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Effect of the addition of potassium and lithium in Pt–Sn/Al_2O_3 catalysts for the dehydrogenation of isobutane

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Abstract

Dehydrogenation of isobutane (iC_4) to isobutene has recently received considerable attention because of the increasing demand for methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE), as additives for gasoline to increase the octane number and to substitute lead. Among several catalysts, Pt–Sn/γ-Al_2O_3 catalyst is one of the most suitable ones. In this study, Pt–Sn, Pt–Sn–K and Pt–Sn–Li catalysts supported on γ-Al_2O_3 have been investigated. The catalysts were prepared by co-impregnation using H_2PtCl_6, $SnCl_2$ as the metal precursors and K_2CrO_4 and LiOH as the promoters. The obtained catalysts were characterized by TPR and XRD techniques. Reaction temperature, feed flow rate (Q), iC_4/H_2 ratio and the catalyst type were the main variables that were investigated. Initially, primary experiments were carried out for the identification of the optimum range of operating variables, then, Taguchi's algorithm was employed to design the experiment. The results revealed that the Pt–Sn–K catalyst showed higher selectivity than Pt–Sn–Li. Under the optimum operating conditions i.e. at 550 °C, feed flow rate of 50 cm^3/min and iC_4/H_2 ratio of 1/3, selectivity toward isobutene of higher than 90% was achieved with the corresponding conversion values of about 15%.

Keywords: Pt/Sn catalyst; Dehydrogenation; Isobutane; Isobutene; Taguchi's algorithm

1. Introduction

There is a growing interest in catalytic dehydrogenation of light alkanes due to the increase in the demand for olefins such as propylene and isobutene [1,2]. Isobutene, a key component of methyl tertiary butyl ether (MTBE) [3] and ethyl tertiary butyl ether (ETBE), is a chemical used as an oxygenate for reformulated gasoline [4,5]. Much research has been undertaken on isobutene synthesis by oxidative, nonoxidative, as well as steam cracking reaction conditions [6]. Supported platinum (Pt)–tin (Sn) catalysts have been widely used in naphtha reforming or alkane dehydrogenation processes due to their high selectivity and stability [7]. Different deposition techniques used in the preparation of Pt–Sn/Al_2O_3 catalysts lead to different adsorbed species after impregnation [8,9]. The deposition of $[PtCl_2(SnCl_3)_2]^{2-}$ complex on the alumina surface with the strong interaction between Pt and Sn is generally achieved by co-impregnation technique [10]. It is shown that the addition of Sn to Pt has the following effects on dehydrogenation reaction:

i — Increases the catalyst stability and decrease the rate of deactivation [11].
ii — Changes the selectivity by inhibiting hydrocracking, oligomerization and coke formation on the catalyst surface [3,12,13].
iii — The metallic crystallites show high degree of dispersion and higher resistance to aging [11].

Supported tin may exist as Sn^{4+}, Sn^{2+} and Sn^o, which cause the complexity of the catalyst. The degree of the tin reduction has been found to depend on the tin loading, temperature of the pretreatment and the presence of surface additives such as chlorine [14]. Generally, platinum–tin alloys are obtained only upon reductive treatments, in which a one-to-one atomic composition (PtSn) is

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the most frequently detected by several techniques. However, all types of platinum–tin alloys are possible [15]. It has been identified that five different stable alloys that can form between Pt and Sn are PtSn, $PtSn_2$, $PtSn_4$, Pt_2Sn_3, and Pt_3Sn [16]. Alloy formation between Pt and Sn is thermodynamically favorable and is expected when the metals are in sufficiently close proximity for the tin oxide to accept "spillover" hydrogen from easily reducible Pt. Indeed, Pt–Sn alloy phases in addition to oxidic tin states have been detected from in situ studies [17].

There are numerous factors that can affect the properties of catalysts such as the acidity of the support, preparation procedure, nature of the precursor compounds, impregnation sequence of metal loading, activation of the solid [1,18] and dispersion of the active metallic species [19]. An example to illustrate the influence of the preparation procedure can be found in the work of Vertes et al. [20], who carried out a series of mossbaura experiments over bimetallic Pt–Sn/γ-Al_2O_3 catalysts obtained by a reaction between $Sn(C_2H_5)_4$ and Pt/γ-Al_2O_3 by an impregnation of $SnCl_2$ onto Pt/γ-Al_2O_3. In order to reduce the acidity of the support, the γ-Al_2O_3 is generally poisoned by the addition of alkali metal ions such as K or Li. The way in which these promoters are added could influence the final properties, not only of the support but also of the metallic phases [21].

For the dehydrogenation of alkanes, a great deal of work has been done to provide better supports for noble metals. Spinel-type structures, which have high thermal stability, low acidity and hydrophobic behavior, are well adapted to the expected conditions forced in dehydrogenation processes. Moreover, it has been reported that spinels such as $ZnA1_2O_4$ or $MgA1_2O_4$ tend to prevent sintering of platinum due to a strong metal-support interaction [15]. Nowadays, several studies are being carried out to evaluate the modification of the stability, selectivity and activity of the metallic catalysts by the addition of some alkali metals such as Li, Ba, K and Ca in Pt–Sn/Al_2O_3 catalyst. The incorporation of Sn and Li improved light-paraffin dehydrogenation and inhibited isomerization and cracking reactions [22]. The effect of K on Pt and Pt–Sn supported on silica, prepared by ion-exchange method, was studied by Cortright et al. [23] for isobutane dehydrogenation. They found that the addition of Sn and K diminished the size of the surface platinum ensembles, suppressing the hydrogenolysis, isomerization and coking reactions. In K–Sn–Pt/SiO_2 catalyst, dehydrogenation rate increased either due to an increase in the number of sites available for hydrogen removal from adsorbed isobutane or to the stabilization of adsorbed isobutane molecules by potassium.

In the present study, Pt–Sn/γ-Al_2O_3, Pt–Sn–K/γ-$Al_2O_3Al_2O_3$ and Pt–Sn–Li/γ-Al_2O_3 catalysts were prepared. The catalysts were characterized by temperature-programmed reduction (TPR) and X-ray diffraction (XRD) techniques. The dehydrogenation of iC_4 on the prepared catalysts was tested in a continuous tubular fixed bed flow reactor. Initially, primary experiments were tested to explore the suitable ranges for the operating variables. Subsequently, the operating conditions were optimized using Taguchi's algorithm with four operating variables such as incorporation of K and Li as a promoter, reaction temperature, feed flow rate (Q) and iC_4/H_2 ratio. Effects of the addition of potassium and lithium as promoters on physical and chemical properties, as well as on the catalytic activity of Pt–Sn/γ-Al_2O_3 catalyst in the dehydrogenation of iC_4 were also investigated.

2. Experimental

2.1. Preparation of catalysts

γ-Al_2O_3 used in this study was obtained from Sigma-Aldrich. All the catalysts were prepared by co-impregnation method. Before the impregnation step, the γ-Al_2O_3 support was calcinated in air at 550 °C for 3 h. The specific surface area of the γ-Al_2O_3 was 115 m^2/g. Subsequently, the support was impregnated using hydrochloric acid solution of $H_2(PtCl_6) \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$. These catalysts were then impregnate with an aqueous solution of K_2CrO_4 and $LiOH \cdot H_2O$ which were used as the promoter agents [24]. Pt loading was held constant at 1 wt.% [1,3,24] while Sn loading was varied from 1 wt.% to 5 wt.% [25]. After the impregnation step, the catalysts were dried at 120 °C for 12 h, followed by calcination in air for 2 h at 500 °C [3]. The compositions of the prepared catalysts are presented in Table 1.

2.2. Catalyst characterization

Catalyst samples were characterized by temperature-programmed reduction (TPR) and X-ray diffraction (XRD) techniques. The bulk reduction behavior of each catalyst was studied using a Micromeritics TPR/TPD 2900 system. 0.05 g of calcined samples was initially heated under He flow (50 cm^3/min) at a rate of 10 °C/min from room temperature to 200 °C for 20 min. Then, the reducing gas (5% H_2 in Ar) was switched on at 20 cm^3/min and the sample temperature was raised at 5 °C/min until it reached 900 °C where it was held constant for 30 min. The effluent gas was passed through a cooling trap (at a temperature of lower than -50 °C) to condense and collect the water generated during the reduction process. A thermal conductivity detector (TCD) was used to determine the amount of H_2 consumed. XRD test was performed on the catalysts by means of using Cu Kα radiation using a Philips PW 3710 powder diffractometer instrument.

2.3. Isobutane dehydrogenation reaction

Isobutane dehydrogenation reaction tests were performed in a continuous tubular fixed bed flow reactor operated at atmospheric pressure. The stainless steel reactor had an inside diameter of 11 mm and was 1 m long. In order to reduce the catalysts, they were charged into the reactor and the temperature

Table 1
Metal composition of prepared catalysts

Catalyst	Pt (wt.%)	Sn (wt.%)	K (wt.%)	Li (wt.%)
1	1	3	–	–
2	1	5	–	–
3	1	3	1	–
4	1	3	–	1