The influence of alumina used as a support on the catalytic properties of Pt/Sn/Al$_2$O$_3$ systems in the dehydrogenation of isobutane

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Abstract

In this research different types of Al$_2$O$_3$ were used as supports to prepare catalysts for dehydrogenation of isobutane to isobutene. These supports were Al$_2$O$_3$ from Merck, Axen and gamma Al$_2$O$_3$ synthesized from Al(OH)$_3$. Sn/Pt/Al$_2$O$_3$ catalysts were prepared by sequential impregnation, at first Pt and then Sn was deposited. Characterization of catalysts was performed by X-ray powder diffraction (XRD) and thermal analysis (TG/DTG) techniques. Elemental analysis of the catalysts was also carried out by wet chemical analysis using inductively coupled plasma (ICP) technique. Isobutane dehydrogenation was studied in a reactor under atmospheric pressure at 848 K. The conversion, selectivity and yield of the prepared catalysts were calculated.

1. Introduction

Catalytic dehydrogenation of isobutane is important because of growing demand for isobutene as a precursor for the production of methyl tert-buthyl ether (MTBE). MTBE is added to gasoline to improve the octane number, yielding cleaner burning fuel [1-5]. The industrial catalytic dehydrogenation of isobutane processes fall into two categories, those based on platinum as the active phase [6, 7] and those based on chromia as the active phase [8].

Platinum-based materials are employed extensively as catalysts for reforming of hydrocarbon streams in the production of petrochemicals and gasoline. Supported bimetallic platinum-tin catalysts are now widely used to dehydrogenate isobutane into isobutene [9-11]. Magnesia-supported platinum–tin catalysts with Pt content of 0.25–3% and atomic ratio of Pt/Sn = 1 are prepared from a Pt–Sn bimetallic complex. These catalysts are among the most selective to isobutene production [9]. Several bimetallic catalysts are prepared by selective hydrogenolysis of Sn(n-C$_4$H$_9$)$_4$ on Pt and the selective dehydrogenation of isobutane into isobutene was studied on

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silica-supported bimetallic Pt-Sn [10]. In other research, Pt–Sn/Al$_2$O$_3$ and Pt–Sn/SiO$_2$ catalysts have been prepared by reacting tris n-butyl-tin hydroxide on the platinum surface, in water solution under atmospheric pressure of hydrogen. High selectivities and activities have been obtained for isobutane dehydrogenation into isobutene [11].

The aim of the preparation of catalytic materials that can be employed on an industrial scale is to obtain a product with high activity, selectivity and stability. To this purpose, the active phase- in our case the metal- must be in a sufficiently high dispersed form which results in a large specific surface area and consequently in a maximum specific activity. In order to reach this objective the active metal component is usually deposited on the surface of a support, a highly porous and thermostable materials (with a high surface area and suitable mechanical strength) which is able not only to disperse the metal, but also to increase its thermal stability and hence the catalyst life. The common preparation methods of dispersed metal catalysts require a combination of different unit operations; which can be described as: introduction of the metal precursor on the support by impregnation, drying, calcinations and reduction. Impregnation method requires that the support is contacted with a certain amount of solution of the metal precursor, usually a salt, and then it is aged, usually for a short time, dried and calcined [12].

2. Experimental

Different types of Al$_2$O$_3$ supports were used for preparation of Sn/Pt/Al$_2$O$_3$ catalysts. To obtain gamma alumina, aluminum hydroxide was heated at 823 K in air for 3 hours. The catalysts were prepared by impregnation. In this method, a homogenous dispersion of metal on the support is achieved especially when dealing with a low metal concentration. Before the impregnation step, the supports were partially dehydrated at 383 K for 6 hours in an oven [12].

In the case of platinum, aqueous solution containing a prescribed amount of chloroplatinic acid (H$_2$PtCl$_6$.6H$_2$O) were prepared to yield 0.75 wt% of platinum/support samples. For tin, aqueous solution containing a prescribed amount of SnCl$_2$.2H$_2$O were prepared to yield of 0.6 wt% of tin/platinum/support samples.

After impregnation, the impregnated material undergoes a drying treatment at a temperature of 383 K for 17 hours to eliminate the solvent used in the previous impregnation step. The impregnated and dried carrier is then calcined at a temperature of 823 K for 2 hours. Calcination has the purpose of decomposing the metal precursor with formation of an oxide and removal of gaseous products (usually water and CO$_2$). The product was in powder form. The powders were converted to pellets under 10 bar pressure. Each pellet weight 50 mg, 2 mm thickness, and 5 mm diameter. Characterization of catalyst was performed by XRD, TG/DTG and ICP techniques. XRD patterns of the samples were recorded using a Bruker Model D8 ADVANCE using *CuK$_\alpha$* radiation over a *2θ* range from 10° to 100°. TG/DTG of the samples was recorded using a Metler thermobalance Model TG50. ICP analysis was performed by an INTEGRA XL2; GBC, Dandenong, instrument.

Isobutane dehydrogenation was performed in a reactor working under atmospheric pressure at 848 K with a ratio isobutene/hydrogen of 2/1. After hydrogen treatment at 823 K, tin and platinum were in reduced form [12]. At 848 K under atmospheric total pressure of isobutane and hydrogen, the conversion, selectivity and yield of this reaction was investigated. Reactants and products were analyzed by PRICHROM 2100 gas chromatograph equipped with an automated gas-sample valve. Products were separated in a packed column (SS 316, 6m, 1/8 inch, 28% DC200 on chromosorb PAW 60/80, ENRO 3015) coupled to a flame ionization detector. Total isobutane conversion is defined as the percentage of isobutane transformed into all products. The selectivity of isobutene is defined as the percentage of the total amount of transformed isobutane which is converted into isobutene. The yield of isobutene is obtained by multiplying the selectivity (%) by the total conversion (%) divided by 100 [13].

3. Result and discussion

3.1. Characterization of catalysts

Platinum and tin contents of catalysts (wt %) determined by elemental analysis with ICP, are represented in Table 1. X-ray diffraction patterns of catalysts are shown in Fig. 1.

Table 1
Metal content of catalysts

Catalyst	Pt (wt %)	Sn (wt %)
Sn/Pt/Al_2O_3 (Merck)	0.74±0.04	0.60±0.03
Sn/Pt/Al_2O_3 (synthesized)	0.66±0.03	0.60±0.04
Sn/Pt/Al_2O_3 (Axen)	0.73±0.04	0.62±0.03
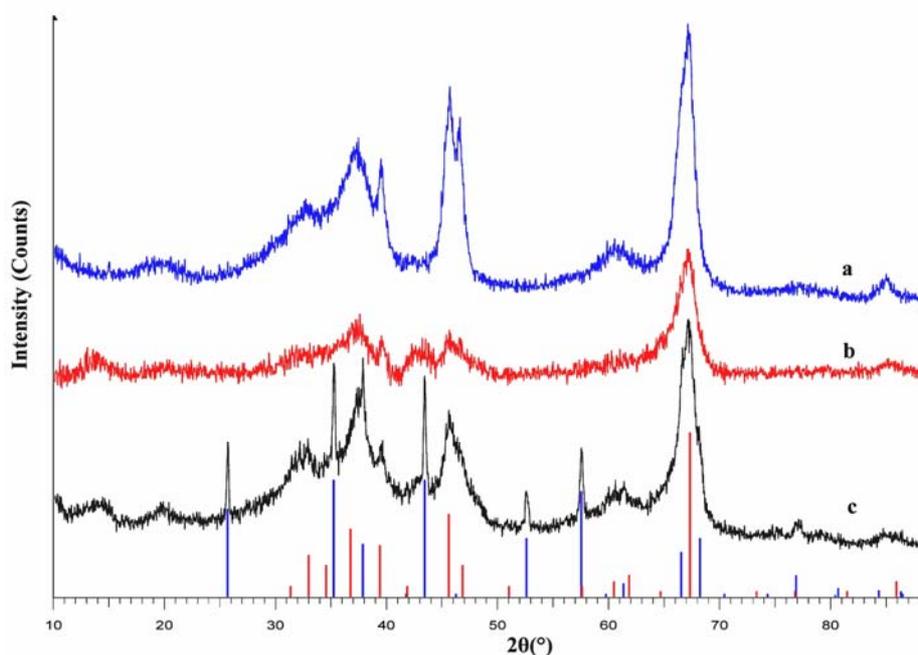
Fig. 1 XRD patterns of different catalysts (a) Axen Al_2O_3, (b) synthesized Al_2O_3, (c) Merck Al_2O_3

XRD patterns of the catalyst prepared by Al_2O_3 from Merck showed two different phases of alpha and gamma Al_2O_3 respectively with corundum and cubic structure, whereas the XRD pattern of the catalyst prepared by Al_2O_3 from Axen showed a single phase of gamma Al_2O_3 with cubic structure. XRD patterns of the catalyst prepared by synthesized Al_2O_3 from aluminum hydroxide showed gamma Al_2O_3 but its structure was not cubic. The XRD patterns of the samples heated of 873 K was unaltered, confirming the thermal stability of products at this temperature. The thermal behavior of the catalysts was studied in the range of 298–873 K in nitrogen atmosphere.

The heating rate was 10 K min^{-1}, Fig. 2. The weight loss of the catalyst prepared by Merck, Axen Al_2O_3 and alumina prepared by aluminum hydroxide in the temperature range 308-383 K was respectively 5.80, 3.81 and 4.50 (wt%) which is due to the dehydration of the samples. Up to 873 K, no thermal event is observed.
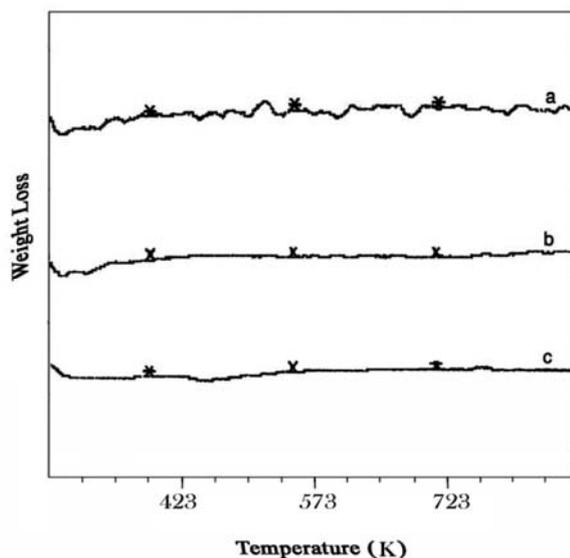
Fig. 2 DTG curves of different catalysts (a) Axen Al_2O_3 (b) synthesized Al_2O_3, (c) Merck Al_2O_3

3.2. Dehydrogenation of isobutane into isobutene

The conversion, selectivity and yield of isobutane dehydrogenation are represented in Fig. 3 and their average in Table 2.
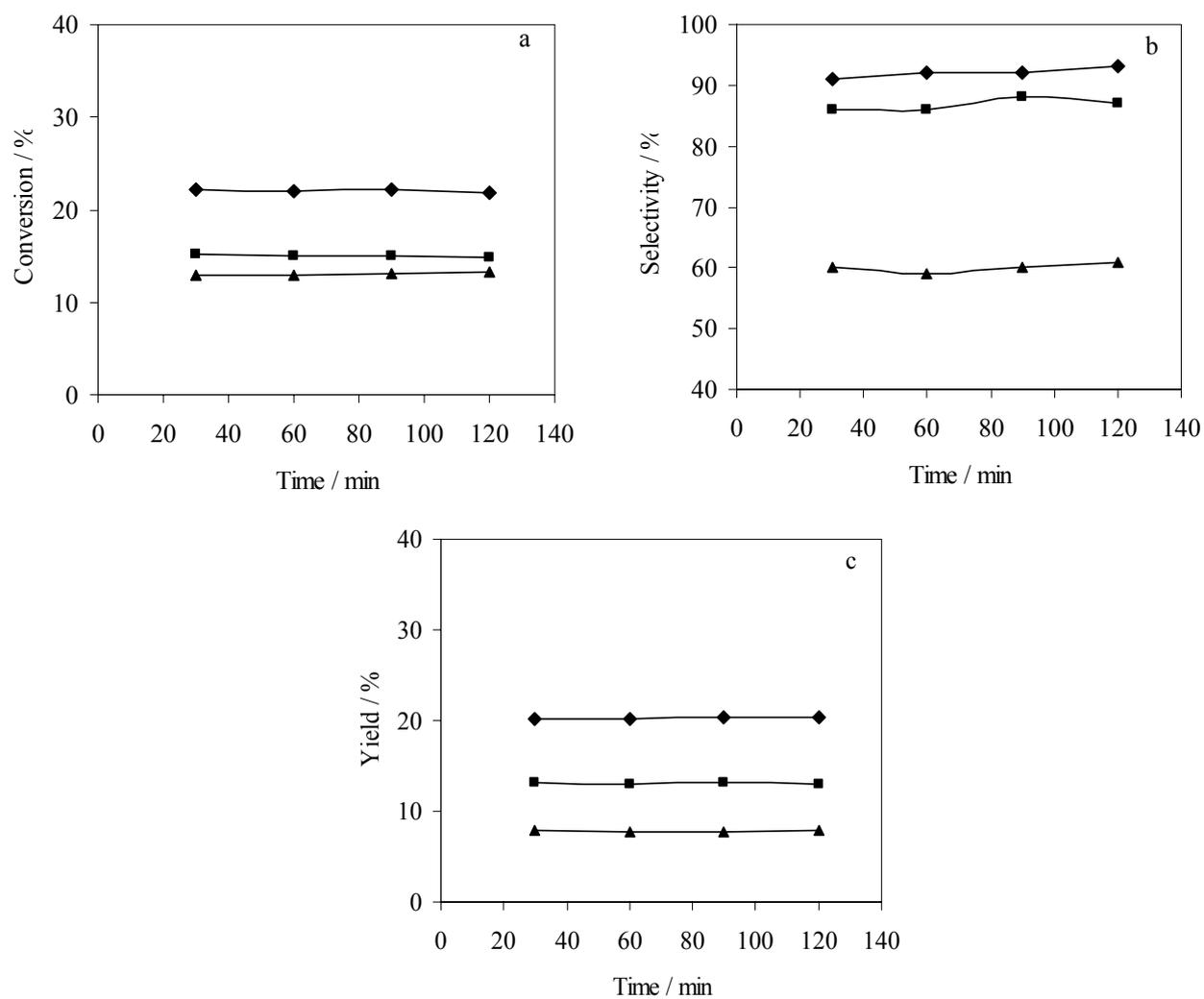
Fig. 3 Conversion (a), Selectivity (b) and Yield (c) of dehydrogenation of catalysts (♦) Sn/Pt/Al_2O_3-Axen,; (■) Sn/Pt/Al_2O_3-synthesized and (▲)Sn/Pt/Al_2O_3-Merck

The catalyst prepared with Axen Al_2O_3 has high values. The structure of this catalyst is gamma Al_2O_3 with cubic structure. The XRD of the catalyst prepared by aluminum hydroxide showed that the support is gamma Al_2O_3. Compare to catalyst with Axen Al_2O_3 the catalyst showed lower conversion, selectivity and yield. The catalyst prepared by Merck alumina showed the least conversion, selectivity and yield that it could be related to the presence of two different phases of alpha and gamma Al_2O_3.

Table 2
Conversion, selectivity and yield of catalysts

Catalyst	Conv (%)	Select (%)	Yield (%)
Sn/Pt/Al$_2$O$_3$ (Axen)	22	92	20.2
Sn/Pt/Al$_2$O$_3$ (synthesized)	15	87	13.1
Sn/Pt/Al$_2$O$_3$ (Merck)	13	60	7.8

$$Conv = \frac{\left[\left(F_{in} \times iC_{4in}\%\right) - \left(F_{out} \times iC_{4out}\%\right)\right]}{\left(F_{in} \times iC_{4in}\%\right)} \times 100\% \qquad (1)$$

$$Sel = \frac{\left(F_{out} \times ISOBUTENE_{out}\%\right)}{\left[\left(F_{in} \times iC_{4in}\%\right) - \left(F_{out} \times iC_{4out}\%\right)\right]} \times 100\% \qquad (2)$$

$$Yeild = \frac{Conv \times Sel}{100} \qquad (3)$$

where F_{in} is the molar inlet flow rate, M_{in} is massive inlet flow rate, F_{out} is molar outlet flow rate and i-C_{4in} % is molar percent inlet isobutane.

4. Conclusion

The results showed that all catalysts are stable up to 873 K. This temperature is higher than operational temperature. Sequential impregnation produces catalysts which in case of Al_2O_3 from Axen is very efficient catalyst for isobutane dehydrogenation.

Acknowledgment

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