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Microwave assisted synthesis of Sn-modified MgAlO as support for platinum catalyst in cyclohexane dehydrogenation to cyclohexene

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ABSTRACT

This paper described an investigation on catalytic properties of Pt nanoparticles supported on hydrotalcite-like oxide (MgAl(Sn)O) calcinated by microwave for cyclohexane dehydrogenation to cyclohexene. The PtSn catalysts were investigated with several state-of-art characterizations such as BET, XRD, NH_3-TPD, H_2-TPR, H_2-TPD and XPS. Particular emphasis was focused on the changes in the Sn-support interaction and in the character of Pt active sites. H_2-TPR showed that the microwave calcination strengthened the interaction between Sn and support. The strengthened interaction could maintain more amounts of Sn in oxidized. H_2-TPD revealed that microwave calcination facilitated Sn in changing the interfacial character between Pt and support. This was beneficial for the migration of carbonaceous materials to the support. These effects resulted in higher activity and stability in cyclohexane dehydrogenation to cyclohexene.

1. Introduction

Caprolactam and adipic acid are important industrial materials for production of nylon-6 and nylon-66, they can produced by selective oxidation of cyclohexane to cyclohexanone and cyclohexanol, and selective hydrogenation of benzene to cyclohexene. In contrast to selective oxidation of cyclohexane, the selective hydrogenation of benzene usually affords higher per-pass yield (~40%) and the process is safer [1–5]. However, owing to severe thermodynamic limitation, the hydrogenation generally obtains undesired cyclohexane, leading to time-wasting and resource-consuming steps to separate products. From the perspective of economics, numerous literatures have devoted to prevent the further hydrogenation to cyclohexane in liquid phase hydrogenation of benzene [6,7]. A recently developed method, oxidative dehydrogenation of cyclohexane to cyclohexene, has been exploited for this target. The routine exhibits low cyclohexene selectivity and produces significant amounts of COx [8,9]. Catalytic dehydrogenation of cyclohexane to cyclohexene as an alternative process with high cyclohexene selectivity is attractive on the basis of atom utilization. The hydrogen it produced is a desirable byproduct that can be used in processes such as hydrocracking and hydrodesulfurization.

Platinum (Pt) catalyst active for dehydrogenation of hydrocarbons is not fully adequate without modification [10–13], leading to low olefins selectivity and rapid deactivation [14]. Modifying Pt catalyst with tin (Sn) notably increases the activity, stability and olefin selectivity. The improved catalytic performance is attributed to the geometric effect and electronic effect [14,15]. The advantageous geometric effect of Sn, depending on the state of Sn, lies in the separation of the platinum ensembles and retaining them in high dispersion. The geometric effect occurs when Sn presents in a nonmetallic state. However, Sn acts as a poison when present in the metallic state [16]. Numerous explanations of the role of Sn reveal that the state of Sn is necessarily related to the interaction between Sn and support. This interaction can prevent the complete reduction of Sn. A proportion of Sn is present under a nonmetallic state for Sn supported on Al_2O_3. However, important quantities of Sn(0) can be observed for Sn supported on SiO_2 [15]. Gomez-Quero et al. demonstrate that the incorporation of Sn into Pt in Pt–Sn/Al_2O_3 enhance the catalytic activity and stability when compared to Pt/Al_2O_3 owing to the Pt–Sn interaction [17]. At this respect, the Pt/ZSM-5(Sn) catalyst with more amounts of Sn in oxidized form by incorporating Sn into the framework of zeolite gives high activity and stability in propane dehydrogenation [18]. Bocanegra et al. also show a good performance of PtSn catalyst supported on $MgAl_2O_4$ with enhanced Sn–support interaction [19].

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Taking into account these behaviors, it is possible to achieve better catalytic performances in alkanes dehydrogenation with enhanced Sn−support interaction.

Stability and olefin selectivity are further enhanced by using a metal oxide support free of acid sties which can promote further conversion via secondary dehydrogenation and isomerization reactions to form coke [20–22]. Moreover, the Al cations present at the support surface can stabilize the dispersed metal particles against sintering [23]. Of these points, calcined hydrotalcite-like MgAlO is ideal as a support for platinum catalyst in alkanes dehydrogenation [24–28]. Previous works studying the effects of modifier demonstrate that the way in which the modifieris added can influence the final catalytic properties. A recently developed method, whereby the modifier(Sn, In, Ga) is primarily buried in hydrotalcite-likeprecursor, provides a general strategy for targeted delivery of the modifying metal to Pt for alloying [29]. In this strategy, Sn is primarily buried in the bulk structure of the precursor and migrates to the surface to form SnOx during the calcination. Recently, microwave assisted heating system distinguished as quick, reproducible, simple, and energy efficient method is developing as a heating way of promoting the calcination processes. The energy interacting at molecular levels results in a rapid and uniform heating of the solid and avoids temperature gradients common in conventional heating [30–32]. Taking into account these behaviors, microwave calcination is used to calcine Sn-modified hydrotalcite-likeprecursors, aiming to yield supports that differ from those generated by conventional calcination.

In this work, hydrotalcite-like precursors were synthesized using the urea-coprecipitation method. The Pt/MgAl(Sn)O catalysts were obtained after dispersing Pt nanoparticles on the surface of the supports calcined by microwave calcination. The catalytic performances of the Pt/MgAl(Sn)O catalyst prepared by microwavewere compared with those of the Pt/MgAlO and Pt/MgAl(Sn)O catalysts prepared by conventional calcination in cyclohexane dehydrogenation to cyclohexene. As is well known, one of important aspects in the study of the advantageous electronic effect of modifier is interpreted in terms of Sn/Pt ratio. To exclude this effect, the same surface Sn/Pt ratio was controlled. Particular emphasis is focused on the changes in the Sn-support interaction and in the character of Pt active sites.

2. Experimental

2.1. Support preparation

All the reactants were analytical grade. Hydrotalcite-like precursors of the MgAl(Sn)O oxides were synthesized, using a urea decomposition methodwith a Urea/Mg/Al molar ratio of 12/3/1. 18.76 g of $Al(NO_3)_3{\cdot}9H_2O$, 38.46 g $Mg(NO_3)_2{\cdot}6H_2O$ and 108.11 g urea were dissolved in 750 ml deionized water at room temperature. Then appropriate amount of $SnCl_2{\cdot}4H_2O$(depending on the desired Sn content) dissolved in 50 ml alcoholic solution was dropwise added into the above solution before adding to a three-neck flask. The flask maintained at 105 °C for 10 h under stirring, and then aged at room temperature for 18 h. The aged solution was filtered and washed with 800 ml deionized water and dried overnight in air at 100 °C. The dried product was then heated by microwave (CEM PHOENIX) in air to 700 °C at 5 °C/min, and maintained at this temperature for 2 h to obtain the support. A series of MgAl(Sn)O supports containing 0.2 wt%, 0.6 wt%, 1.0 wt%, 1.2 wt% Sn were prepared. The samples calcined at 700 °C by muffle furnace were also prepared for comparative study.

The hydrotalcite-like precursors were designated as follows: MA O-HT for the hydrotalcite-like precursor of MgAlO support; MASOx-HT for the hydrotalcite-like precursor of MgAl(Sn)O support. x indicated wt% of Sn.

The synthesized supports were designated as follows: MASOWx and MASOMx where W and M represented microwave calcination and conventional calcination, respectively; x indicated wt% of Sn. MAOM for the support without Sn prepared by conventional electric calcination; MASOW0.2 for support with 0.2 wt% Sn prepared by microwave calcination; MASOW0.6 for support with 0.6 wt% Sn prepared by microwave calcination; MASOM0.8 for support with 0.8 wt% Sn prepared by conventional calcination; MASOW1.0 for support with 1.0 wt% Sn prepared by microwave calcination; MASOW1.2 for support with 1.2 wt% Sn prepared by microwave calcination.

2.2. Catalyst preparation

Pt/MgAl(Sn)O catalysts were prepared by impregnation of Pt onto the support in aqueous solution of hexachloroplatinic acid at 30 °C for 24 h with weight ratio of support to $H_2[PtCl_6]$ solution equal to 1:4, and dried at 80 °C. The samples were then calcined by muffle furnace at 550 °C for 5 h to obtain the catalysts. In all cases, the Pt content of was controlled at 0.2 wt% determined by ICP-OES analysis.

2.3. Catalytic reaction

The cyclohexane dehydrogenation reaction was carried out in a fixed bed microreactor. The inner diameter of quartz reactor was 6 mm, in which 0.25 ml of prepared catalyst was placed. The catalyst was previously reduced by H_2(30 ml/min) at 600 °C for 1 h and cooled to the reaction temperature before the reactant with the composition of $C_6H_{12}/H_2/N_2 = 1/1/1$(molar ratio) was fed to the reactor. Gaseous products (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8) were analyzed by TCD-GC (Shimadzu 2014C with a column of Porapak Q, 8 m). The column temperature was 120 °C. Liquid products(C_6H_{12}, C_6H_{10}, C_6H_6) were analyzed by FID-GC (Agilent 6820 with DB-1701,30m). The column temperature was 40 °C.

The conversion of cyclohexane (reaction temperature <550 °C) was determined from Eq. (1), and the selectivities to products were determined from Eqs. (2) and (3).

$$C_6H_{12}\text{Conversion} = \frac{[C_6H_{10}] + [C_6H_6]}{[C_6H_{12}]_{\text{out}} + [C_6H_{10}] + [C_6H_6]} \times 100\% \qquad (1)$$

$$C_6H_{10}\text{Selectivity} = \frac{[C_6H_{10}]}{[C_6H_{10}] + [C_6H_6]} \times 100\% \qquad (2)$$

$$C_6H_6\text{Selectivity} = \frac{[C_6H_6]}{[C_6H_{10}] + [C_6H_6]} \times 100\% = 100 - C_6H_{10}\text{Selectivity} \qquad (3)$$

where $[C_6H_{10}]$, $[C_6H_6]$ and $[C_6H_{12}]_{\text{out}}$ represented cyclohexene, benzene and cyclohexane of the liquid products, respectively.

The conversion of cyclohexane (reaction temperature >550 °C) was determined from Eq. (7), and the selectivities to products were determined from Eq. (8).

$$\begin{aligned} N_{\text{gas}} = V \cdot \{ & C[CH_4] + 2C[C_2H_4] + 2C[C_2 \\ & H_6] + 3C[C_3H_6] + 3C[C_3H_8] + 6C[C_6H_6] + 6C[C_6H_{10}] \} /6 \end{aligned} \qquad (4)$$

$$N'_{\text{gas}} = V \cdot C[C_6H_{12}] \qquad (5)$$

$$N_{\text{liq}} = N_{\text{liq}}^{C6H12} + N_{\text{liq}}^{C6H10} + N_{\text{liq}}^{C6H6} \qquad (6)$$

$$C_6H_{12}\text{Conversion} = \frac{N_{\text{gas}} + N_{\text{liq}}^{C6H10} + N_{\text{liq}}^{C6H6}}{N_{\text{gas}} + N'_{\text{gas}} + N_{\text{liq}}} \qquad (7)$$