

SYNTHESIS OF Pt-Re-Sn NANO-CATALYST: ROLE OF NANO-PARTICLE SIZE ON ACTIVITY AND SELECTIVITY IN N-HEPTANE REFORMING

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Received July 8, 2018; Accepted September 28, 2018

Abstract

The bimetallic and trimetallic 0.3 wt. % Pt–0.3 wt. % Re–x wt. % Sn/Al₂O₃ catalysts (x = 0, 0.07, 0.2, 0.3, 0.4) were prepared through impregnation technique and applied in n-heptane reforming as a model fuel. The catalysts were characterized using ICP-AES, BET, TPR, H₂ chemisorption, and Volhard–Charpentier method. All catalysts were assessed in terms of their activity, selectivity and products' yield in a fixed bed micro reactor for n-heptane reforming process. The results showed that the most appropriate percentage of tin metal, as a promoter, was 0.3%. At least the trimetallic catalyst was synthesized using Chemical Vapor Deposition (CVD) technique with the optimized catalyst compositions. According to TEM pictures, the catalysts produced with CVD technique have smaller particles with very narrow particle size distributions. The nano-particles synthesized by the proposed CVD technique increased catalyst activity (g HC/g cat. hr) and the selectivity of isoparaffin to both of aromatics and undesirable light gaseous products from 37% and 39.5% to 51% and 51.62% respectively, and the selectivity of methane decreased from 1.23% to 0.71%.

Keywords: -Heptane reforming; Impregnation; CVD, Pt-Re-Sn/Al₂O₃ catalyst; Dispersion.

1. Introduction

The naphtha reforming process is very important in the petroleum refining and petrochemical industries because it is one of the main suppliers of high octane gasoline and aromatic hydrocarbons. Great improvements in the process have been occurred since 1949 when a bifunctional metal–acid catalyst was introduced [1-2]. The metal function is provided by Pt, which is supported over the acid function, chlorinated gamma alumina. Alumina support has important industrial applications in the petroleum industry in reforming and hydrotreating processes. The catalytic properties of Pt can be improved by the addition of another metal, such as Re, Sn or Ge. The major reactions promoted by bifunctional catalysts are hydrogenation, dehydrogenation, isomerization, cyclization and hydrocracking, Therefore, the reaction to produce aromatic compounds is bifunctional since it uses both the metal and the acid sites [3-4]. The adverse effect of hydrogenolysis reaction that generate light and volatile hydrocarbons stops by sulphidation. Sulphidation venoms the hydrogenolysis active sites and the catalyst activity decreases, also sulphidation is costly operation and catalyst need to rebuild. Recently, trimetallic catalysts were studied in order to replace the sulphidation of the metallic Pt–Re [1, 4-6]. The wet impregnation method has traditionally been used to prepare bimetallic reforming catalysts. It seems necessary to do studies to improve the catalysts performance through employing different methods of synthesis. In this sense, the Chemical Vapor Deposition (CVD) method has been reported as an alternative to produce better catalysts. The CVD process includes reactions of gaseous reactant in an active environment such as heat, light,

plasma which is used to form a stable solid product. The CVD technique for catalyst preparation, enables the control of metal particle size with a narrow particle size distribution, regardless of metal content [7-11].

Bilone and Helle mentioned that with increasing in the distribution of metal particles, dehydrogenation reaction increases [1, 12]. Gaseous light product was decreased and liquid product and the selectivity of isoparaffin to both of aromatics and undesirable light gaseous increased by CVD synthesized catalysts. This matter can be attributed to the high dispersion and uniform distribution of active metal particles on the support in CVD synthesized catalyst in comparison to impregnated catalysts [13-18].

In this study bimetallic and trimetallic 0.3 wt.% Pt–0.3 wt.% Re–x wt.% Sn/Al₂O₃ catalysts (x =0, 0.07, 0.2, 0.3, 0.4) were prepared through impregnation technique. The catalysts were assessed in terms of their activity, selectivity, stability and products' yield in a fixed bed micro reactor at 500°C and 1 bar for n-heptane reforming as model fuel. The results showed that the most appropriate percentage of tin metal, as a promoter. At least the trimetallic catalyst was synthesized using CVD technique with the optimized catalyst compositions. All catalysts also were characterized by BET, TPR, H₂ chemisorption, ICP-AES, XRD and Volhard–Charpentier method.

2. Experimental

2.1. Catalysts preparation

The support used was a commercial high-purity γ -alumina (Cyanamid Ketjen CK300) and main impurities were Na (5 ppm), Fe (150 ppm) and S (50 ppm). The extruded alumina pellets were sieved and the 35–80 mesh fractions was separated and dried at 70°C for 8 hr, 120°C overnight and then calcined at 450°C for 3 hr under flow of air (60 cm³/min.gr). The specific surface area of this support was 212.40 m²g⁻¹, the pore volume 0.57 cm³. Impregnation method was used in order to synthesize 0.3 wt.% Pt–0.3 wt.% Re–x wt.% Sn/Al₂O₃ (x= 0, 0.07, 0.2, 0.3, 0.4) catalysts. The concentration of Pt and Re and Sn were adjusted using aqueous solutions of H₂PtCl₆ and HReO₄ and SnCl₂ (Merck). The catalysts prepared by means of this protocol were denoted as Cat₁–Cat₅. Next, the catalyst was dried at 120°C and calcined at 370°C for 3 hr and slowly exposed to an oxygen atmosphere during the cooling step. The catalyst with the optimum percentage of tin (x= 0.3 wt%) synthesized by the CVD method through direct liquid injection (DLICVD). Precursor used in this method is SnCl₄ and was adsorbed on catalyst surface and the catalyst was dried, calcined according to above procedure. The catalyst prepared by this method, denoted as Cat₆. The compositions in all calcined catalysts were verified by an ICP-AES system. The catalysts nomenclature and properties are listed in Table 1.

Table 1. Chemical composition and chlorine content of the catalysts

Catalyst	Targeted composition (wt. %)				Measured composition (wt. %)			
	Pt	Re	Sn	Cl	Pt	Re	Sn	Cl
Cat ₁	0.3	0.3	0	0.8	0.291	0.289	0	0.78
Cat ₂	0.3	0.3	0.07	0.8	0.291	0.292	0.067	0.77
Cat ₃	0.3	0.3	0.2	0.8	0.289	0.295	0.19	0.78
Cat ₄	0.3	0.3	0.3	0.8	0.296	0.297	0.294	0.78
Cat ₅	0.3	0.3	0.4	0.8	0.290	0.293	0.398	0.79
Cat ₆	0.3	0.3	0.3	0.8	0.288	0.293	0.288	0.84

2.2. Catalyst characterization

Morphology of all catalysts (Cat₁–Cat₆) were characterized by Volhard–Charpentier method, BET, TPR, and H₂ chemisorptions according to procedure previously reported [1].

2.3. Catalyst activity and selectivity

One gram of each catalyst (diluted with 4 g quartz) was charged in an Inconel fixed bed reactor of 2.54cm internal diameter, forming a bed of 54cm height. The catalyst was reduced in situ with hydrogen (60 ml/min) for 4 h at 500°C. Then n-heptane (Merck, 99.9%) as a model fuel (molar ratio of H₂/n-heptane =7.5) was injected to the reactor and the reaction was carried out for 6 hr at 500°C, 0.1 MPa. The reaction products were analyzed in a HP 5890 SERIES II Gas Chromatograph equipped with flame ionization and thermal conductivity detectors. The products' yields were obtained from the chromatographic data. The yield or the percentage of n-heptane converted into any product is calculated as [1-2]:

$$\text{Yield}_i = \frac{\%C_i 100X}{\sum \%C_i} \quad (1)$$

where X is the total conversion; the notification i is any compound concentration in the reaction products; $\sum \%C_i$ the sum of concentration of all reaction products (n-heptane is not included).

For each experiment, the sum of all the C_i yields was in agreement with the n-heptane conversion. The Carbon balance was considered satisfactory when the error was < 3 %. Fig. 1 shows a schematic view of experimental setup.

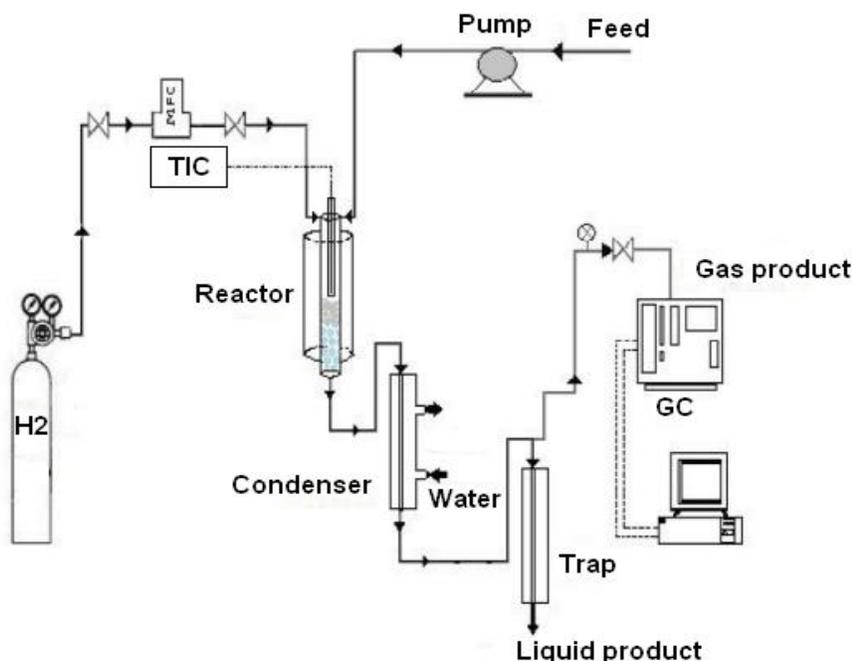


Fig. 1. Schematic view of experimental setup

3. Result and discussion

3.1. Catalyst characterization

The chlorine content and elemental compositions of the calcined catalysts, measured by Volhard–Charpentier [1, 19] and ICP method, are given in Table 1. The measured metal loadings were found to be slightly lower compared to the targeted values. As shown, the chlorine content in the catalyst prepared by CVD technique is higher than the targeted value. This can be due to the presence of chloride in precursor (SnCl₄) used for catalyst preparation.

Table 2 presents the surface morphological characterization results for support, the bimetallic and trimetallic catalysts synthesized in both CVD and impregnation methods. The results

of BET surface area (S_{BET}) in this table show that in all cases the metal incorporation reduced the specific surface area of the catalysts when compared to the support. Lower S_{BET} and pore volume of the Cat₁-Cat₆ catalysts indicate some pore blockage due to Pt-Re loading on the support. However, this table shows that the amount of pore blockage is lower in the case of the catalyst prepared by CVD technique. In case of Cat₄ and Cat₆ catalysts, with equal amount of active metals and promoter loading, have different S_{BET} , which is attributed to synthesis technique of catalysts. The CVD technique increased the dispersion and caused the promoter particles on the support were distributed and formed a film on the entire surface. The uniform and small metal particles size produced through CVD technique increases the efficiency of the catalyst and also prevents sintering of active metals particles [16-18, 20-22].

Table 2. Textural properties of the catalysts

Sample	Preparation procedure	S_{BET} (m^2/g)	pore volume (mL/g)	Average pore diameter (\AA)
Cat1	Impregnation	209.45	0.53	80.89
Cat2	Impregnation	208.66	0.52	79.40
Cat3	Impregnation	205.15	0.51	75.36
Cat4	Impregnation	203.14	0.49	73.20
Cat5	Impregnation	192.59	0.48	65.45
Cat6	CVD	206.25	0.50	67.50
Support	-	212.40	0.57	99.80

The reducibility of the catalysts in H_2 atmosphere was determined by TPR experiments. The TPR spectra of the calcined catalysts are shown in Fig. 2.

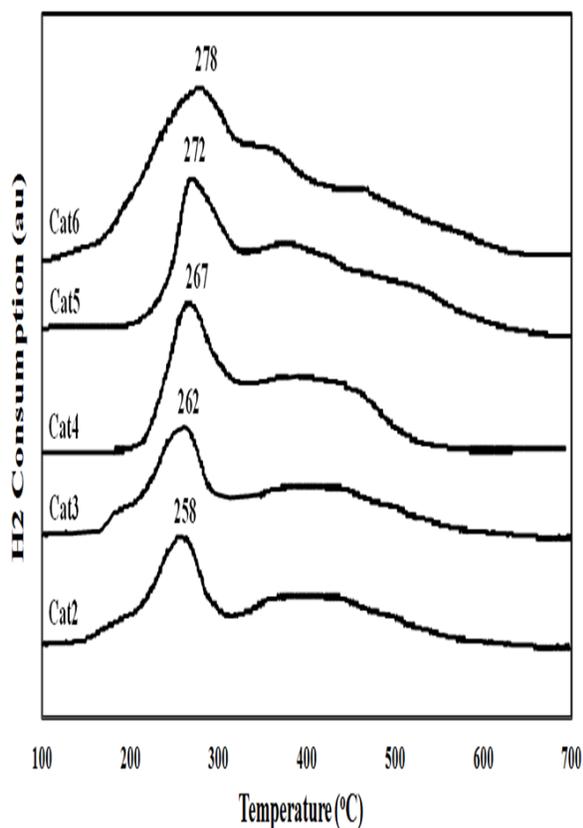


Fig. 2. TPR curves for catalysts

The Cat₄ & Cat₆ which contain the same contents of active metals and promoter have different hydrogen consumption and the hydrogen consumption of Cat₆ was more than Cat₄. This

TPR peak temperatures and the TPR area for all samples are presented in Table 3. This technique allows getting information about the interaction of the metal components by means of the measurement of the hydrogen consumption during the reduction of the oxides at a constant heating rate. The temperature at which reduction occurs and the number of reduction peaks depend on the oxidation state of the metals, the interaction of the metal oxides with each other and with the support. As shown, the TPR peak for tin oxide is very broad, starting at 150°C and ending at 550°C , with two main reduction regions in the $200\text{--}300^\circ\text{C}$ and $380\text{--}520^\circ\text{C}$ ranges. This is an indication of interaction of Sn oxide with alumina that is able to produce tin aluminates. According to this figure the reduction peak of catalyst synthesized by CVD technique (Cat₆) shifted to higher temperature compared to the catalyst prepared by impregnation method (Cat₄). This can be attributed to difficult reduction for small particles produced in this method. In TPR spectra, the peak area is assigned to hydrogen uptake of each catalyst, so results of Table 3 show the hydrogen consumption increases when the promoters' content increase.

is attributed to small metal particles size and more and regular distribution of tin metal nano-particles in CVD synthesized catalyst which prevents sintering of active metals particles [21-24].

Table 3. Hydrogen consumption and TPR results of catalysts

Catalysts	TPR peak (oC) Sn+4→Sn0	TPR area peak	Catalysts	TPR peak (oC) Sn+4→Sn0	TPR area peak
Cat2	258	2 721	Cat5	372	4 522
Cat3	262	3 063	Cat6	378	4 017
Cat4	367	3 556			

The results of H₂ chemisorption are given on Table 4. As shown, changes in catalyst synthesis method from impregnation to CVD increase the percentage dispersion. In CVD preparation technique the promoter particles on the support were distributed through gases and sediments of atoms and formed a film on the entire surface. This method of sedimentation can produce high purity materials with structural nanometer.

Table 4. H₂ chemisorption results

Catalyst	Dispersion (%)
Cat4	15.1
Cat6	37

3.2. Reaction

Table 5 shows the results of catalysts activity and the different products' yield in n-heptane reforming reaction. The tin was added to the bimetallic catalyst to increase the isomerization step and decrease gaseous undesirable products. In the presence of tin, n-heptane is broken mostly from intermediate carbons instead of the first and last carbons of molecules [2, 6]. In case of Cat₁-Cat₄ catalysts prepared by impregnation technique, with increasing the percentage of tin promoter the activity of catalysts increased from 20.48 to 37.65, and then the catalyst activity decreased. The activity (g HC/g cat.hr) of proposed catalyst synthesized by CVD technique (Cat₆) was 51.25 compared to 37.65 for traditionally impregnated catalyst (Cat₄) with the equal amount of Sn loading. The Cat₆ is approximately two times more active, and it can be attributed to small and uniform particles size and consequently the higher dispersion of metals particles on the surface of CVD synthesized catalyst [16-18]. Comparative studies of Cat₄ & Cat₆ catalysts show that Cat₆ have smaller particle size, less pore blockage, higher S_{BET}; pore volume and percentage of dispersion which can be responsible for it's higher catalyst activity [16-18, 25].

Table 5 also shows Cat₆ synthesized through CVD technique with smaller Pt-Re ensembles (a site composed of a large number of contiguous active metal atoms) has a methane yield of 0.71% compared to the Cat₄ catalyst with methane yield of 1.23%. This is logical, since hydrogenolysis occurs better on a large ensemble, so decrease in the metals particle size is effective in inhibiting the hydrogenolytic activity of the Pt-Re ensembles [1, 26].

It must be taken into account that methane is produced mainly from a hydrogenolysis reaction catalyzed by the metal sites, while propane is formed by a bifunctional mechanism controlled by the acid function of the catalyst. As shown in this table, for impregnated catalysts series (Cat₁-Cat₄), with increasing percentage of tin from 0.07 to 0.3 wt%, gaseous light and undesirable products decreased. Comparing the product yields for impregnation catalysts (Cat₁-Cat₄), it can be seen that, benzene and toluene and methyl cyclohexane yields increased from 3.28%, 2.78% and 2.39% to 10.87%, 5.54% and 9.74% respectively. In this catalysts series, higher benzene, toluene and methyl cyclohexane yields belong to Cat₄ and it is related to the increase in dehydrogenation step through the catalytic process.

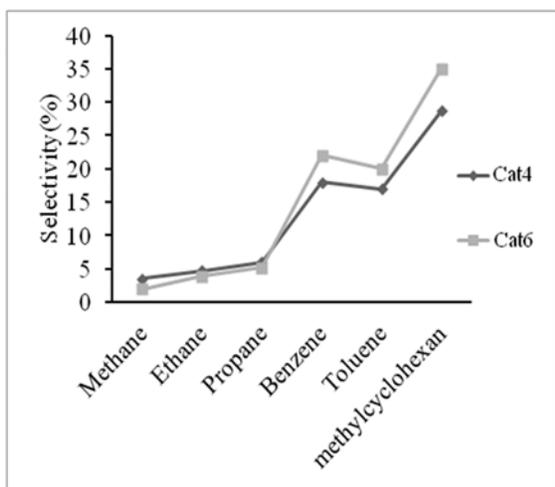


Fig. 3. Comparison selectivity of Cat4 and Cat6

As shown in Table 5 and Fig 3, Cat₆ decreased gaseous light, increased liquid products with high octane number and selectivity of isoparaffins to aromatics, in comparison to Cat₄. This matter can be attributed to the high dispersion and uniform distribution of active metal particle on the support in CVD synthesized catalyst in comparison to impregnated catalysts, which can cause to increase dehydrogenation reactions through n-heptane reforming. On the other hand, uniform distribution of small active metal particles causes olefin intermediate molecules produced on a metal site easily adsorb on adjacent metal site and don't traverse long trajectory and possible expos to existing acidic sites (capable to cracking reaction) on

the catalyst support. Therefore in CVD synthesized catalyst the possibility of two-factor reactions that lead to the production of gaseous undesirable products reduced.

Table 5. Catalysts' activity and yield of different products in n-heptane reforming reaction

Catalyst	Activity (g HC/g cat. h)	Yield (%)					
		Benzene	Toluene	Ethane	Methane	Propane	MCyH*
Cat1	20.48	3.28	2.78	5.45	3.87	7.52	2.39
Cat2	29.52	5.54	3.36	4.74	3.22	6.51	4.46
Cat3	31.36	9.63	4.70	3.65	2.24	4.45	7.32
Cat4	37.65	10.87	5.54	3.09	1.23	3.23	9.74
Cat5	35.2	10.10	5.32	3.1	1.54	3.18	8.82
Cat6	51.25	12.60	7.52	1.84	0.71	2.31	14.25

*MCyH –methyl cyclohexane

4. Conclusion

The bimetallic and trimetallic 0.3 wt.% Pt–0.3 wt.% Re–x wt.% Sn/Al₂O₃ (x = 0, 0.07, 0.2, 0.3, 0.4) catalysts were synthesized by impregnation and 0.3%Pt-0.3%Re-0.3%Sn/Al₂O₃ (optimized catalyst compositions) was synthesized by CVD method and applied in n-heptane reforming process as a model fuel. According to H₂ chemisorptions data and S_{BET}, the CVD technique produces small and uniform nano-particles and consequently increases the dispersion of nano-particles on the alumina supports. According to TPR profile, these Pt-Re nano-particles were reduced at higher temperatures due to increasing metal-support interactions. It was also found that activity and selectivity of the catalysts are dependent to the synthesize method. The proposed Pt-Re-Sn nano-catalyst synthesized by CVD technique increased the catalyst activity and the yield of benzene; toluene; and methyl cyclohexane. Also the yields of undesirable products like methane decreased.

5. Acknowledgements

The authors are thankful to the Iran National Science Foundation (INSF) for their support of this work.

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