chemical compositions on the surface.

2.3. Catalyst test

Dehydrogenation of ethylbenzene was conducted using a continuous gas-flow reactor with a fixed bed catalyst (Autoclave Engineers Ltd. Model 401C 0286) at atmospheric pressure. In the dehydrogenation reactions, typically 0.15 g of catalyst, which had been pelletized to the particles 0.3–0.8 mm in diameter, was loaded into the reactor. The catalyst was pre-treated in a He gas flow (100 ml min^{-1}) at 550 °C for 1 h. The reaction was started by introducing a gas mixture of ethylbenzene and He into the reactor. Ethylbenzene (0.08 ml min^{-1}; ca. 0.7 mmol min^{-1}) was fed by micro-feeder under a He flow (100 ml min^{-1}). Helium was used as a carrier gas instead of N_2, because N_2 can be activated to form NH_3 in the presence of H_2 over Fe catalysts. The reaction was carried out for 3 h of time-on-stream at 550 °C. The effect of reaction tem-