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The properties and catalytic performance of PtIn/Mg(Al)O catalysts for the propane dehydrogenation reaction: Effects of pH value in preparing Mg(Al)O supports by the co-precipitation method

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ABSTRACT

PtIn/Mg(Al)O-p*X* catalysts were prepared with co-precipitation method at different pH values ($X = 6$–12), with the aim of investigating the effect of pH value on their catalytic performance for the propane dehydrogenation reaction. It was found that the co-precipitation pH value could strongly influence the crystalline phase, the specific surface area, the surface morphology, the distribution of surface acidity, the reduction properties of the metal phase, the surface chemical state, the distribution of metal particles, and coke formation, giving rise to different catalytic performance. All the results reveal that the catalyst prepared at pH 8 shows the best catalytic performance; it possesses the primary crystal phase of periclase (MgO) and the highest specific surface area of support, the lowest fraction of strong acidic sites and In^0 species, the strongest interaction between the metal phase and support, the highest Pt dispersion (41.6%), the best distribution of Pt particles with the smallest Pt particle size (1.8 nm), and the lowest coke amount. Furthermore, the highest once-though yield of 0.37 mol propylene can be obtained over PtIn/Mg(Al)O-p8, in which 0.60 mol propane is consumed in a whole dehydrogenation reaction period (28 h).

1. Introduction

In recent years, there has been growing interest in the production of propene by a propane dehydrogenation (PDH) process, since propene is an important raw material for the production of commodity and specialty chemicals [1–4]. Currently, many studies in PDH are devoted to developing novel catalysts such as ceria-based catalysts [5], Al–Cu catalysts [6], Co/SiO_2 catalysts [7], and In_2O_3–Ga_2O_3–Al_2O_3 catalysts [8]. ZnO-modified ZSM-5 (or Y) zeolites [9] and [Fe]ZSM-5 [10] catalytic systems based on novel materials are reported to be considerable catalysts for propane dehydrogenation. However, compared with other catalysts, Pt-based catalysts are still considered as the most promising catalysts used in propane dehydrogenation process, even if with very low Pt content [11], especially with indium as a promoter to further improve catalytic performance [12–14].

The textural properties of the support materials, such as specific surface area, acid–base properties, and thermal stability, can influence the catalytic performance of Pt-based catalysts for the PDH process [15,16]. During the past several years, many attempts have been made to investigate the support materials of catalysts for the PDH reaction, such as Al_2O_3, MgO, SiO_2, Zr_2O, spinel $MgAl_2O_4$ (or $ZnAl_2O_4$), and calcined hydrotalcite or hydrotalcite-like materials [12,17–22]. Of all these supports, calcined hydrotalcite (Mg(Al)O) or hydrotalcite-like materials were especially attractive due to their moderate basic characteristics, high thermal stability, and high metal dispersion [23–25]. Our previous work investigated the influence of Mg/Al molar ratio in Mg(Al)O-*x* materials prepared by a co-precipitation method on the properties of PtIn/Mg(Al)O-*x* catalysts, demonstrating that Mg(Al)O material with a Mg/Al ratio of 4:1 was the optimal support material for the PDH reaction [13].

It is well known that various synthesis conditions such as identity of precursor, preparation methods, preparation temperature, molar ratios of metals, and preparation pH value have significant effects on the structural properties of support materials [26–31]. In particular, the pH value in the co-precipitation step is known to be a key factor in the successful design of catalysts. Jeong et al. [32] have prepared a series of Cu/ZnO_X catalysts by a co-precipitation method with variation of pH value ($X = 6$–10), and they clarified the effect of pH value on the catalytic properties and activity of Cu/ZnO_X for alcohol-assisted low-temperature methanol synthesis from syngas. Meshkani et al. [33] investigated the influence of pH value on the structural and catalytic properties

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of Fe–Cr–Cu catalysts prepared by co-precipitation in the high-temperature water gas shift reaction. Jung et al. [34] reported a kind of γ-Bi_2MoO_6 catalyst and probed the effect of pH in the preparation of the catalyst for oxidative dehydrogenation of *n*-butene to 1,3-butadiene. Furthermore, the effects of pH in the preparation of $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ [35] and $ZnFe_2O_4$ [36] catalysts were also verified by them. Based on these reports, it can be noted that no investigation of the effects of pH value in the preparation of Mg(Al)O materials on Pt-based catalysts for the PDH reaction has been reported. This current situation invites us to carry out a systematic study in this field.

The objective of this work is to clarify the effect of pH value in the preparation of Mg(Al)O supports via a co-precipitation method on the properties of PtIn/Mg(Al)O-p*X* catalysts. The Mg(Al)O-p*X* supports were synthesized by a co-precipitation method with a variation of pH value, and then bimetallic PtIn catalysts supported by these materials were applied to the propane dehydrogenation (PDH) reaction. Various methods of characterization such as XRD, BET, field emission scanning electron microscopy (FESEM), TEM, H_2 TPR, X-ray photoelectron spectroscopy (XPS), CO chemisorption, temperature-programmed oxidation (TPO), thermogravimetry (TG) and NH_3 TPD analyses were employed to discuss the correlations between the catalytic properties and performance of PtIn/Mg(Al)O-p*X* catalysts.

2. Experimental

2.1. Catalyst preparation

Calcined hydrotalcite (referred to as Mg(Al)O) was prepared by a co-precipitation process and subsequent heat treatment with $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ as precursors, as described in detail in our previous work [14]. In the preparation process, the solution pH was set at 6, 8, 10, and 12, respectively. The obtained support materials were denoted as Mg(Al)O-p*X*, where *X* represents the solution pH value in the preparation process.

PtIn/Mg(Al)O-p*X* catalysts were prepared using the same routine as in our previous work [14], and the content of Pt and In in all the catalysts was fixed at 0.6 and 1.5 wt.%, respectively. All the raw materials were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

2.2. Catalyst characterization

The XRD patterns of PtIn/Mg(Al)O-p*X* catalysts were collected on a Bragg–Brentano diffractometer (Rigaku D/Max-2000) with monochromatic Cu Kα radiation (λ = 1.5418 Å). The textural properties of samples were measured by N_2 adsorption–desorption at liquid nitrogen temperature with an automatic analyzer (NOVA 4000, Quantachrome, USA). The morphologies of PtIn/Mg(Al)O-p*X* catalysts were examined by FESEM (HITACHI S-4800) operated at 5.0 KV. NH_3 TPD measurements were implemented to analyze the surface acidity of catalysts. The TEM images of the as-synthesized catalysts were captured with a JEM-2010 microscope operated at 200 kV. H_2 TPR experiments were implemented in a programmable temperature system. The XPS of the prereduced PtIn/Mg(Al)O-p*X* catalysts was recorded on a Perkin–Elmer PHI 5000C ESCA using Al Kα radiation. The binding energies (BE) were calibrated using the C_{1s} level at 284.8 eV as an internal standard. The Pt dispersion of the prereduced PtIn/Mg(Al)O-p*X* catalysts was determined by CO chemisorption on an autosorb-iQ unit (Quantachrome, USA). The spent catalysts were analyzed by TG tests and TPO experiments to describe their coking behaviors. The details of all the characterization experiments can be referred to from our previous work [13,14].

2.3. Propane dehydrogenation reaction

2.3.1. Catalytic activity measurement

The propane dehydrogenation reaction was carried out in a fixed-bed quartz reactor with 0.3 g fresh catalyst at 620 °C and 0.1 MPa. Prior to the dehydrogenation reaction, the catalyst was reduced with H_2 at 580 °C for 2.5 h. Then a feed flow consisting of H_2, C_3H_8, and Ar ($H_2/C_3H_8/Ar$ molar ratio = 7:8:35, WHSV = 3.3 h^{-1}) was added to the reactor. A gas chromatograph (GC, SP-6890) equipped with a FID detector and an AT-PLOT PORA-Q capillary column was employed to analyze the products. The propane conversion and propylene selectivity were calculated from the total number of carbon atoms balance [14].

2.3.2. Calculation of turnover frequencies

On the basis of the dispersion of exposed Pt species in the catalyst, the TOF value was calculated according to the equation

$$\mathrm{TOF}(\mathrm{min}^{-1}) = \frac{F_{\mathrm{propane}} \times X_{\mathrm{propane}}}{m_{\mathrm{cat}} \times X_{\mathrm{Pt}} \times D_{\mathrm{Pt}}/M_{\mathrm{Pt}}}, \tag{1}$$

where X_{propane} is the propane conversion, F_{propane} is the flow rate of propane in mol min^{-1}, m_{cat} is the amount of catalyst, X_{Pt} is the Pt loading in the catalyst, D_{Pt} is the dispersion of Pt, and M_{Pt} is the molar weight of Pt (195.1 g mol^{-1}).

3. Results and discussion

3.1. Effect of pH on the structural properties

3.1.1. X-ray diffraction evaluations

Fig. 1 shows the XRD patterns of PtIn/Mg(Al)O-p*X* catalysts prepared at different co-precipitation pH values. All the catalyst samples exhibit well-crystallized patterns; the crystalline phases observed were identified by the Joint Committee on Powder Diffraction Standards (JCPDS). From Fig. 1, the characteristic peaks ascribed to spinel $MgAl_2O_4$ and periclase (MgO) can easily be observed in PtIn/Mg(Al)O-p6 catalyst prepared under weak acidic condition (pH 6). In contrast, when the Mg(Al)O materials were synthesized under alkali conditions (pH 8, 10, and 12), MgO seems to be the primary crystal phase in the catalysts. These observations suggest that the $MgAl_2O_4$ phase can be obtained by the initial preparation of co-precipitation in acidic environment. Additionally, it is interesting to find that PtIn/Mg(Al)O-p8 and PtIn/Mg(Al)O-p10 catalysts (prepared at pH 8 and 10) present a minor XRD

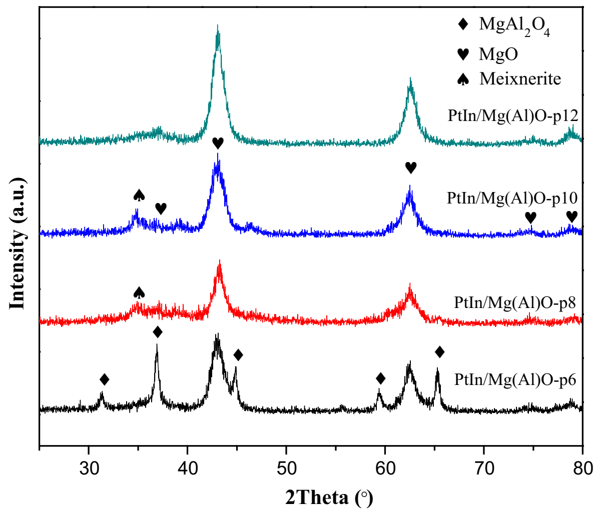

Fig. 1. XRD patterns of different catalysts.