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Effect of microwave calcination on catalytic properties of Pt/MgAl(Sn)Ox catalyst in cyclohexane dehydrogenation to cyclohexene

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ABSTRACT

This paper describes an investigation on catalytic properties of Pt nanoparticles supported on MgAl(Sn)Ox mixed oxide for cyclohexane dehydrogenation to cyclohexene. The MgAl(Sn)Ox supports were synthesized by microwave calcined hydrotalcite-derived precursors, and Pt/MgAl(Sn)Ox catalysts were prepared by an incipient wetness impregnation method. The catalysts were characterized by X-ray diffraction (XRD), hydrogen temperature-programmed reduction (H_2-TPR), hydrogen temperature-programmed desorption (H_2-TPD), X-Ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The results showed that the microwave calcination changed the interfacial character between Pt and support, and strengthened the interaction between tin and support, and facilitated the high dispersion of Pt nanoparticles presented on the support. These effects resulted in higher activity, stability and cyclohexene selectivity in cyclohexane dehydrogenation to cyclohexene.

1. Introduction

Cyclohexene is widely used as building blocks for the production of nylons and fine chemicals. It is currently produced by the partial hydrogenation of benzene [1]. Recently, oxidative dehydrogenation of cyclohexane to cyclohexene has been intensively investigated as alternative routine to obtain cyclohexene [2,3]. However, this routine exhibits low cyclohexene selectivity and produces significant amounts of COx. Catalytic dehydrogenation of cyclohexane to cyclohexene is of industrial interest because it can be carried out without COx and the hydrogen it produced is a desirable byproduct that can be used in processes such as hydrocracking and hydrodesulfurization. To the best of our knowledge, this attractive alternative has not yet been studied extensively and systematically.

Platinum is very active for dehydrogenation of hydrocarbons. However, platinum bonds too strongly to the unsaturated carbon intermediates, leading to low alkene selectivity and rapid deactivation [4–8]. Addition of tin as modifier has been found to be effective in increasing alkene selectivity and suppressing coke formation [9]. Geometric effect, electronic effect and acidic site poison have been proposed to explain its roles in modifying the catalyst surface [10]. Stability and alkene 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 [11–13]. Recently, hydrotalcite-derived support (MgAlOx) is broadly used because it is moderately basic and exhibits high thermal stability and the Al cations help stabilize the dispersed Pt nanoparticles against sintering [14–16]. Moreover, a further attraction is that it can be prepared with elements other than Al, e.g, Zn, Ga, In [17–19].

The advantageous geometric effect of tin lies in the separation of the platinum ensembles and retaining them in high dispersion, occurring when tin presents in a nonmetallic state. However, tin acts as a poison when present in the metallic state. Tin, as reported, is not reducible because of being chemically complexed by the support. The oxidation state of tin and the possibility of alloy formation after reduction are closely related to the interaction of tin with the support [20].

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Additionally, it is well established that the catalytic performances of PtSn bimetallic catalysts mainly depend on the corresponding preparation methods [10]. As shown by comparison with the catalytic properties of the catalysts prepared by various methods, the advantageous electronic effect of modifying tin is restricted to the PtSn bimetallic composition [21–25]. For example, separate stoichiometric metallic phases of Pt_3Sn, PtSn and $PtSn_2$ being effectively controlled by selection of the starting inorganic complexes are studied by the conversions of hydrocarbons (cyclohexane, propane and isobutane), the catalytic properties are interpreted in terms of Sn/Pt ratio [26–28]. Any alloy containing more than 25% Sn (e.g., PtSn, $PtSn_2$) is inactive as a catalyst. For the majority of PtSn bimetallic catalyst, tin is primally introduced by impregnation and followed by calcination. Although such techniques are widely used due to their simplicity and low cost, they offer little control over particle structure. Several methods have been developed for targeted delivery of a second metal to Pt for alloying. A recently developed method, whereby a second metal is delivered via hydrotalcite-derived support, provides a general strategy for controlled delivery [29]. In this strategy, tin is primarily buried in the bulk structure of the precursor and migrates to the surface to form SnOx during the calcination. Taking into account these behaviors, it is possible to produce the supports with uniformity distribution of SnOx. Recently, microwave assisted heating systems is distinguished as quick, reproducible, simple, and energy efficient method. The energy interacting at molecular levels results in a rapid and uniform heating of the solid and avoids temperature gradients common in conventional heating, therefore, it is developed as a heating way of promoting the calcination process. Solid materials prepared by microwave calcination can obtain products that differ from those generated by conventional heating. Examples of this method include ceramic materials with improved microstructure, layered hydrotalcite-type oxide with strong basicity and nano-powders with low reaction temperature [30–32].

In consequence, hydrotalcite-derived precursors containing tin were synthesized using the coprecipitation method and microwave calcination was applied to obtain the supports with superior properties. A series of Pt/MgAl(Sn)Ox catalysts were obtained after dispersing Pt nanoparticles to the surface of the supports calcined at different temperatures. In this work, effect of microwave calcination on catalytic properties in cyclohexane dehydrogenation to cyclohexene was investigated using various techniques.

2. Experiment

2.1. Supports preparation

All the reactants were analytical grade. Hydrotalcite-derived precursors of MgAl(Sn)Ox mixed oxides were prepared by the urea decomposition method with a Mg/Al molar ratio of 3.0. Typically, 18.76 g of $Al(NO_3)_3{\cdot}9H_2O$ and 38.46 g $Mg(NO_3)_2{\cdot}6H_2O$ were dissolved in 750 ml deionized water which added into a three-neck flask. 108.11 g urea (urea/Mg/Al molar ratio of 12/3/1) was dissolved in the above solution. A 50 ml alcoholic solution containing 0.09 g $SnCl_2{\cdot}4H_2O$ was dropwise added with stirring at room temperature. The flask was soaked in oil previously heated at 105 °C before the hydrolysis reaction. The solution was maintained at 105 °C for 10 h under stirring, and then aged at 30 °C for 18 h. The resulting suspension was filtered and washed with 800 ml deionized water and subsequently dried at 100 °C for 18 h. The product was then calcined by the microwave furnace (CEM PHOENIX), using feedback-control to maintain the temperature ramp and a constant temperature in the isothermal region. In this work, the samples were heated in air to 700 °C, 800 °C and 900 °C at 5 °C/min, and temperatures were maintained for 2 h to obtain the supports. The samples calcined by muffle furnace at 700 °C, 800 °C and 900 °C were also prepared for comparative studies.

The synthesized supports were designated as follow: MASO-HT, the hydrotalcite-derived precursor of MgAl(Sn)O support; MAO, MgAlO support calcined by muffle furnance at 700 °C; MASOM, calcined by muffle furnance; MASOM700, calcined by muffle furnace at 700 °C; MASOM800, calcined by muffle furnace at 800 °C; MASOM900, calcined by muffle furnace at 900 °C; MASOW, calcined by microwave; MASOW700, calcined by microwave at 700 °C; MASOW800, calcined by microwave at 800 °C; MASOW900, calcined by microwave at 900 °C.

2.2. Catalysts preparation

The precursors of supported platinum catalysts were prepared by impregnation of the support in aqueous solution of hexachloroplatinic acid at 30 °C for 24 h. After the impregnation, all the samples were dried at 80 °C for 12 h. For the impregnation of the supports, the Pt concentration in the impregnating solutions was 0.5 $g\,L^{-1}$ and the impregnating volume/support weight ratio was 4.0 $ml\,g^{-1}$. Then the catalysts were obtained after calcined by muffle furnace at 550 °C for 5 h. In all cases, the nominal compositions were for platinum 0.2 wt% and for tin 1.0 wt%.

2.3. Catalytic reaction

Dehydrogenation of cyclohexane was carried out in a fixed bed microreactor. A sample (0.25 ml) previously reduced by H_2 (30 ml/min) at 550 °C for 1 h was placed in a quartz reactor (6 mm in diameter). Then the feed compositions of N_2, H_2, and C_6H_{12} (N_2:H_2:C_6H_{12} (molar ratio) = 1:1:1) were added to the reactor. Cyclohexane was introduced into the reactor using a syringe pump. Gaseous and liquid products were analyzed by TCD-GC (Shimadzu 2014C with a column of Porapak Q) and FID-GC (Agilent 6820), respectively.

2.4. Catalyst characterizations

The N_2 adsorption/desorption isotherms of the samples were determined by the automatic analyzer (NOVA 2200e, Quantachrome, USA) at liquid nitrogen temperature. X-ray diffraction (XRD) analysis was performed on D/MAX 2500. Diffraction patterns were recorded with Cu Kα with 0.03°(2θ) steps over 5–70°.

Hydrogen-temperature-programmed reduction (H_2-TPR) studies were carried out with Quantachrome's CHEMBET3000 instrument. The samples (100 mg) were placed in U-shaped quartz reactor for pretreatment at 300 °C at 10 °C/min for 30 min in helium-atmosphere (30 ml/min), and then cooled to room temperature in helium-atmosphere (30 ml/min) before heated from room temperature to 800 °C at 10 °C/min with the existence of 10 % H_2/Ar reduction gas (30 ml/min). The H_2 consumption was recorded by TCD detector and was normalized with the mass of the sample. In order to obtain semi-quantitative comparison of the profiles, the curve fitting of the peaks was conducted using the Gaussian deconvolution method. Then the total area and the maximum temperature (T_M) were achieved from the multiple peaks fit reports and the peak fraction was calculated using peak area.

Hydrogen-temperature-programmed desorption (H_2-TPD) was measured with the same apparatus as that of H_2-TPR. The samples (100 mg) were reduced in flowing H_2 (10% H_2/Ar 30 ml/min) at 550 °C at 10 °C/min for 1 h and cooled to 30 °C in Ar gas atmosphere (30 ml/min) before exposed to H_2 (10% H_2/Ar, 30 ml/min) until surface saturation. The weakly adsorbed H_2 was removed by flushing Ar (30 ml/min) for 0.5 h. After the base line became stable, the desorptions were programmed at 900 °C at 10 °C/min and the amount of H_2 desorption was recorded by TCD detector.