

The Catalytic Properties of PtSn/Al₂O₃ for Acetic Acid Hydrogenation

Mingchuan Zhou, Haitao Zhang, Hongfang Ma, Weiyong Ying

Abstract—Alumina supported platinum and tin catalysts with different loadings of Pt and Sn were prepared and characterized by low temperature N₂ adsorption/desorption, H₂-temperature programmed reduction and CO pulse chemisorption. Pt and Sn below 1% loading were suitable for acetic acid hydrogenation. The best performance over 0.75Pt1Sn/Al₂O₃ can reach 87.55% conversion of acetic acid and 47.39% selectivity of ethanol. The operating conditions of acetic acid hydrogenation over 1Pt1Sn/Al₂O₃ were investigated. High reaction temperature can enhance the conversion of acetic acid, but it decreased total selectivity of ethanol and acetyl acetate. High pressure and low weight hourly space velocity were beneficial to both conversion of acetic acid and selectivity to ethanol.

Keywords—Acetic acid, hydrogenation, PtSn, operating condition.

I. INTRODUCTION

CARBOXYLIC acid hydrogenation is a very important reaction to synthesis of corresponding fatty alcohols [1]. Fatty alcohols have attained considerable importance as nonionic surfactants and intermediates for synthesis of lubricants, resins and perfumes [2]. In comparison with many carbonyl hydrogenations, weak polarity of carbonyl group from carboxylic acid makes the hydrogenation of carboxylic acid more difficult [3]. Many researchers [4]-[6] have explored the catalysts and reaction conditions on carboxylic acid hydrogen. The reactions with different catalysts both showed extreme conditions to obtain high selectivity of desired alcohols. Hence, an appropriate catalyst for carboxylic acid hydrogenation should be developed to meet milder and more selective hydrogenation of carboxylic acid.

Acetic acid as the simplest fatty acid can be used as a model to test carboxylic acid adsorption and hydrogenation. Ethanol has been also considered as a transportation fuel and feedstock for the synthesis of variety of chemicals, fuels, and polymers [7]. The researches on acetic acid hydrogenation to ethanol have been focused on by many groups. Pestman et al. found that adding platinum to oxides enhanced selectivity and activity in

hydrogenation of acetic acid to acetaldehyde [8]. Rachmady and Vannice published the catalytic behavior of acetic acid hydrogenation over Pt supported on TiO₂, SiO₂, Al₂O₃ and Fe₂O₃ [9]. Alcalá et al. demonstrated the reaction mechanism of acetic acid hydrogenation to ethanol over Pt(111) and PtSn through density functional theory calculations [10]. It is concluded that PtSn catalysts, compared with Pt catalysts, can enhance catalytic activity and selectivity to ethanol and ethyl acetate, which was also experimentally verified by acetic acid hydrogenation over carbon nanotube supported PtSn catalyst [11] and alumina supported PtSn catalyst [12].

Considering the characteristic of bimetal catalysts, loading proportion of two metals can impact catalytic performance of acetic acid hydrogenation. PtSn/Al₂O₃ catalysts with different loading amounts of platinum and tin were prepared and evaluated to figure out the appropriate loading proportion of two metals and operating condition.

II. EXPERIMENT

A. Catalyst Preparation

Supported bimetallic catalysts were prepared via co-impregnation impregnation methods. Before the impregnation step, the γ -Al₂O₃ support was calcined in air at 823 K for 4h. The support was co-impregnated by using mixed solution of H₂(PtCl₆)•6H₂O and SnCl₄•5H₂O (denoted as PtSn/Al₂O₃). After impregnation step, the catalysts were dried at 383 K for 12h, followed by calcination in air at 823 K for 4h. The loadings of platinum and tin were respectively varied with 0.75 wt.%, 1wt.%, and 1.25wt.%.

B. Catalyst Characterization

The BET surface area, pore volume and pore size of catalysts were measured by using a Micromeritics ASAP 2020M automated system. All samples were degassed at 500 K, 1.3 Pa for 6h before N₂ adsorption.

H₂-Temperature programmed reduction (TPR) and CO pulse chemisorption were studied by using Micromeritics Autochem II 2020 chemisorption apparatus.

For H₂-TPR experiment, calcined sample was pre-treated in Ar (99.99%) atmosphere at 773 K for 1h and cooled down to room temperature. Then, it was subjected to a flow of reducing gas (50 ml/min) containing a mixture of H₂: Ar (10:90) with a heating rate of 10 K/min from room temperature to 1073 K. The hydrogen consumption was monitored by a thermal conductivity detector (TCD) after the base line was stable.

CO pulse chemisorption was conducted to analyze the Pt dispersion of catalyst. The sample was pre-treated at 773 K for 1h and cooled down to room temperature. Then, the sample was

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reduced under H_2 (99.99%, 30 ml/min) at 623 K for 2h and cooled down to 323 K in a stream of helium. The 0.1 cm^3 pulses of CO were repeatedly introduced to the reactor until no more CO was consumed, and the time between each pulse was 4 min.

C. Catalyst Test

The hydrogenation evaluation of the catalysts was carried out in a 10-mm-inner-diameter stainless steel tubular fixed bed at the condition of 2 MPa, 548 K and 0.9 h^{-1} . About 2.8 g catalysts were placed in constant temperature zone of reactor, and both sides of catalyst bed were filled with quartz powders. 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 623K and maintained at 623 K for 2h. Acetic acid was pumped into the reactor using constant-flux pump and preheated to vapor phase, which was introduced into reactor with H_2 : AcOH mole ratio of 10:1. The liquid product separated by condenser was collected for 12h after steady state 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 \times 1/8 in \times 2.1 mm) and a Hayesep Q packed column (8 ft \times 1/8 in). In the other loop, C_1 - C_6 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 \times 0.53 mm \times 40 μ m) and an HP-INNOWAX (30 m \times 0.53 mm \times 1 μ m) 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 nitrogen adsorption/desorption isotherm of different catalysts and support were demonstrated in Fig. 1. According to IUPAC classification, the support displayed type IV isotherms and exhibited an H1 hysteresis loop, which had the adsorption and desorption branches to be almost vertically parallel within a wide interval of adsorbed amount [13]. The closure of hysteresis loop at $P/P^0 > 0.40$ indicates the absence of micropores and the formation of well-defined mesoporous texture. The loading of platinum and tin didn't change the pore structure of Al_2O_3 . Textural properties of different catalysts and support were listed in Table I. After impregnation, specific surface area (S_{BET}) had no obvious decrease and pore volume (V_{total}) and pore size (D_{pore}) have slight decrease, which might be affected by corrosion of acid media during during impregnation of H_2PtCl_6 and $SnCl_4$.

Co-impregnation of two metal precursors into support might generate the alloy form of Pt and Sn. In Fig. 2, TPR profiles of 1Pt1Sn/ Al_2O_3 had one peak of reduction, which means that the peak at 550 K-600 K was considered as the reduction of PtSn alloy [14]. From TPR profiles of other catalysts, the peak at 450 K can be assigned to reduction of Pt(II) to metal Pt and the peak at 700-800 K belonged to the reduction of Sn^{4+}/Sn^{2+} and/or

Sn^{2+}/Sn^0 species [15]. If platinum had lower loading than Sn loading on support, TPR profiles show more obvious reduction peak of Sn and lower reduction peak of PtSn alloys. More loading of platinum on support also led to the presence of metal Pt, which did not interact well with Sn. According to TPR profiles and the results of CO pulse chemisorption, 0.75Pt1Sn/ Al_2O_3 had the best dispersion of platinum and most platinum with tin turned into alloy form. If the loading of Sn exceeded 1%, platinum may be wrapped around excess Sn because the support could not offer enough surface to disperse the metal, which led to decrease the dispersion of Pt. If the loading of Pt exceeded 1%, part of Pt seems not interact with Sn and it cause bad dispersion of Pt. Hence, the formation of PtSn was conducive to the dispersion of Pt.

B. Comparison of Different Comparison of Different Catalysts

The performance over different catalysts for acetic acid hydrogenation is shown in Table II. It is found out that the conversion of acetic acid had correspondence with the dispersion of Pt on different catalysts. If the loading of Pt exceeded 1%, the conversion of acetic acid decreased by 35%. The conversion of acetic acid increased with decreasing loading of tin on support. Excess Sn or excess Pt loading on limited surface of support generated large particle of metal and caused decrease of conversion. In addition, the form of metal on support can also affect the distribution of production. Excess Sn or Pt also caused increase of methane and acetyl acetate and decrease of ethanol. Low loading of Pt or Sn can enhance the selectivity of ethanol and decrease the selectivity of acetyl acetate, which means that the presence of PtSn alloy may have benefit for acetic acid hydrogenation to ethanol.

TABLE I
TEXTURAL PROPERTIES AND CHEMISORPTION CAPACITY OF DIFFERENT CATALYSTS AND SUPPORT

Catalyst	S_{BET} (cm ² /g)	V_{total} (cm ³ /g)	D_{pore} (nm)	d_p (%)
Al_2O_3	160	0.370	9.26	-
1Pt1Sn/ Al_2O_3	154	0.351	9.12	47.36
1Pt0.75Sn/ Al_2O_3	157	0.351	8.95	50.09
1Pt1.25Sn/ Al_2O_3	155	0.358	9.02	42.27
0.75Pt1Sn/ Al_2O_3	159	0.347	8.96	65.26
1.25Pt1Sn/ Al_2O_3	158	0.353	8.89	42.85

TABLE II
THE PERFORMANCE OVER DIFFERENT CATALYSTS FOR ACETIC ACID HYDROGENATION ^a

Catalyst	AcOH Conversion (%)	Selectivity (%)			
		CH_4	C_2H_6	EtOH	EtOAc
1Pt1Sn/ Al_2O_3	83.51	2.74	2.29	41.57	48.49
1Pt0.75Sn/ Al_2O_3	87.55	2.78	2.15	47.39	39.40
1Pt1.25Sn/ Al_2O_3	75.48	3.12	2.61	31.55	59.41
0.75Pt1Sn/ Al_2O_3	83.88	2.69	2.26	43.33	44.77
1.25Pt1Sn/ Al_2O_3	48.43	4.42	2.88	27.04	62.04

^a reaction operation: T=548K, P=2MPa, WHSV=0.9h⁻¹, $H_2/CH_3COOH=10$

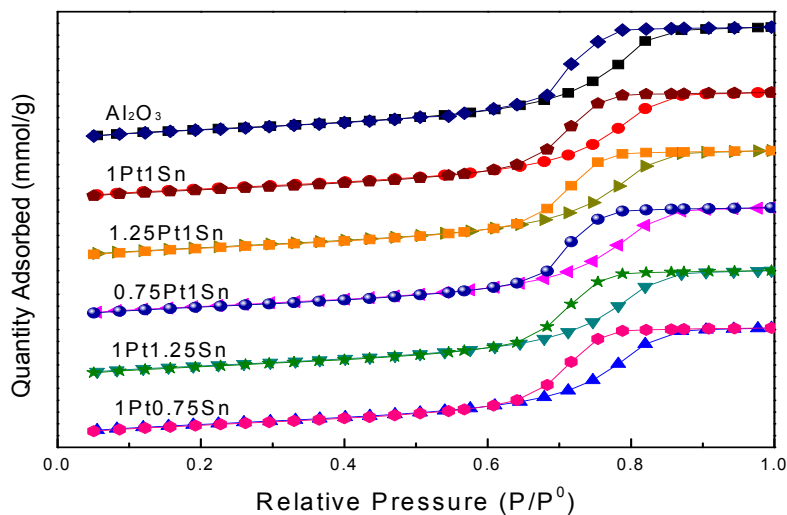


Fig. 1 The nitrogen adsorption/desorption isotherm of different catalysts and support

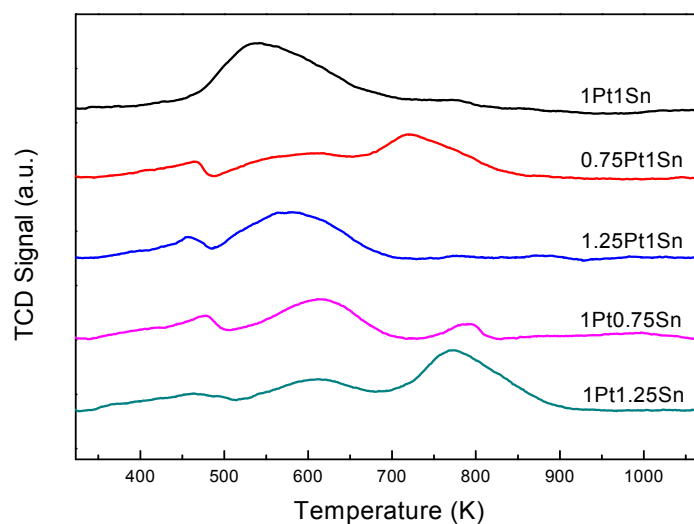
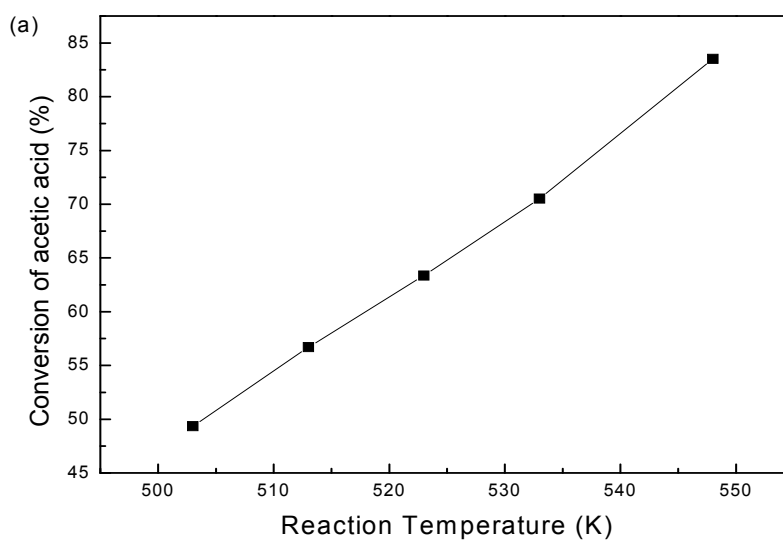


Fig. 2 H₂-TPR profiles of different catalysts



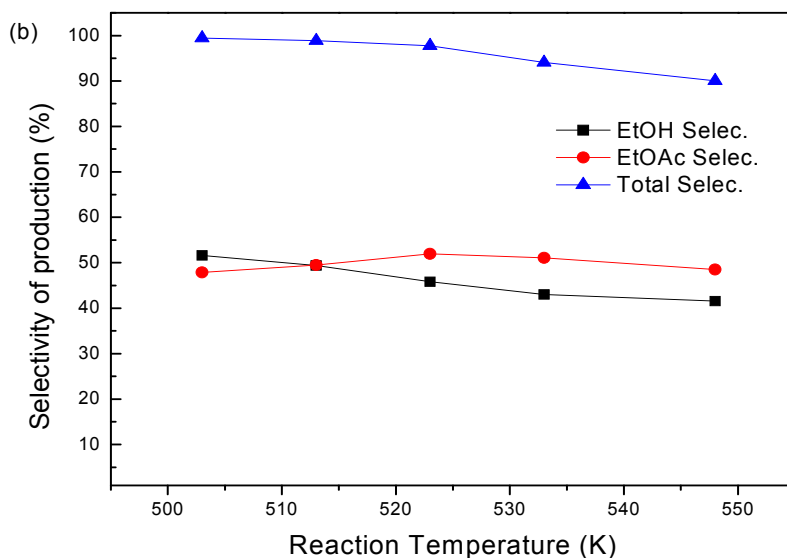


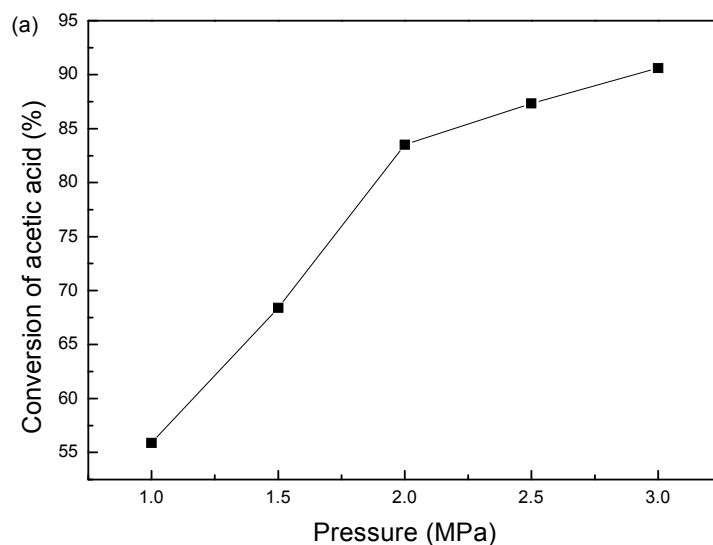
Fig. 3 (a) Conversion of acetic acid and (b) selectivity of production over 1Pt1Sn/ Al_2O_3 catalyst with different reaction temperatures

C. Effect of Temperature on Performance

The performances of acetic acid hydrogenation over 1Pt1Sn/ Al_2O_3 with different reaction temperatures were evaluated and presented in Fig. 3. Other conditions were fixed ($P=2$ MPa, $\text{WHSV}=0.9 \text{ h}^{-1}$, $\text{H}_2/\text{CH}_3\text{COOH}=10$). The conversion of acetic acid increased by 30% with increasing reaction temperature from 503 K to 548 K, which almost had a linear relationship. According to kinetics of acetic acid hydrogenation to ethanol, high reaction temperature accelerated reaction rates and converted more acetic acid per unit time. In view of the distribution of production, the selectivity of ethanol decreased and the selectivity of acetyl acetate increased firstly then decreased at high reaction temperature. However, high reaction temperature also led to the increase of methane because of ability of C-C cleavage on Pt. So, total selectivity of ethanol and acetyl acetate decreased slightly with increasing reaction temperature.

D. Effect of Pressure on Performance

The influence of pressure on the performance over 1Pt1Sn/ Al_2O_3 catalyst were investigated and shown in Fig. 4. Other conditions were fixed ($T=548 \text{ K}$, $\text{WHSV}=0.9 \text{ h}^{-1}$, $\text{H}_2/\text{CH}_3\text{COOH}=10$). The conversion of acetic acid increased fast firstly with increasing pressure from 1 MPa to 2 MPa. High pressure can enhance polarity of carboxylic acid and made hydrogenation easily. While the pressure increased from 2 MPa to 3 MPa, the conversion of acetic acid increased slowly. It is possible that the reaction at high pressure nearly closed to the thermodynamic equilibrium conversion. High pressure led to increase of selectivity to ethanol, decrease of selectivity to acetyl acetate and increase of total selectivity. These might be related to thermodynamic equilibrium. High pressure could improve acetic acid hydrogenation to ethanol because of the reaction of reduced volume.



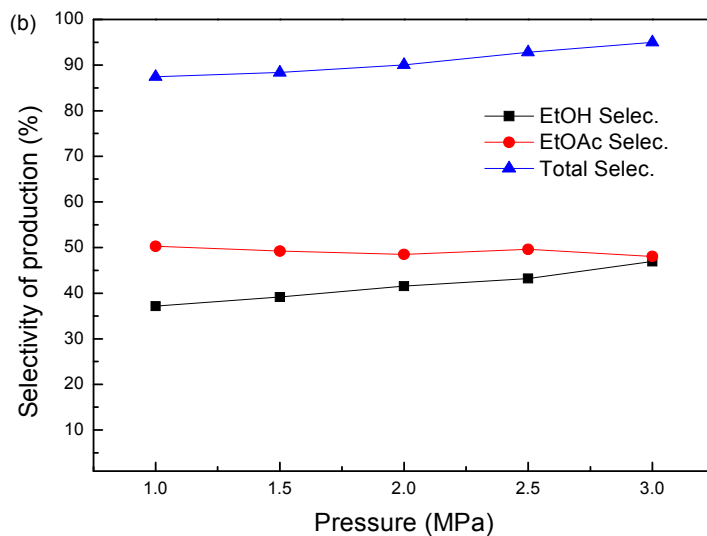


Fig. 4 (a) Conversion of acetic acid and (b) selectivity of production over 1Pt1Sn/Al₂O₃ catalyst with different pressures

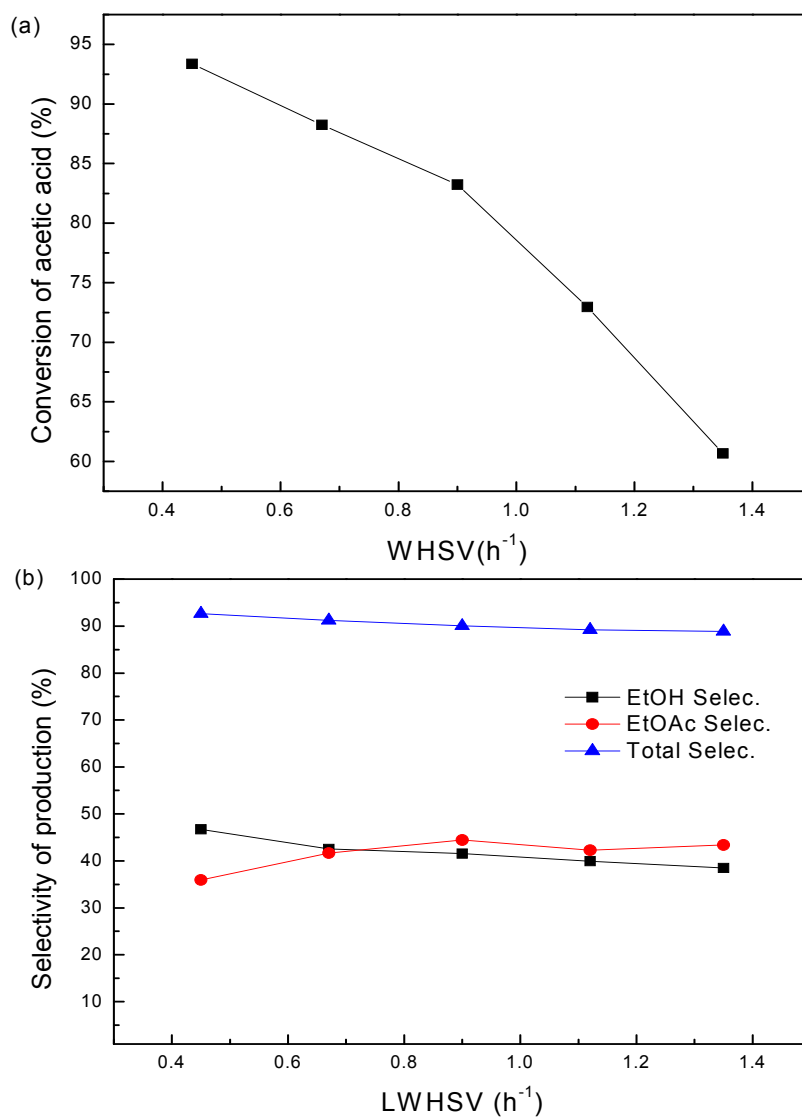


Fig. 5 (a) Conversion of acetic acid and (b) selectivity of production over 1Pt1Sn/Al₂O₃ catalyst with different WHSVs

E. Effect of WHSV on Performance

The effect of weight hourly space velocity (WHSV) on conversion of acetic acid and selectivity of production were displayed in Fig. 5. Other conditions were fixed ($T=548\text{ K}$, $P=2\text{ MPa}$, $H_2/CH_3COOH=10$). As WHSV increased from 0.4 h^{-1} to 1.35 h^{-1} , the conversion of acetic acid decreased by 30% because of short residence time. High WHSV led to slight increase of selectivity to acetyl acetate and slight decrease of selectivity to ethanol. WHSV had no effect on total selectivity of acetyl acetate and ethanol.

IV. CONCLUSION

Acetic acid hydrogenation to ethanol over $PtSn/Al_2O_3$ catalysts with different loading of Pt and Sn were carried out at the condition of 548 K , 2 MPa , $H_2/CH_3COOH=10$ and $WHSV=0.9\text{ h}^{-1}$. Loading of Pt or Sn exceeding 1% had no benefit for acetic acid hydrogenation. According to H_2 -TPR and CO pulse chemisorption, low loading of Pt or Sn can generate PtSn alloys easily and had better dispersion. Low temperature N_2 adsorption/desorption isotherm showed mesoporous texture of Al_2O_3 . The operating conditions of acetic acid hydrogenation were investigated over $1Pt1Sn/Al_2O_3$. High reaction temperature was good for the conversion of acetic acid, but the selectivity of ethanol decreased and the selectivity of acetyl acetate increased firstly then decreased at high reaction temperature. The conversion of acetic acid increased with increasing pressure and low WHSV. Both high pressure and low WHSV led to increase of selectivity to ethanol.

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