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 carboxyl hydrogenations, weak polarity of carboxyl 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 hydrogenation. 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 to test carboxylic acid adsorption and hydrogenation. Ethanol should be developed to meet milder and more selective conditions to obtain high selectivity of desired alcohols. Hence, a catalyst with high activity and selectivity is desired. The reaction conditions can influence the activity and selectivity of the catalysts.

Acetic acid hydrogenation has been extensively studied due to its importance in fuel synthesis [7]. The researches on acetic acid hydrogenation to ethanol over Pt(111) and 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 proportions 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-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...
redistributed under H₂ (99.99%, 30 ml/min) at 623 K for 2 h and
cooled down to 323 K in a stream of helium. The 0.1 cm³ 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 623 K
and maintained at 623 K for 2 h. Acetic acid was pumped into
the reactor using constant-flux pump and preheated to vapor
phase, which was introduced into reactor with H₂: AcOH mole
ratio of 10:1. The liquid product separated by condenser was
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 1 mol/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/P₀ > 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 Al₂O₃. Textural properties of different catalysts and
support were listed in Table I. After impregnation, specific
surface area (S₅₇₅) had no obvious decrease and pore volume
(V₅₇₅) and pore size (D₅₇₅) have slight decrease, which might
be affected by corrosion of acid media during impregnation of H₂PtCl₆ and SnCl₄.

Co-impregnation of two metal precursors into support might
generate the alloy form of Pt and Sn. In Fig. 2, TPR profiles of
1Pt1Sn/Al₂O₃ had one peak of reduction, which means that the peak
at 550 K-600 K was considered as the reduction 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/ Al₂O₃ had the best dispersion of platinum and most platinum
with tin turned into alloy form. If the loading of Pt 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

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
cause 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>
<thead>
<tr>
<th>Catalyst AcOH Conversion (%)</th>
<th>Selectivity (%)</th>
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<tr>
<td></td>
<td>CH₄</td>
</tr>
<tr>
<td>1Pt1Sn/Al₂O₃</td>
<td>83.51</td>
</tr>
<tr>
<td>Pt6.75Sn/Al₂O₃</td>
<td>87.55</td>
</tr>
<tr>
<td>1Pt1.25Sn/Al₂O₃</td>
<td>75.48</td>
</tr>
<tr>
<td>0.75Pt1Sn/Al₂O₃</td>
<td>83.88</td>
</tr>
<tr>
<td>1.25Pt1Sn/Al₂O₃</td>
<td>48.43</td>
</tr>
</tbody>
</table>

TABLE II

The performance over different catalysts for acetic acid
hydrogenation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>AcOH Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₄</td>
<td>CH₃COOH</td>
</tr>
<tr>
<td>1Pt1Sn/Al₂O₃</td>
<td>83.51</td>
<td>2.74</td>
</tr>
<tr>
<td>Pt6.75Sn/Al₂O₃</td>
<td>87.55</td>
<td>2.78</td>
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<td>1Pt1.25Sn/Al₂O₃</td>
<td>75.48</td>
<td>3.12</td>
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<tr>
<td>0.75Pt1Sn/Al₂O₃</td>
<td>83.88</td>
<td>2.69</td>
</tr>
<tr>
<td>1.25Pt1Sn/Al₂O₃</td>
<td>48.43</td>
<td>4.42</td>
</tr>
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</table>

* reaction operation: T=548K, P=2MPa, WHSV=0.9h⁻¹, H₂/CH₃COOH=10

TABLE I

Textural Properties and Chemisorption Capacity of Different
Catalysts and Support

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S₅₇₅(cm²/g)</th>
<th>V₅₇₅(cm³/g)</th>
<th>D₅₇₅(nm)</th>
<th>d₅⁵⁰⁰(%)</th>
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<tr>
<td>Al₂O₃</td>
<td>160</td>
<td>0.370</td>
<td>9.36</td>
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</tr>
<tr>
<td>1Pt1Sn/Al₂O₃</td>
<td>154</td>
<td>0.351</td>
<td>9.12</td>
<td>47.36</td>
</tr>
<tr>
<td>1Pt0.75Sn/Al₂O₃</td>
<td>157</td>
<td>0.351</td>
<td>8.95</td>
<td>50.09</td>
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<tr>
<td>1Pt1.25Sn/Al₂O₃</td>
<td>155</td>
<td>0.358</td>
<td>9.02</td>
<td>42.27</td>
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<tr>
<td>0.75Pt1Sn/Al₂O₃</td>
<td>159</td>
<td>0.347</td>
<td>8.96</td>
<td>65.26</td>
</tr>
<tr>
<td>1.25Pt1Sn/Al₂O₃</td>
<td>158</td>
<td>0.353</td>
<td>8.89</td>
<td>42.85</td>
</tr>
</tbody>
</table>
Fig. 1 The nitrogen adsorption/desorption isotherm of different catalysts and support

Fig. 2 H₂-TPR profiles of different catalysts

(a) Conversion of acetic acid (%) vs. Reaction Temperature (K)
C. Effect of Temperature on Performance

The performances of acetic acid hydrogenation over 1Pt1Sn/Al₂O₃ with different reaction temperatures were evaluated and presented in Fig. 3. Other conditions were fixed (P=2 MPa, WHSV=0.9 h⁻¹, H₂/CH₃COOH=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/Al₂O₃ catalyst were investigated and shown in Fig. 4. Other conditions were fixed (T=548 K, WHSV=0.9 h⁻¹, H₂/CH₃COOH=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 3MPa, 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 K, P=2 MPa, H₂/CH₃COOH=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/Al₂O₃ catalysts with different loading of Pt and Sn were carried out at the condition of 548 K, 2 MPa, H₂/CH₃COOH=10 and WHSV=0.9 h⁻¹. Loading of Pt or Sn exceeding 1% had no benefit for acetic acid hydrogenation. According to H₂-TPR and CO pulse chemisorption, low loading of Pt or Sn can generate PtSn alloys easily and had better dispersion. Low temperature N₂ adsorption/desorption isotherm showed mesoporous texture of Al₂O₃. The operating conditions of acetic acid hydrogenation were investigated over 1Pt1Sn/Al₂O₃. 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.

**References**


