The Performance of PtSn/Al$_2$O$_3$ with Cylindrical Particles for Acetic Acid Hydrogenation

Mingchuan Zhou, Haitao Zhang, Hongfang Ma, Weiyong Ying

Abstract—Alumina supported PtSn catalysts with cylindrical particles were prepared and characterized by using low temperature N$_2$ adsorption/desorption and X-ray diffraction. Low temperature N$_2$ adsorption/desorption demonstrate that the tableting changed the texture properties of catalysts. XRD pattern indicate that the crystal structure of supports had no change after reaction. The performances over particles of PtSn/Al$_2$O$_3$ catalysts were investigated with regards to reaction temperature, pressure, and H$_2$/AcOH mole ratio. After tableting, the conversion of acetic acid and selectivity of ethanol and acetyl acetate decreased. High reaction temperature and pressure can improve conversion of acetic acid. H$_2$/AcOH mole ratio of 9.36 showed the best performance on acetic acid hydrogenation. High pressure had benefits for the selectivity of ethanol and other two parameters had no obvious effect on selectivity.

Keywords—Acetic acid hydrogenation, ethanol, PtSn, cylindrical particles.

I. INTRODUCTION

ETHANOL is used widely as a gasoline addictive, a transportation fuel and a feedstock for the synthesis of variety of chemical [1]. A growing worldwide interest has been put in the production of ethanol from biomass and possibly from other readily available carbonaceous sources such as coal and petroleum [2], [3]. However, the fermentation from biomass has a high cost and long production cycle [4], and the hydration of ethylene from petrochemical has very low conversion per pass [5]. A reasonable route for producing ethanol industrial scale should be economic and reliability.

Mass of acetic acid have been easily obtained through well developed technology of methanol carbonylation [6], [7]. Theoretically, acetic acid can be efficiently hydrogenated to ethanol over appropriate catalyst. Pestman et al. [8]-[10] explored the reactions of carboxylic acids on oxides to verify the possibility of acetic acid reduction. Rachmady and Vannice [11] concluded that Pt as a source of activated hydrogen atoms can be supported on oxides to enhance the hydrogenation of acetic acid. Recently, carbon nanotube supported PtSn catalyst

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[12] and alumina supported PtSn catalyst [13] have been studied on acetic acid hydrogenation to ethanol and 1%Pt1%Sn (wt.) catalysts show the best activity with acetic acid conversion of more than 80%. Hence, hydroconversion of acetic acid to ethanol should be a process to apply to mass production of ethanol.

Since Al$_2$O$_3$ support has wide applications on chemical industry, PtSn/Al$_2$O$_3$ catalysts with cylindrical particles of 0.005 m × 0.005 m were prepared and evaluated at various operating conditions to figure out the catalytic performance on acetic acid hydrogenation to ethanol.

II. EXPERIMENT

A. Catalyst Preparation

Supported bimetallic catalyst were prepared via co-impregnation methods. Before the impregnation step, the γ-Al$_2$O$_3$ powders were calcined in air at 823 K for 4h. The supports were co-impregnated using mixed solution of H$_2$(PtCl$_6$)•6H$_2$O and SnCl$_4$•5H$_2$O (denoted as PtSn/Al$_2$O$_3$-P). The powders of PtSn/Al$_2$O$_3$ were tableted into cylindrical particles of 0.005 m × 0.005 m (denoted as PtSn/Al$_2$O$_3$-C). The loadings of Pt and Sn were held constant at 1 wt.% respectively.

B. Catalyst Characterization

The BET surface area, pore volume and pore size of catalysts were measured using a Micromeritics ASAP 2020M automated system. All samples were degassed at 500 K, 1.3 Pa for 6h before N$_2$ adsorption.

X-ray diffraction (XRD) powder patterns of the catalysts were recorded with a Rigaku D/max 2550 diffractometer using nickel filtered Cu Kα radiation (λ=1.54056 A) at room temperature. The X-Ray tube was operated at 40 Kv ,100 mA and scanned from 10°~80° at a speed of 2°/min (stepwise, 0.02) and the patterns were recorded with a 6° position sensitive detector.

C. Catalyst Test

The hydrogenation of acetic acid (AcOH) was carried out at 548 K with LWHSV of 0.67 h^{-1} using 2.8 g of catalyst under the pressure of 2.0 MPa. The reactor is a 10-mm-inner-diameter tubular stainless steel fixed-bed reactor. Before each experiment, the sample was reduced in a pure hydrogen (99.99%) flow (120 ml/min). The temperature during the reduction increased slowly from room temperature to 623 K and maintained at 623 K for 2h. After reduction, liquid acetic acid was pumped and preheated to vapor phase, which is introduced into reactor with H$_2$: AcOH mole ratio of 9.36:1. The liquid product separated by condenser was collected for

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12h after steady sate of reaction and detected off-line by GC Agilent 7890A. Other products in form of gas phase were detected on-line. In one sampling loop, CH_4, C_2H_6, H_2, and H_2O were analyzed with a thermal conductivity detector (TCD) furnished with a molecular sieve 5A packed column (6 ft×1/8 in×2.1 mm) and a Hayesep Q packed column (8 ft × 1/8 in). In the other loop, C1-C6 oxy-compounds which mainly contain ethanol (EtOH) and ethyl acetate (EtOAc) were analyzed with a flame ionization detector (FID) coupled with an HP-PLOT/Q capillary column (30 m × 0.53 mm × 40 μm) and an HP-INNOWAX (30 m × 0.53 mm × 1 μm) capillary column. Particularly, acetic acid left in the liquid was determined by titration of 1mol/L solution of NaOH.

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

The process of tableting may change the porous structure of catalysts. Through low-temperature N_2 adsorption/desorption, Table I shows the textural property of $PtSn/Al_2O_3$ with powders and cylindrical particles. After tableting, specific surface area (S_{BET}), pore volume (V_{total}) and pore size (D_{pore}) had obvious decrease because of large pore compaction under some tableting pressure.

TABLE I
TEXTURAL PROPERTY OF PTSN/AL$_2$O$_3$ WITH POWDERS AND CYLINDRICAL PARTICLES

Catalyst	S_{BET}(cm^2/g)	V_{total} (cm^3/g)	D_{pore}(nm)
PtSn/Al$_2$O$_3$-P	171	0.396	9.24
PtSn/Al$_2$O$_3$-C	154	0.323	8.36

XRD pattern of $PtSn/Al_2O_3$ with cylindrical particles (a) fresh, (b) after reaction are shown in Fig. 1. The characteristic diffraction peaks at 33.0°, 36.5°, 39.2°, 46.2°, 61.2° and 67.3° indicate that the support Al_2O_3 had well crystal structure [14] and this structure didn't change after reaction. The characteristic peak of metal platinum at 39.7° was found over $PtSn/Al_2O_3$ with cylindrical particles after reaction [15], [16]. The diffraction peak at 26.6° belonged to graphite [16], which was mixed with catalyst powders in order to lubricate cylindrical particles during depanning.
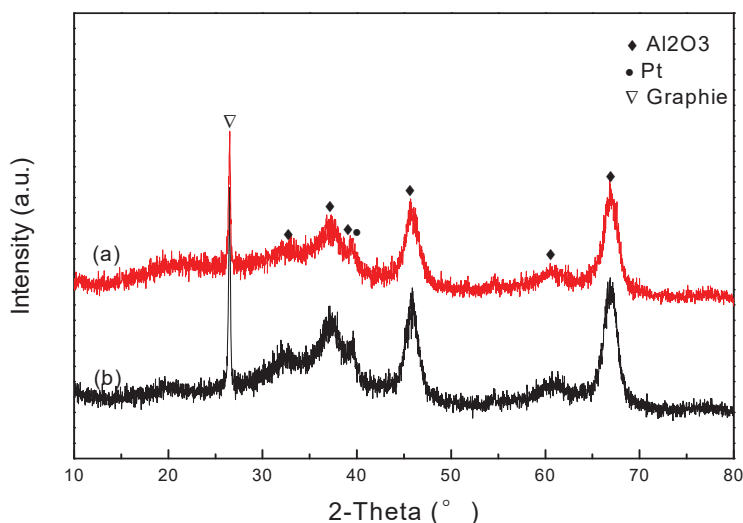

Fig. 1 XRD pattern of PtSn/Al$_2$O$_3$ with cylindrical particles (a) at fresh, (b) after reaction

B. Comparison of Catalyst Powders and Particles

The performances of $PtSn/Al_2O_3$ catalysts with powders and particles were evaluated, and the results are displayed in Table I. As we see, the catalyst particles show worse performance than that of powders. It is speculated that severe internal diffusion limitation existed during acetic acid hydrogenation over $PtSn/Al_2O_3$ catalyst particle. After tableting, ethyl acetate became main product instead of ethanol. Internal diffusion resistance caused that most of acetic acid cannot be able to be hydrogenated in the pore channel of catalyst particles and the conversion of acetic acid decreased obviously from 83.51% to 48.43%. Part of ethanol product had no time to diffuse to outside surface and proceeded the Fisher esterification reaction with acetic acid, then ethyl acetate became main product instead of ethanol. The selectivity of CH_4 increased from 2.74%

to 4.42% because ethanol had longer time to be dehydrated, cracked, and hydrogenated to methane in the interior surface.

TABLE II
THE PERFORMANCES OF PTSN/AL$_2$O$_3$ CATALYSTS WITH POWDERS AND PARTICLES^A

Catalyst	AcOH Conversion (%)	Selectivity (%)			
		CH$_4$	C$_2$H$_6$	EtOH	EtOAc
PtSn/Al$_2$O$_3$-P	83.51	2.74	2.29	41.57	48.49
PtSn/Al$_2$O$_3$-C	48.43	4.42	2.88	27.04	62.04

a   reaction   operation: T=548K,   P=2MPa,   LWHSV=0.9h^{-1}, H$_2$/CH$_3$COOH=9.36

C. Effect of Temperature on Performance

The performances over $PtSn/Al_2O_3$ catalysts with cylindrical particles of 0.005 m × 0.005 m as function of reaction temperature are shown in Fig. 2. The reactions were carried out under temperature range from 513 K to 533 K and other

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condition are constant (P=2 MPa, LWHSV=0.67 h^{-1}, H$_2$/CH$_3$COOH=9.36). High reaction temperature can accelerate the reaction rate and more reactant acetic acid can be assumed under same residence time. So, the conversion of acetic acid increased from 47.5% to 64.5% with reaction temperature from 513 K to 553 K. Reaction temperature had no obvious effect on selectivity of ethanol and acetyl acetate. But, the total selectivity of ethanol and acetyl acetate had slight decrease with increasing reaction temperature. It might be explained by the increase of methane and ethane at high reaction temperature.

D. Effect of Pressure on Performance

The influence of pressure on performance over PtSn/Al$_2$O$_3$ catalysts with cylindrical particles has been investigated in Fig. 3 (T=548K, LWHSV=0.67h^{-1}, H$_2$/CH$_3$COOH=9.36). As reaction pressure increased from 1 MPa to 3 MPa, and other condition are still fixed, the conversion of acetic acid increased from 58% to 74%. This trend almost belonged to a linear relationship. At high pressure, the performance over PtSn/Al$_2$O$_3$ catalysts with cylindrical particles had high selectivity of ethanol and low selectivity of acetyl acetate. However, pressure had no impact on total selectivity of ethanol and acetyl acetate. High pressure might affect reactivity of the polar C=O and hydrogenated easily [17]. There is another possibility that high pressure increased the density of gas and made molecular collision more violent. The enhancement of pressure on selectivity of ethanol can be explained by thermodynamics. Acetic acid hydrogenation to ethanol is a reaction of reduced volume and esterification of acetic acid and ethanol to ethyl acetate is a reaction of constant volume. Hence, high pressure can improve the production of ethanol.
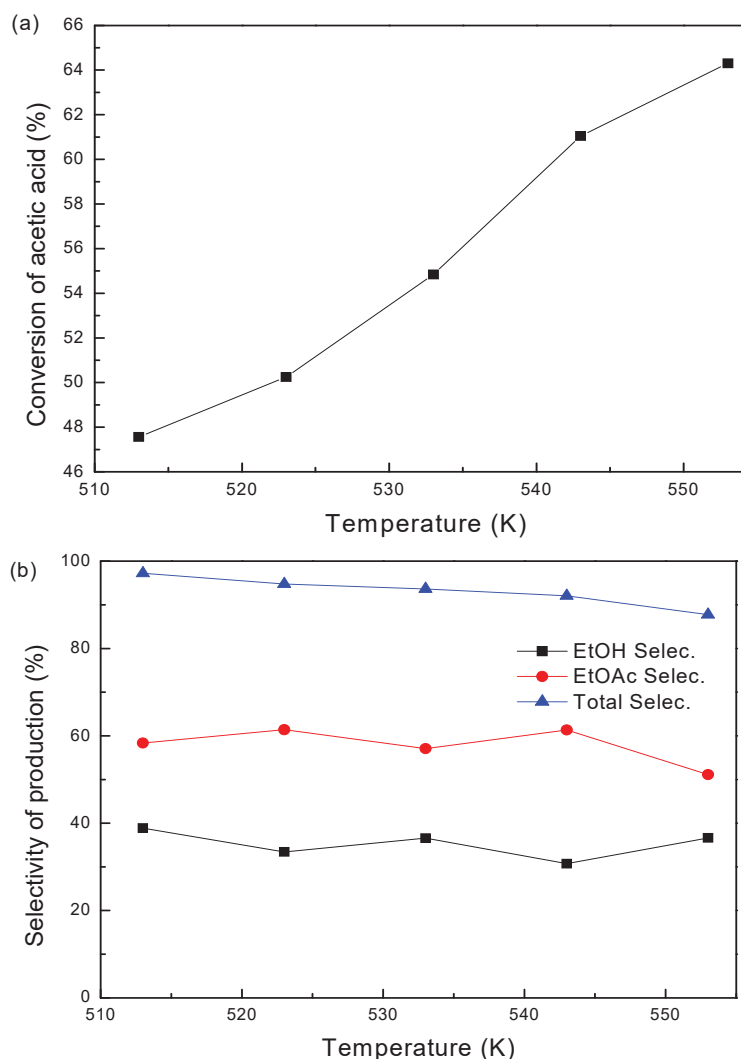

Fig. 2 (a) Conversion of acetic acid and (b) selectivity of production over PtSn/Al$_2$O$_3$ catalysts with cylindrical particles of 0.005 m × 0.005 m as function of reaction temperature

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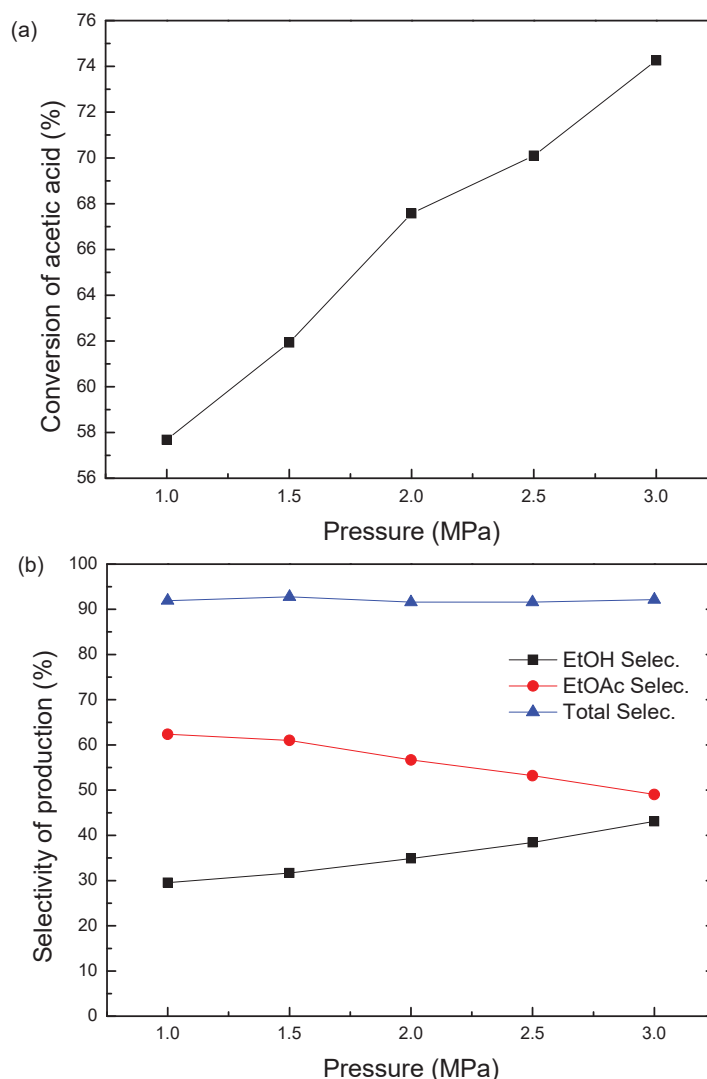International Journal of Chemical and Molecular Engineering
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Fig. 3 (a) Conversion of acetic acid and (b) selectivity of production over PtSn/Al₂O₃ catalysts with cylindrical particles of 0.005 m × 0.005 m as function of reaction pressure

E. Effect of H₂/AcOH Mole Ratio on Performance

The performances over PtSn/Al₂O₃ catalysts with cylindrical particles with different H₂/AcOH mole ratios were evaluated and displayed in Fig. 4 (T=548 K, P=2 MPa, LWHSV=0.67 h⁻¹). Fig. 4 (a) shows that the conversion of acetic acid increased firstly and then decreased with increasing H₂/AcOH mole ratios. The change of H₂/AcOH mole ratio can affect the partial pressure of hydrogen and gaseous hourly space velocity. The kinetics of acetic acid hydrogen suggested that high partial pressure of hydrogen can enhance the reaction rate as a result of first increase of conversion. As H₂/AcOH mole ratio increased, total volume of reaction gas increased and gaseous hourly space velocity became larger, which led to short residence time, but liquid weight hourly space velocity did not change. While H₂/AcOH mole ratio exceeded 9.36, adverse effect from short residence time made control of conversion and led to decrease of conversion. It seems that H₂/AcOH mole ratio had no distinct effect on selectivity of ethanol and acetyl acetate.

IV. CONCLUSION

Alumina supported PtSn catalysts with cylindrical particles of 0.005 m × 0.005 m have been investigated in acetic acid hydrogenation at 548K, 2MPa, H₂/AcOH=9.36 and LWHSV=0.67 h⁻¹. Low temperature N₂ adsorption/desorption show that texture properties of catalysts had some change after tabletting. XRD pattern indicate that reaction can't change the crystal structure of supports. In comparison with the powders of PtSn/Al₂O₃, the performance over cylindrical particles of PtSn/Al₂O₃ showed an obvious decrease of conversion of acetic acid and selectivity of acetyl acetate as well as decrease of byproduct methane and product ethanol. Under investigation of reaction condition, conversion of acetic acid had positive relationship with reaction temperature and pressure. H₂/AcOH mole ratio of 9.36 showed best activity of 66% conversion on acetic acid hydrogenation. High pressure enhanced the selectivity of ethanol, and both temperature and H₂/AcOH mole ratio had no obvious effect on selectivity of ethanol. At the range of 513K-523K, the conversion of acetic acid increased by

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17%. Pressure ranging from 1MPa to 3MPa increased conversion of acetic acid increased from 58% to 74% and selectivity of ethanol from 30% to 40%.
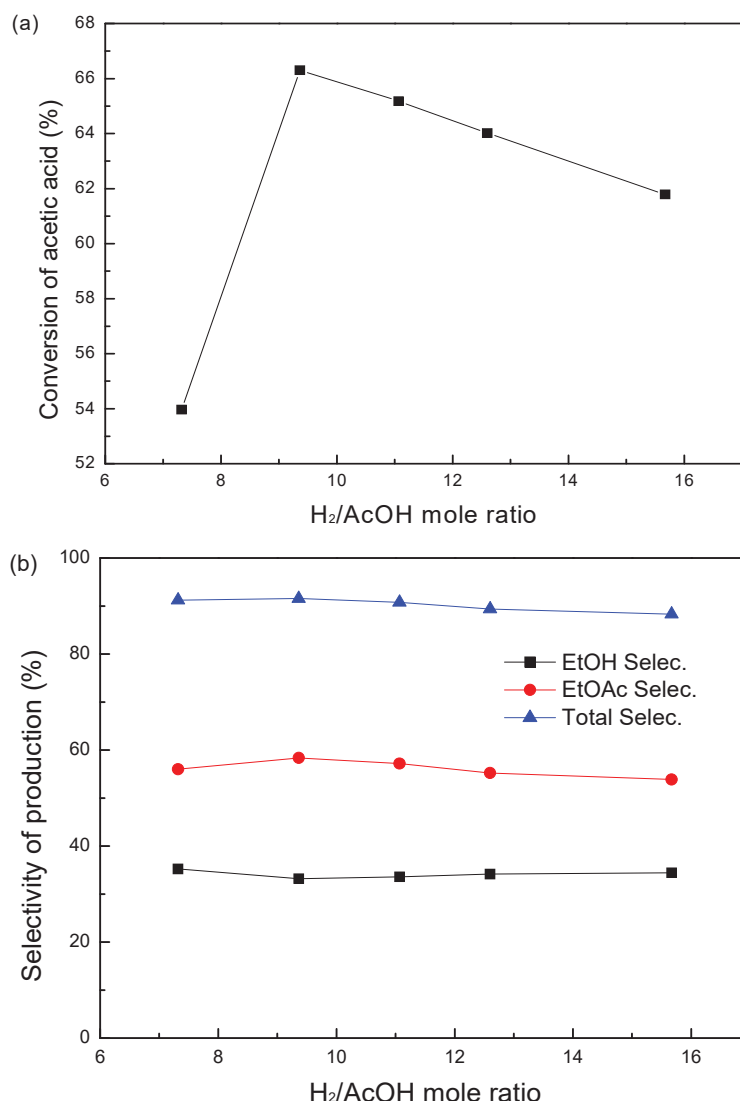
Fig. 4 (a) Conversion of acetic acid and (b) selectivity of production over PtSn/Al₂O₃ catalysts with cylindrical particles of 0.005 m × 0.005 m as function of H₂/AcOH mole ratio

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