

# Dehydrogenation of Isobutane Over Nanoparticles of Pt/Sn Alloy on Pt/Sn/Na-Y Catalyst: the Effect of Tin Precursor on the Catalyst Behavior

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**ABSTRACT:** *In this research Na-Y was synthesized by hydrothermal method and used as support for preparation of Sn/Pt/Na-Y catalysts using two different tin precursors,  $Bu_3Sn(Cl)$  and  $SnCl_2 \cdot 2H_2O$ , by sequential impregnation, in which the Pt was deposited first and in the next step Sn was deposited. The catalysts were characterized by  $H_2$  chemisorption, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray powder diffraction (XRD) and, thermogravimetric analysis (TG) techniques. Elemental analysis of the catalysts was also carried out by X-ray fluorescence analysis (XRF). Dehydrogenation of isobutane was studied in a reactor under atmospheric pressure at 848 K. The conversion, selectivity and the yield of product and the efficiency of prepared catalysts were calculated. The aim of this work was to investigate effect of different Sn precursor and Pt dispersion on the performance of the prepared catalysts.*

**KEY WORDS:** *Zeolite-Y, Bimetallic catalysts, Supported platinum-tin catalysts, Isobutane dehydrogenation, Isobutene.*

## INTRODUCTION

Heterogeneous catalytic systems, which composed of more than one metal component, are of paramount importance in modern catalysis [1]. Multicomponent catalysts have found widespread use because combination of two or more metals can lead to synergistic effects such as increasing of catalytic activity, enhancing the catalyst lifetime, and improving the product selectivity [2, 3].

Although an extraordinarily large number of bimetallic catalysts have been examined by various researchers, a brief survey of recent literature demonstrates the great interest in the Pt/Sn catalytic system [4-13]. Multicomponent catalysts based on the Pt/Sn combination have found widespread industrial usage, such as naphtha reforming [14, 15], reduction of

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nitrogen oxides in flue gases [16], and the dehydrogenation of light alkanes [17]. The deactivation of Pt-based catalysts used in reforming and dehydrogenation reactions is generally a fast process. It is known that the addition of elements like Re [2], Sn [18] and In [19] increases the lifespan of these catalysts.

Platinum-based materials are employed extensively as catalysts for the reforming of hydrocarbon streams in the production of petrochemicals and gasoline [20]. Supported bimetallic platinum-tin catalysts are now widely used to dehydrogenate isobutane into isobutene [21].

Preparation of catalytic materials that can be employed on an industrial scale and show high activity, selectivity and stability is an area of interest. In this manner, the active phase 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 material (with a high surface area and suitable mechanical strength).

Such immobilization not only disperses the metal, but also increases its thermal stability and hence the catalyst life. The common preparation methods of dispersed metal catalysts require a combination of different unit operations; which include the introduction of the metal precursor on the support by impregnation, drying and calcination, 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 for a short time, dried and calcined [22].

It is reported that in the silica-supported Pt/Sn catalysts, tin interacts with platinum to form Pt/Sn alloy particles, which reduces the size of surface Pt ensembles and inhibits the formation of highly dehydrogenated surface species required for the competing isomerization, hydrogenolysis, and coking reactions [20].

The direct one-step conversion of n-butane to isobutene was also investigated over H-Y zeolite supported platinum and platinum-tin catalysts. Catalytic results over monometallic Pt catalysts showed that dispersion of Pt mainly affects the selectivity towards reaction products, larger Pt ensembles resulting in a higher degree of cracking/hydrogenolysis reactions and consequently to a lower n-butenes and isobutene formation.

Addition of tin has been found to significantly improve both the selectivity to isobutene and the resistance of the catalytic system toward deactivation. The improved stability of Pt/Sn catalysts has been related to the lower surface acidity of the system in the presence of Sn, which results in a reduced formation of carbonaceous deposits responsible for catalysts deactivation [23].

## EXPERIMENTAL

All of materials were prepared from Merck and Degussa.

### *Synthesis of Na-Y-zeolite*

The zeolite Y seeds were prepared as following: To a solution of aluminum powder (0.612 g) in distilled water (18 mL) was added sodium hydroxide (7.5 g) and stirred for 60 min (solution A). To a solution of sodium hydroxide (7.5 g) in distilled water (20 mL) was added colloidal silica (7.5 g) at 343K (solution B). Solution A was added to solution B and stirred for 110 min. This mixture was used as seed solution. A solution of hydrated aluminum sulfate (10.5 g) in distilled water (40 mL) was added to a solution of sodium hydroxide (5.2 g) and colloidal silica (10 g) in distilled water (25 mL) to prepare the aluminosilicate gel. After addition of seed solution (7.0 g) to aluminosilicate gel (22.5 g), the mixture was transferred into an autoclave (stainless steel with Teflon internal wall) and heated at 366-368 K for 24 h. The solids were filtered, washed with distilled water several times and dried at 383 K for 12 h [24, 25].

### *Preparation of catalysts*

The catalysts were prepared by sequential impregnation. Before the impregnation step, the supports were dehydrated at 383 K for 6 h in an oven [22].

A prescribed amount of chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) was prepared to yield 0.50 wt % of platinum/support samples. Aqueous solution containing a prescribed amount of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and ethanol solution of  $\text{Bu}_3\text{Sn}(\text{Cl})$ , were also prepared to yield 0.6 wt % of tin/platinum/support samples.

After impregnation, the impregnated material undergoes a drying treatment at 383 K for 17 h to eliminate the solvent used in the previous impregnation step. The impregnated and dried carrier was then calcined at 823 K for 2 h. During the calcinations procedure,

Table 1: Results of XRF analysis of synthesized catalysts.

Catalyst	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	PtO <sub>2</sub>	SnO <sub>2</sub>	LOI
Sn <sub>1</sub> /Pt/Na-Y	15.08	53.19	10.36	0.58	0.74	20.05
Sn <sub>2</sub> /Pt/Na-Y	15.11	53.70	10.48	0.56	0.71	19.44

metal precursor decomposes with formation of an oxide and removal of gaseous products (usually water, CO<sub>2</sub>). In this technique, a homogenous dispersion of metal on support is achieved especially when dealing with a low metal concentration.

The obtained powders were converted to pellets under 10 bar pressure. Each pellet has a 50 mg weight, 2 mm thickness, and 5mm diameter. The catalysts were characterized by H<sub>2</sub> chemisorption, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray powder diffraction (XRD) and, thermogravimetric analysis (TG) techniques. Elemental analysis of the catalysts was also carried out by X-ray fluorescence analysis (XRF). H<sub>2</sub> uptake was measured in a static system operating at room temperature. Before the measurements, the samples have been reduced in H<sub>2</sub> at 823 K for 1 h then cooled to room temperature. Chemisorptions' measurements were performed using a Micromeritics ASAP 2000. The particle size of the metal loaded on catalysts was estimated by transmission electron microscopy. The catalysts, stored under air, were suspended in ethanol and ultrasonically dispersed. Drops of the dispersions were applied on a copper grid-supported carbon film. A Philips CM12 transmission electron microscope, operated at 120 kV, was used to investigate the samples. Scanning electron microscopy and energy dispersive X-ray (EDX) analysis were performed with a Philips XL30. XRD patterns of the samples were recorded on a Bruker D8 ADVANCE using CuK<sub>α</sub> radiation. TG of the samples was recorded using a Metler thermobalance TG50 instrument. Elemental analysis by XRF was performed with S4 PIONEER (BRUKER).

Isobutane dehydrogenation was performed in a reactor working under atmospheric pressure at 848 K with an isobutane/hydrogen ratio of 2/1 and flow rate dimension was (mL/min). After hydrogen treatment at 823 K, tin and platinum is in reduced form and in which the tin atoms are located on the surface of the metallic particles [20].

Reactants and products were analyzed by PRICHROM 2100 gas chromatograph equipped with an automatic gas-sample valve. Products were separated in a packed column (SS 316, 6 m, 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 which is converted into all products. The selectivity of isobutene is defined as the percentage of the total amount of consumed isobutane which is converted into isobutene. The yield of isobutene is obtained by multiplying the selectivity (%) by the total conversion (%) divided by 100. These calculations were carried out by the following [26].

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

$$\text{Sel} = \frac{(F_{\text{out}} \times \text{ISOBUTENE}_{\text{out}} \%)}{[(F_{\text{in}} \times iC_{4\text{in}} \%) - (F_{\text{out}} \times iC_{4\text{out}} \%)]} \times 100 \%$$

$$\text{Yield} = \frac{\text{Conv} \times \text{Sel}}{100} \%$$

F<sub>in</sub>: molar inlet flow rate

M<sub>in</sub>: massive inlet flow rate

F<sub>out</sub>: molar outlet flow rate

i-C<sub>4</sub><sub>in</sub> %: molar percent of inlet isobutane

## RESULTS AND DISCUSSION

### Characterization of catalysts

XRF analysis of catalysts is shown in table 1. The results show that SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of synthesized zeolite-Y as support was 6. Thermal decomposition temperature of zeolite-Y is under 1273 K. Therefore, loss on ignition (LOI) of these catalysts was 19-20 % that it was obtained according to ASTM test method D 1208.

XRD pattern of zeolite-Y is shown in Fig. 1 (JCPDS: 38-0239), before and after impregnation that it does not show any changes (Fig. 1 (A)). It was observed that the crystallinity of Sn/Pt/Na-Y is kept after impregnation of metal. XRD patterns of Sn<sub>1</sub>/Pt/Na-Y and Sn<sub>2</sub>/Pt/Na-Y

Table 2: XRD data of synthesized cataly.

Reference	2 $\theta$	6.176	15.616	23.580	31.362	20.305
	I/I <sub>0</sub>	100	31	30	24	20
Synthesized zeolite-Y	2 $\theta$	6.102	15.622	23.601	31.381	20.317
	I/I <sub>0</sub>	100	30	28	22	19

Table 3: Lists the H/Pt ratios determined for the both catalyts.

Catalyst	H/Pt <sub>total</sub>	H/Pt <sub>strong</sub>
Sn <sub>1</sub> /Pt/Na-Y	0.40	0.19
Sn <sub>2</sub> /Pt/Na-Y	0.44	0.23

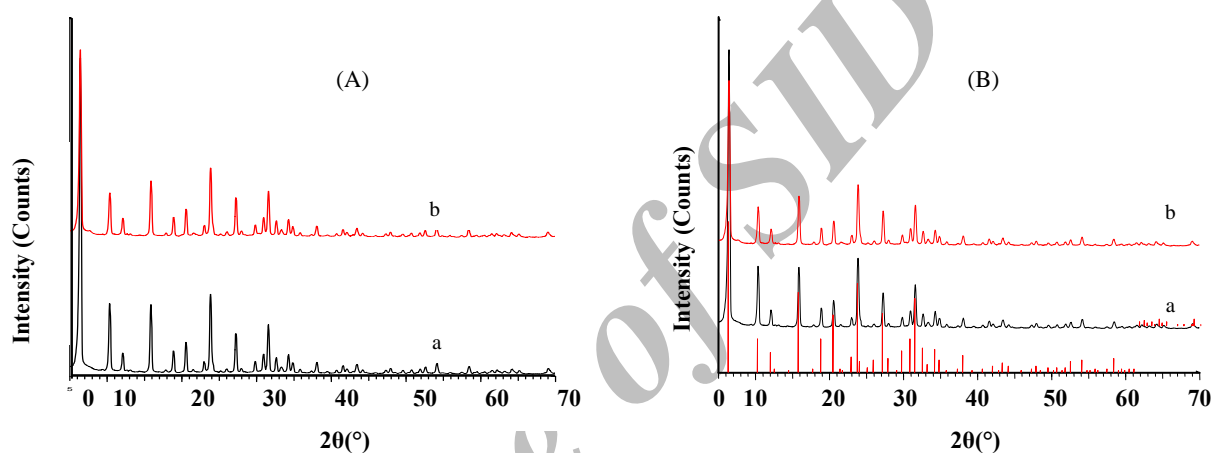


Fig. 1. X-ray diffraction pattern of (A) zeolite-Y before (a) and after (b) impregnation and (B) Sn<sub>1</sub>/Pt/zeolite-Y (a) and Sn<sub>2</sub>/Pt/zeolite-Y (b).

catalysts are shown in Fig. 1 (A) that it does not show any changes. XRD technique has been used for identification and quantification of zeolite. Several reports are available on using XRD method for estimating crystallinity [27, 28]. Crystallinity has been estimated for the synthesized sample as following:

$$\frac{\sum \text{Relative intensities of sample}}{\sum \text{Relative intensities of standard}} \times 100 \%$$

Therefore, the crystallinity percent of zeolite-Y was estimated 97.1 % (table 2).

The thermal behavior of the catalyts was studied in the range of 298-873 K in nitrogen atmosphere and the heating rate was 10 K.min<sup>-1</sup> by TG technique. Final weight loss of the catalyts prepared by Bu<sub>3</sub>Sn(Cl) and SnCl<sub>2</sub>.2H<sub>2</sub>O was 19.44 % and 20.05 %, respectively, which is due to the dehydration of the samples. Up to 873 K,

no more thermal event is observed. The XRD patterns of the samples heated at 873 K was unaltered. This confirms the thermal stability of products at this temperature.

Typically in the Chemisorption's measurements, 0.5 g of catalyts was dried in flowing helium at 523 K for 1 h with subsequent evacuation at 323 K for 1 h. The samples were reduced in hydrogen at 673 K for 1 h, cooled down in hydrogen to 473 K, and evacuated for 1 h at this temperature. Subsequently the sample was cooled down to room temperature. The first isotherm was obtained at 308 K. The H/Pt<sub>total</sub> ratios were determined based on the adsorbed amounts of hydrogen determined with this isotherm by extrapolation of the linear part to zero pressure. After the first isotherm was measured, the sample was evacuated at 308 K for 1 h and the second isotherm was obtained. The H/Pt<sub>strong</sub> ratios were calculated by subtracting the ratios obtained with the second isotherms from the H/Pt<sub>total</sub> ratios. Table 3 lists

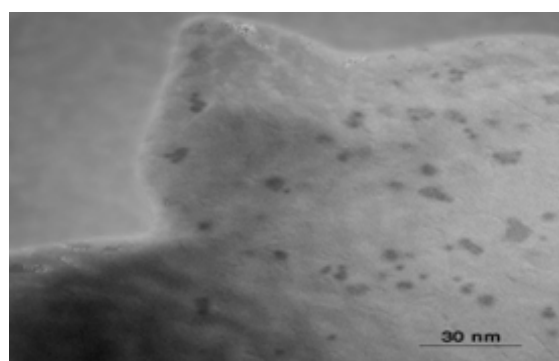
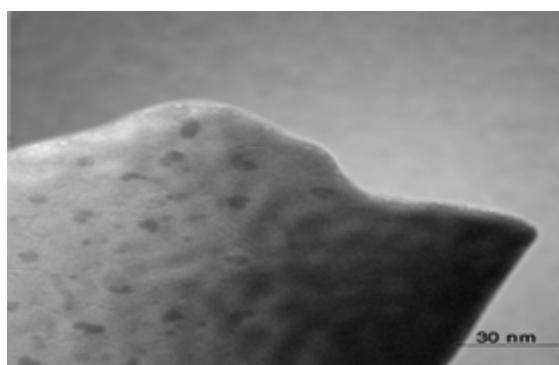


Fig. 2: TEM images of  $\text{Sn}_1/\text{Pt}/\text{Zeolite-Y(a)}$  and  $\text{Sn}_2/\text{Pt}/\text{Zeolite-Y(b)}$  catalysts.

the H/Pt ratios determined for the both catalysts. Both the ratios obtained in the first isotherm,  $\text{H}/\text{Pt}_{\text{total}}$ , and the ratios obtained after subtraction of the amount of removable hydrogen at 308 K,  $\text{H}/\text{Pt}_{\text{strong}}$ , vary significantly. However, the  $\text{H}/\text{Pt}_{\text{total}}$  ratio is for each catalyst about twice as high as the  $\text{H}/\text{Pt}_{\text{strong}}$  ratio, which shows that the correlation with Pt surface area is the same for both numbers. According to conventional use, the catalysts are compared on the basis of  $\text{H}/\text{Pt}_{\text{strong}}$  ratios. The  $\text{H}/\text{Pt}_{\text{strong}}$  ratio of impregnated zeolite in  $\text{Sn}_1/\text{Pt}/\text{Na-Y}$  and  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$  is 0.19 and 0.23 respectively.

Although quantification of the platinum surface sites on the basis of hydrogen chemisorption results is controversial, the observed difference in H/Pt ratio for different catalysts based on the same support must be due to a difference in dispersion.

The size of Platinum particles in the  $\text{Sn}_1/\text{Pt}/\text{Na-Y}$  were obtained in the range 6-10 nm (Fig. 2) while no platinum particles larger than 6 nm were observed on the  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$ . The TEM images of  $\text{Sn}_1/\text{Pt}/\text{Na-Y}$  and  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$  were analyzed as described in experimental section. TEM analysis of the Pt on zeolite-Y catalyst

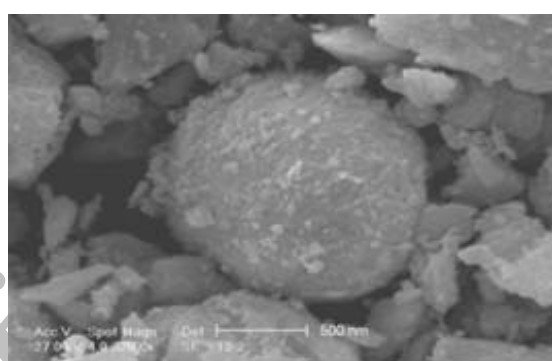
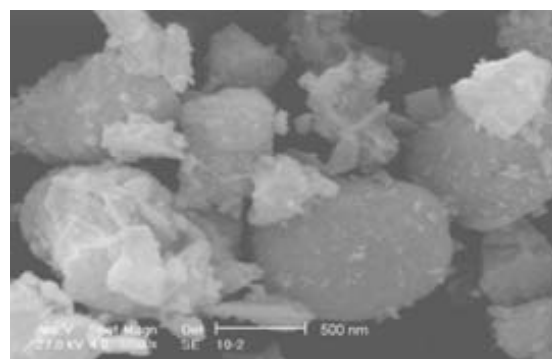


Fig. 3: SEM images of  $\text{Sn}_1/\text{Pt}/\text{Zeolite-Y(a)}$  and  $\text{Sn}_2/\text{Pt}/\text{Zeolite-Y(b)}$  catalysts after calcination.

showed the platinum to be well dispersed in the  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$  catalyst. These distributions showed that the average size of the Pt particles of the  $\text{Sn}_1/\text{Pt}/\text{Na-Y}$  catalyst is higher than that of the  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$  catalyst. Moreover, the number of particles per gram of  $\text{Sn}_1/\text{Pt}/\text{Na-Y}$  is higher than that per gram of  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$ .

Transmission Electron micrographs (TEM) of the  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$  indicated that the metal particles in this system were evenly dispersed and were 4-6 nm size range, while for the  $\text{Sn}_1/\text{Pt}/\text{Na-Y}$  the metal nanoparticles were unevenly distributed with a size range from 6-10 nm.

SEM images of  $\text{Sn}_1/\text{Pt}/\text{Na-Y}$  and  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$  catalysts are shown in Fig. 3. Homogenous dispersion of the metallic clusters on the support is provided by using the impregnation method. In this manner, the active phase must be in a sufficiently high dispersed form which results in a large specific surface area and consequently in a maximum specific activity. EDX analysis established that bimetallic particles were formed in both  $\text{Sn}/\text{Pt}/\text{Na-Y}$  catalysts.

The need for the extremely low heating rate for the preparation of highly dispersed Pt particles inside zeolite

Y is explained by the slow desorption of water and ammonia from the zeolite Y micropores. In addition, the zeolite micropores might well be able to stabilize mobile Pt species [29].

#### Dehydrogenation of isobutane into isobutene

The inlet isobutane was analyzed and the gas composition was  $\text{CH}_4=0.05\%$ ,  $\text{C}_2\text{H}_6=0.08\%$ ,  $\text{C}_3\text{H}_6=0.89\%$ ,  $\text{iC}_4=98.65\%$ ,  $\text{nC}_4=0.34\%$ . After dehydrogenation reaction, the conversion, selectivity and yield of the product was calculated, according to the products analysis.

The reaction was studied in the range of 773 to 873 K. The experimental conditions (WHSV) were fixed such that the conversions were low and not limited by the thermodynamics (Fig. 4). Extrapolation of the data can give the thermodynamic conversion value of the catalysts.

To study the effect of tin precursor, two catalysts with two different tin precursors were synthesized. Dehydrogenation reaction was carried out at present of hydrogen and isobutane under following conditions:

Catalyst weight (2 g); temperature reaction (848 K); pressure (1 atmosphere), isobutane/hydrogen molar ratio was 2/1 and WHSV ( $2.5\text{ h}^{-1}$ ).

The reactor testing system that has been used for dehydrogenation of isobutane, was designed and constructed in Petrochemical Research Company. All of connecting lines were made by stainless steel. A quartz tube was used as reactor with 60 cm length and 10 mm diameter.

The conversion, selectivity and yield of isobutane dehydrogenation are calculated and represented in Fig. 5 as diagrams. It was known that the catalysts with higher Pt dispersion show higher selectivity to isobutene and produces smaller amounts of other products [23].

#### CONCLUSIONS

In this work  $\text{Sn}/\text{Pt}/\text{Na-Y}$  catalysts were prepared from two different tin precursors,  $\text{Bu}_3\text{Sn}(\text{Cl})$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , by sequential impregnation. The results showed that the synthesized catalysts are stable up to 873 K. This temperature is higher than operational temperature. The conversion, selectivity and yield of isobutane dehydrogenation showed when  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$  catalyst was used; higher conversion, selectivity and yield were

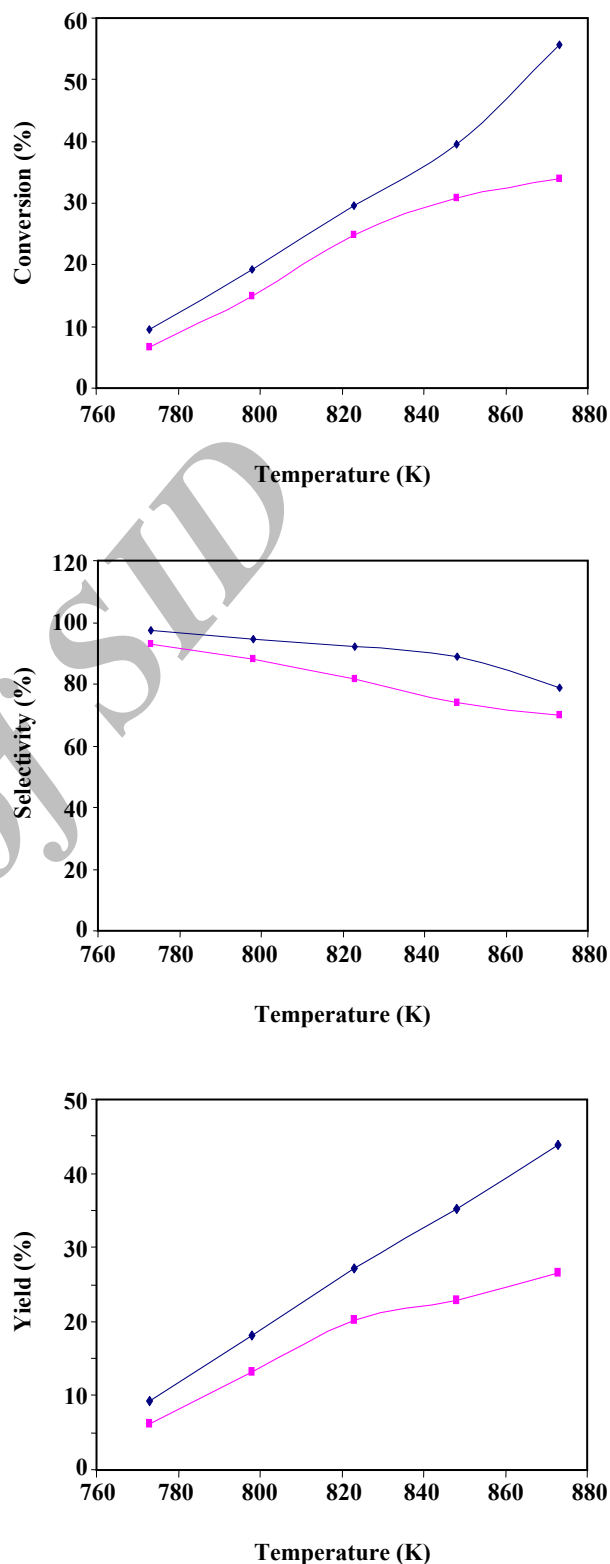


Fig. 4: Conversion (a), selectivity (b) and yield (c) of  $\text{Sn}_2/\text{Pt}/\text{Na-Y}$  catalyst (■) and  $\text{Sn}_2/\text{Pt}/\text{Y-zeolite}$  catalyst (◆) in the range of 773-873 K.

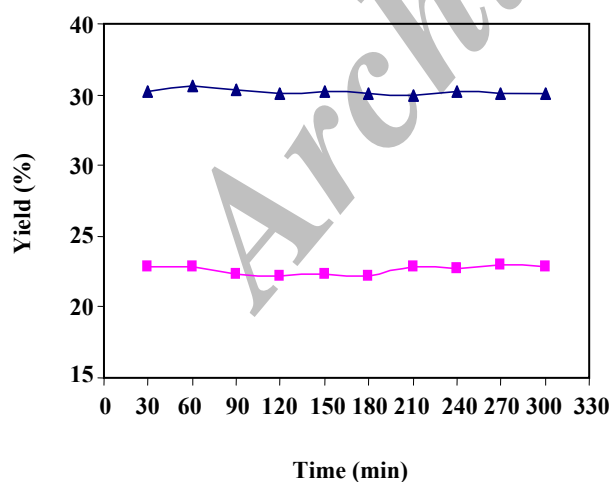
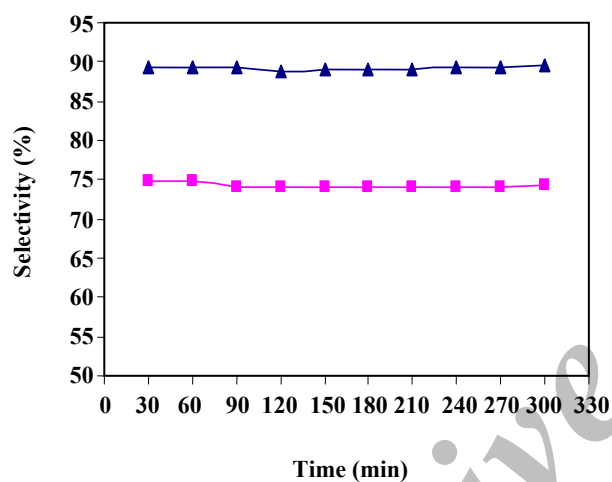
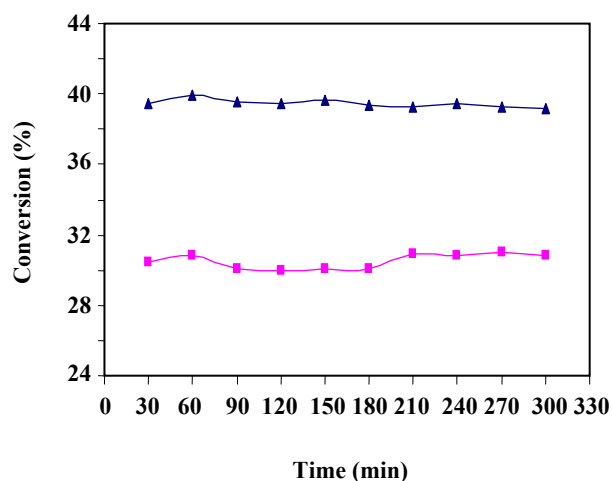


Fig. 5: Conversion (a), selectivity (b) and yield (c) of Sn<sub>1</sub>/Pt/Na-Y catalyst (■) and Sn<sub>2</sub>/Pt/Y-zeolite catalyst (▲) at 848 K.

obtained. It is believed that the presence of tin in the catalyst surface enhances formation of Sn-Pt particles and prevents formation of local platinum clusters. The Sn-Pt also prevents the association of dehydrogenated products on the catalyst surface, which compete with main reactants and cause coke formation [22].

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