

# Hydrogenation of Acetic Acid on Alumina-Supported Pt-Sn Catalysts

Ke Zhang, Fang Li, Haitao Zhang, Hongfang Ma, Weiyong Ying, and Dingye Fang

**Abstract**—Three alumina-supported Pt-Sn catalysts have been prepared by means of co-impregnation and characterized by XRD and N<sub>2</sub> adsorption. The influence of catalyst composition and reaction conditions on the conversion and selectivity were investigated in the hydrogenation of acetic acid in an isothermal integral fixed bed reactor. The experiments were performed on the temperature interval 468-548 K, liquid hourly space velocity (*LHSV*) of 0.3-0.7h<sup>-1</sup>, pressures between 1.0 and 5.0Mpa. A good compromise of 0.75%Pt-1.5%Sn can act as an optimized acetic acid hydrogenation catalyst, and the conversion and selectivity can be tuned through the variation of reaction conditions.

**Keywords**—Acetic acid, hydrogenation, Pt-Sn catalysts, ethanol.

## I. INTRODUCTION

ETHANOL is frequently used either in the production of beverages, dyes, and flavors or as fuels, such as gasohol [1], which is a mixture of ethanol and gasoline. Traditionally, there are two routes for the mass production of ethanol [2], namely fermentation of agricultural products, such as corn and sugar cane, as well as hydration of ethylene from petrochemical. However, the food crisis and the oil depletion make the aforementioned routes unattractive for the large scale production of ethanol.

A desirable synthesis method should be direct and robust and applicable on an industrial scale. Catalytic hydrogenation of acetic acid would meet these demands if suitable catalyst is

Ke Zhang is with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China (e-mail: zhangke0124@gmail.com).

Fang Li is with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China.

Haitao Zhang is with Engineering Research Center of Large Scale Reactor Engineering and Technology of the Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China.

Hongfang Ma is with Engineering Research Center of Large Scale Reactor Engineering and Technology of the Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China.

Weiyong Ying is with Engineering Research Center of Large Scale Reactor Engineering and Technology of the Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China (phone: 86-21-64252193; fax: 86-21-64252192; e-mail: wying@ecust.edu.cn).

Dingye Fang is with Engineering Research Center of Large Scale Reactor Engineering and Technology of the Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China.

available because theoretically acetic acid can be catalytic reduced to ethanol according to the following stoichiometry,



R. Pestman et al. have accomplished a series of experiments to explore the reactions of carboxylic acids on oxides [3-5]. Studies conducted by Willy Rachmady and M. Albert Vannice indicated that Pt supported on oxides is a promising catalyst for acetic acid hydrogenation and the most active catalyst they reported is Pt/TiO<sub>2</sub> with a product distribution of 50% ethanol, 30% ethyl acetate and 20% ethane[6-7].

Sn added to platinum-based catalysts has been proven to be beneficial to the activity maintenance and can modify the selectivity of catalysts. Pt-Sn/alumina catalysts have been used in soot oxidation [8], isobutane dehydrogenation [9], n-octane dehydrocyclization [10], transformation of olefins [11], crotonaldehyde hydrogenation [12] and citral hydrogenation [13].

In this study, three alumina-supported Pt-Sn catalysts with different Pt and Sn loading were prepared and tested at various operation conditions in order to maximize the selectivity of ethanol and minimize the production of byproducts.

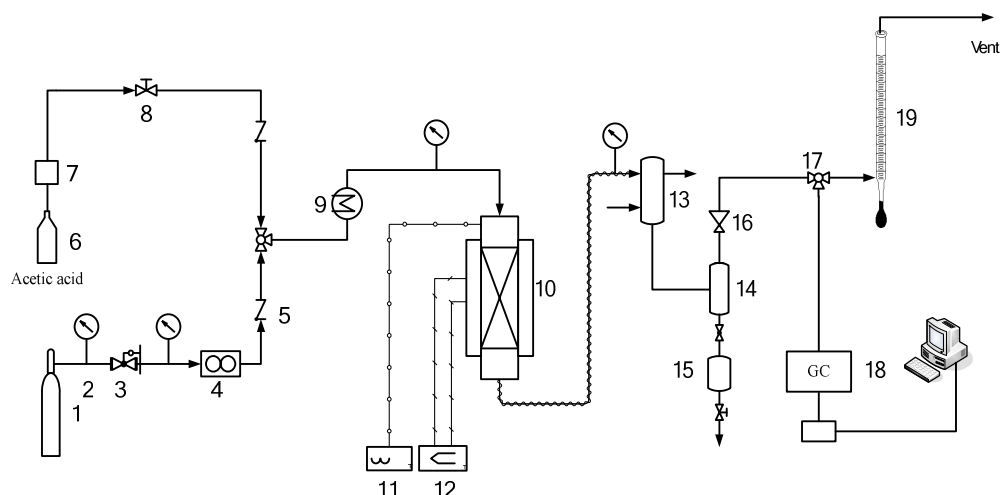
## II. EXPERIMENT

### A. Catalyst Preparation

Three bimetallic catalysts with different Pt, Sn content were prepared by co-impregnation. The Al<sub>2</sub>O<sub>3</sub> support was ground and sieved to desired size (0.2-0.3mm) and calcined at 823K for 12h to remove organic impurities before impregnation with a solution of tin salt and platinum salt, which was prepared by dissolving certain amount of SnCl<sub>2</sub>·4H<sub>2</sub>O and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in deionized water. All the catalysts were dried in an oven at 293K overnight after aged for 12h at ambient and then calcined at static air at 823K for 12h. The catalyst was denote as aPt-bSn/Al<sub>2</sub>O<sub>3</sub> where a and b represents the nominal weight percentage of each metal based on the mass of the catalyst.

### B. Activity Testing

The activity and selectivity of the various catalysts prepared were tested for the hydrogenation of acetic acid in an isothermal integral fixed bed reactor (Φ14×2×650mm). Generally, the catalyst ( 2.8g, 4ml ) was heated from ambient temperature to 623K with a ramp of 2K/min in N<sub>2</sub> atmosphere and then held at



1-Gas cylinder; 2-Pressure gauge; 3-Reducing valve; 4-Mass flow meter; 5-Non-return valve; 6-Acetic acid container; 7-Advection pump; 8-Ball valve; 9-Preheater; 10-Isothermal integral reactor; 11-Thermocouple; 12-Furnace; 13-Condenser; 14-Separator; 15-Fluid reservoir; 16-Back pressure valve; 17-Three-way valve; 18-Gas chromatograph ;19-Soap film flowmeter

Fig. 1 Scheme of the catalyst evaluation system

623K for 2h in  $H_2$  (0.1MPa) flow. The catalyst was cooled to the selected reaction temperature under  $N_2$  flow and the reaction started as acetic acid was transferred into the system by  $H_2$ . The mixture of acetic acid and  $H_2$  was preheated to maintain gas phase before entering the reactor. After passing through the condenser and the liquid-vapor separator, the effluent was sampled every 12h so as to get a steady-state performance. Composition of the tail gas was monitored on-line and the products in the liquid phase were determined off-line by a gas chromatograph Agilent 7890A. In one sampling loop,  $CO$ ,  $CH_4$ ,  $C_2H_6$ ,  $N_2$  and  $H_2$  were analyzed with a molecular sieve 5A packed column (6FT $\times$ 1/8IN $\times$ 2.1mm), a Hayesep Q packed column (8FT $\times$  1/8IN), and a thermal conductivity detector (TCD). In the other loop, C1-C6 oxy-compounds were analyzed with an HP-PLOT/Q capillary column (30m $\times$ 0.53mm $\times$ 40 $\mu$ m), a HP-INNOWAX (30m $\times$ 0.530mm $\times$ 1 $\mu$ m) capillary and a flame ionization detector (FID). Particularly, the concentration of acetic acid in the liquid phase was determined by titration. The setup of the employed catalyst evaluation system was depicted in Fig. 1. The carbon balance is within 5% error and the conversion, selectivity were determined with an accuracy of 5% according to the following formulas:

$$X_{HOAc} = \frac{N_{HOAc,in} - N_{HOAc,out}}{N_{HOAc,in}} \times 100\% \quad (2)$$

$$S_{EtOH} = \frac{N_{EtOH,out}}{N_{HOAc,in} - N_{HOAc,out}} \times 100\% \quad (3)$$

$$S_{EtOAc} = \frac{2N_{EtOAc}}{N_{HOAc,in} - N_{HOAc,out}} \times 100\% \quad (4)$$

### C. Catalyst Characterization

The BET (Brunauer Emmett Teller) surface area, average pore size diameters, and pore size distribution were determined by means of nitrogen physisorption using a Micromeritics ASAP 2020 M automated system. All samples were degassed at 400K, 1.33Pa for 6h before adsorption.

X-ray diffraction (XRD) powder patterns of the catalysts were recorded with a Rigaku D/max 2550 diffractometer using nickel filtered  $Cu K\alpha$  radiation ( $\lambda=1.54056 \text{ \AA}$ ) at room temperature. The X-Ray tube was operated at 40Kv, 100mA and scanned from  $10^\circ \sim 80^\circ$  at a speed of  $2^\circ/\text{min}$  (stepwise, 0.02) and the patterns were recorded with a  $6^\circ$  position sensitive detector.

### III. RESULTS AND DISCUSSION

A number of reactions [14] related to acetate acid can occur on supported Pt catalysts as depicted in Fig. 2. Apart from ethanol and ethyl acetate (originated from the esterification of ethanol and acetic acid), there are also a small amount of  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$  and acetaldehyde in the products (totally less than 5%).

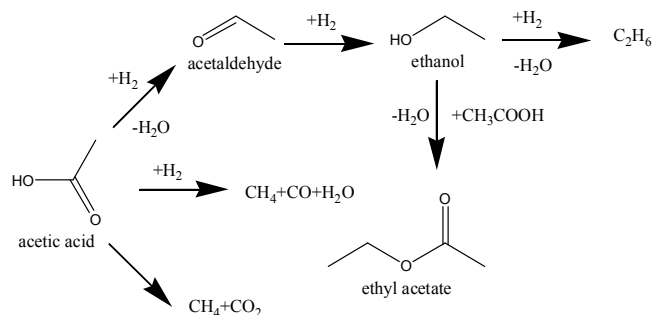


Fig. 2 Schematic diagram of stoichiometric reactions involved in the conversion of acetic acid over Pt

#### A. The Behavior of Various Catalysts

The performance of catalysts with different Pt, Sn loading was studied and the results are presented in Table I. The activity of the catalysts follows the order of: 0.75 Pt-1.5 Sn > 0.5 Pt-1.5 Sn > 0.5 Pt-5.0 Sn in terms of acetic acid conversion. Obviously, 0.5Pt-1.5Sn and 0.5Pt-5.0Sn shows distinct activity and selectivity. On one hand, the conversion of acetic acid increased from 67.48% to 84.54% with Sn loading declined from 5.0% to 1.5%, so was the selectivity of ethyl acetate (from 57.24 % to 32.50 %); on the other hand, the selectivity of ethanol increased from 38.94 % to 62.55 %. But Sn content was not the only conclusive factor, since the activity of 0.75Pt-1.5Sn was higher than that of 0.5Pt-1.5Sn though the variation of selectivity was not that remarkable.

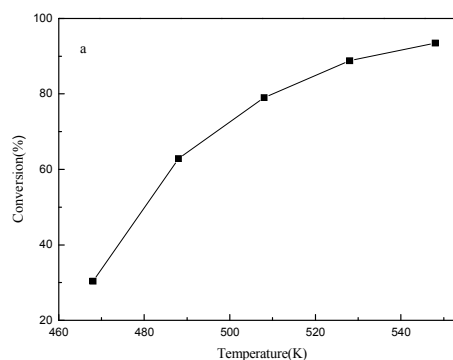
TABLE I  
PERFORMANCE OF CATALYSTS WITH DIFFERENT PT, SN LOADING<sup>A</sup>

Catalyst	Conversion %	Selectivity (mol. %)		
		ETOH	ETOAC	Others <sup>b</sup>
0.5Pt-5.0Sn	67.48	38.94	57.24	3.82
0.5Pt-1.5Sn	84.54	62.55	32.50	4.95
0.75Pt-1.5Sn	88.09	64.36	30.83	4.81

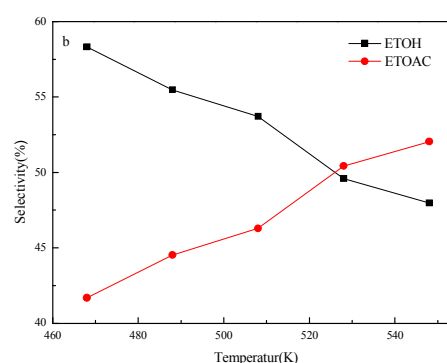
<sup>a</sup> Reaction conditions: T=528K, P=3MPa, H<sub>2</sub>/CH<sub>3</sub>COOH=10, LHSV=0.3h<sup>-1</sup>, <sup>b</sup> Others including acetaldehyde, CH<sub>4</sub> C<sub>2</sub>H<sub>6</sub>.

#### B. The Effect of Temperature

The impact of reaction temperature on the activity and selectivity of ethanol and ethyl acetate over 0.75Pt-1.5Sn was studied from 468 to 548K (P=5MPa, H<sub>2</sub>/CH<sub>3</sub>COOH=10, LHSV=0.3h<sup>-1</sup>) and displayed in Fig.3. It is shown that the conversion of acetate acid increased dramatically from 30.39% to 93.42% over the range studied due to the promotion of reaction rate caused by the rise of temperature, and the higher the temperature, the less significant the acceleration of the conversion of acetate acid. The selectivity of ethanol dropped markedly as the on-going increase of temperature and the trend of selectivity of ethyl acetate is against that of ethanol.



(a) The conversion of acetic acid

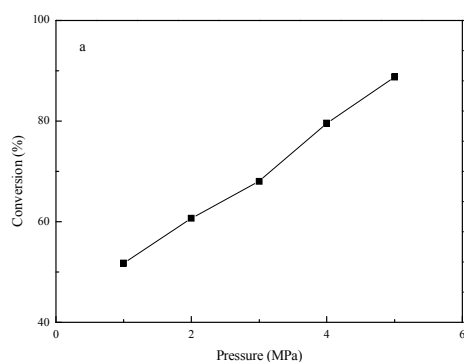


(b) The selectivity of ethanol and ethyl acetate

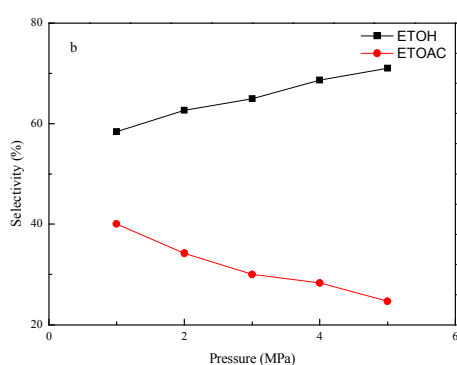
Fig. 3 The effect of temperature on the conversion and selectivity

#### C. The Effect of Pressure

The influence of pressure has been investigated over the range of 1.0-5.0MPa when other operation conditions were fixed (T=528K, H<sub>2</sub>/CH<sub>3</sub>COOH=10, LHSV=0.3h<sup>-1</sup>) and the results are presented in Fig. 4. The conversion of acetic acid rose along with the increase of pressure, which is result from the enhanced density of active acetate surface species and the improved collision probability of reactants and catalyst. At the same time, the selectivity of ethanol increased while that of ethyl acetate decreased, and that can be explained from the perspective of thermodynamics. There are 2 consecutive reactions in the system: the reduction of acetic acid to ethanol and the esterification of acetic acid and ethanol to ethyl acetate. The former one is a molecules reduced reaction and the number of molecules of the latter one is constant. Thus, the increase of pressure is beneficial to the production of ethanol.



(a) The conversion of acetic acid



(b) The selectivity of ethanol and ethyl acetate

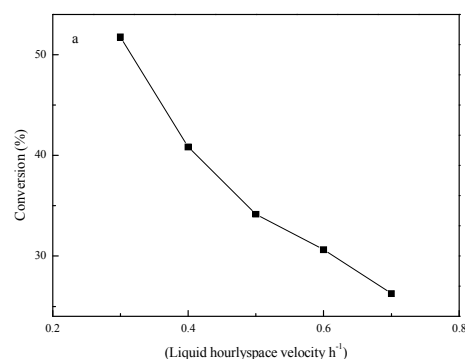
Fig. 4 The effect of pressure on the conversion and selectivity

#### D. The Effect of LHSV

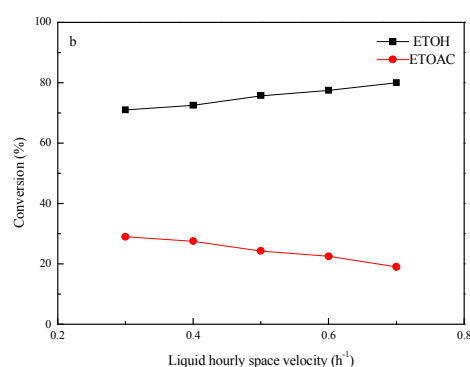
The effects of liquid hourly space velocity (*LHSV*) on acetic acid conversion and product selectivity were evaluated ( $T=428\text{K}$ ,  $P=1\text{MPa}$ ,  $\text{H}_2/\text{CH}_3\text{COOH}=10$ ) and show in Fig. 5. As *LHSV* was raised from 0.3 to  $0.7\text{h}^{-1}$ , the conversion of acetate acid decreased from 51.75 % to 30.64 % due to a shortened contact time between the reactants and the surface of the catalyst result from an increase of *WHSV*. As to the selectivity, that of ethanol was improved with continued increase of *LHSV* and reached a maximum at  $0.7\text{h}^{-1}$  while that of ethyl acetate bear a decline and dropped to 22.51% at  $0.7\text{h}^{-1}$ .

#### E. Catalysts Characterization

The XRD patterns of the catalysts and the support were shown in Fig. 6. There are 3 obvious peaks located at  $2\theta=38, 46$  and  $67^\circ$ , which can be ascribed to  $\gamma\text{-Al}_2\text{O}_3$  [15]. The presence of Pt, Sn and Pt-Sn alloy phases were not detected in our samples, probably due to that the Pt and Sn are highly dispersed on the alumina support and/or that the size of the crystallite is too small to be detected by XRD detection.



(a) The conversion of acetic acid



(b) The selectivity of ethanol and ethyl acetate

Fig. 5 The effect of pressure on conversion and selectivity

The BET surface area ( $S_{\text{BET}}$ ), pore volume ( $V_p$ ), and average pore diameter ( $D_p$ ) of the catalysts and the support are listed in Table 2. For  $\text{Al}_2\text{O}_3$  support, the surface area is formed by the micro/meso-pores and it is capillary effect that dominates the impregnation procedure [16]. The surface area, pore volume and average pore diameter of the catalysts is lower than that of the support due to the blockage of parts of small pores caused by metal loading, and the differences among the catalysts is slight because of a low metal loading. The  $\text{N}_2$  adsorption-desorption isotherms (Fig. 7) reveal that the catalysts and support all showed the properties of typical mesoporous materials.

TABLE II  
 $S_{\text{BET}}$ ,  $V_p$  AND  $D_p$  OF THE SAMPLES

Sample	$S_{\text{BET}}(\text{m}^2\cdot\text{g}^{-1})$	$V_p(\text{cm}^3\cdot\text{g}^{-1})$	$D_p(\text{nm})$
support	313.11	0.50	6.38
0.5Pt-5.0Sn	299.85	0.44	5.54
0.5Pt-1.50Sn	305.83	0.45	5.52
0.75Pt-1.50Sn	307.35	0.45	5.52

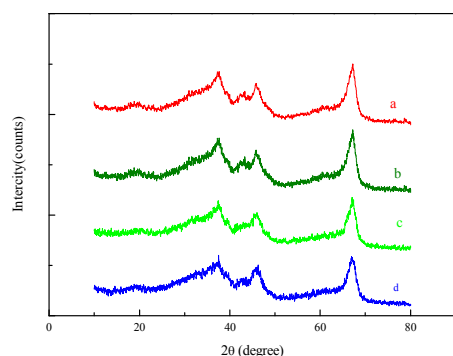


Fig. 6 XRD patterns of the samples; a-0.75Pt-1.5Sn; b-0.5Pt-1.5Sn; c-0.5Pt-5.0Sn; d- $\text{Al}_2\text{O}_3$

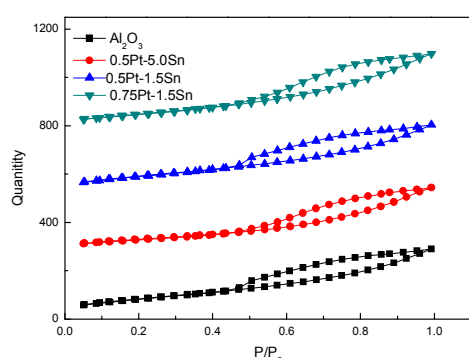


Fig. 7  $\text{N}_2$  adsorption-desorption isotherms of the samples

#### IV. CONCLUSIONS

Alumina supported Pt-Sn catalysts have been evaluated in the acetic acid hydrogenation at 528K, 3MPa,  $\text{H}_2/\text{CH}_3\text{COOH}=10$  and  $\text{LHSV}=0.6\text{h}^{-1}$ . Among the three catalysts, 0.75Pt-1.5Sn shows the highest acetic acid conversion (88.09%) and ethanol selectivity (64.36%). The effect of reaction conditions (temperature, pressure,  $\text{LHSV}$ ) on the activity of 0.75Pt-1.5Sn was studied and results show that product distribution could be achieved feasibly by adopting different temperature, pressure and  $\text{LHSV}$ . The catalysts and the support were characterized by  $\text{N}_2$  adsorption and XRD and results show that the impregnation of Pt, Sn caused little change to the texture properties of the support.

#### ACKNOWLEDGMENT

The authors acknowledge financial support in this research from the National Key Technology R&D Program of China (No. 2006BAE02B02).

#### REFERENCES

- [1] F. L. Pryor, "The economics of gasohol," Contemporary economic policy, vol. 27, pp. 523-537, 2009.
- [2] B. Roozbehani, S. I. Moqadam, M. Mirdrikvand, A. C. Roshan, "Modeling direct ethylene hydration over zirconium tungsten catalyst:

Fundamental of ethanol production using the biggest global ethylene feeding pipeline in Iran," Energy and environment research; vol. 2, pp. 28-36, 2012.

- [3] R. Pestman, R. M. Koster, E. Boellaard, A. M. van der Kraan, et al., "Identification of the active sites in the selective hydrogenation of acetic acid to acetaldehyde on iron oxide catalysts," Journal of catalysis, vol. 174, pp. 142-152, 1998
- [4] R. Pestman, A. van Duijne, J.A.Z. Pieterse, V. Ponce, "The formation of ketones and aldehydes from carboxylic acids, structure-activity relationship for two competitive reactions," Journal of molecular catalysis A: chemical, vol. 103, pp. 175-180, 1995.
- [5] R. Pestman, R. M. Koster, J. A. Z. Pieterse, and V. Ponce, "Reactions of carboxylic acids on oxides: 1. Selective hydrogenation of acetic acid to acetaldehyde," Journal of catalysis, vol. 168, pp. 255-264, 1997.
- [6] W. Rachmady, M. A. Vannice, "Acetic acid hydrogenation over supported platinum catalysts," Journal of catalysis, vol. 192, pp. 322-334, 2000.
- [7] W. Rachmady, M. A. Vannice, "Acetic acid reduction by  $\text{H}_2$  over supported Pt catalysts: A DRIFTS and TPD/TPR study," Journal of catalysis, vol. 207, pp. 317-330, 2002.
- [8] G. Corro, J. L. G. Fierro, F. B. Romero, "Catalytic performance of Pt-Sn/ $\square$ - $\text{Al}_2\text{O}_3$  for diesel soot oxidation," Catalysis communications, vol. 7, pp. 867-874, 2006.
- [9] G.J. Siri, J. M. Ramallo-López, M. L. Casellaa, J. L.G. Fierrod, et al., "XPS and EXAFS study of supported PtSn catalysts obtained by surface organometallic chemistry on metals: Application to the isobutane dehydrogenation", Applied catalysis A: General, vol. 278, pp. 239-249, 2005.
- [10] D.L. Hoang, S.A.-F. Farrage, J. Radnik, M.-M. Pohl, et al., A comparative study of zirconia and alumina supported Pt and Pt-Sn. catalysts used for dehydrocyclization of n-octane .Applied catalysis A: General, vol. 333, pp. 67-77, 2007.
- [11] I. Coletó, Ra. Roldán, C. Jiménez-Sanchidrián, J. P. Gómez, et al. , "Transformation of  $\alpha$ -olefins over Pt-M (M = Re, Sn, Ge) supported chlorinated alumina," Fuel, vol. 86, pp. 1000-1007, 2007
- [12] J.C. Serrano-Ruiz, G. W. Huber, M.A. Sánchez-Castillo, J. A. Dumesic, et al., "Effect of Sn addition to Pt/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts: An XPS, 119Sn Mössbauer and microcalorimetry study," Journal of catalysis, vol. 241, pp. 378-388, 2006.
- [13] P. D. Zgolicz, V. I. Rodríguez, I. M. J. Vilella, S. R. de Miguel, et al., "Catalytic performance in selective hydrogenation of citral of bimetallic Pt-Sn catalysts supported on MgAl<sub>2</sub>O<sub>4</sub> and -Al<sub>2</sub>O<sub>3</sub>," Applied catalysis A: General, vol. 392, pp. 208-217, 2011.
- [14] K. I. Gursahani, R. Alcalá, R. D. Cortright, J. A. Dumesic, "Reaction kinetics measurements and analysis of reaction pathways for conversions of acetic acid, ethanol, and ethyl acetate over silica-supported Pt." Applied catalysis A: General, vol. 222, pp. 369-392, 2001.
- [15] B. K. Vu, M. B. Song, I. Y. Ahn, Y. -W. Suh, et al. , "Location and structure of coke generated over Pt-Sn/Al<sub>2</sub>O<sub>3</sub> in propane dehydrogenation," Journal of industrial and engineering chemistry, vol. 17, pp. 71-76, 2011
- [16] A. M. Zhao, W. Y. Ying, H. T Zhang, H. F. Ma, "Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for syngas methanation: Effect of Mn promoter," Journal of energy chemistry, vol. 21, pp. 170-177, 2012.