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 nonionc 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 hydrogenation of carboxylic acid should be developed to meet milder and more selective hydrogenation of carboxylic acid.

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reduced 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 collected for 12 h after steady state of reaction and detected by off-line by GC Agilent 7890A. Other products in form of gas 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 Haysep 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 K can be assigned to reduction of Pt(II) to metal Pt and the peak at 550 K-600 K was considered as the reduction of PtSn alloys. More loading of Pt 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 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>
<thead>
<tr>
<th>Catalyst</th>
<th>AcOH Conversion (%)</th>
<th>Selectivity (%)</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>EtOH</th>
<th>EtOAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Pt1Sn/Al₂O₃</td>
<td>83.51</td>
<td></td>
<td>2.74</td>
<td>2.29</td>
<td>41.57</td>
<td>48.49</td>
</tr>
<tr>
<td>1Pt0.75Sn/Al₂O₃</td>
<td>87.55</td>
<td></td>
<td>2.78</td>
<td>2.15</td>
<td>47.39</td>
<td>39.40</td>
</tr>
<tr>
<td>1Pt1.25Sn/Al₂O₃</td>
<td>87.48</td>
<td></td>
<td>3.12</td>
<td>2.61</td>
<td>31.55</td>
<td>59.41</td>
</tr>
<tr>
<td>0.75Pt1Sn/Al₂O₃</td>
<td>83.88</td>
<td></td>
<td>2.69</td>
<td>2.26</td>
<td>43.33</td>
<td>44.77</td>
</tr>
<tr>
<td>1.25Pt1Sn/Al₂O₃</td>
<td>48.43</td>
<td></td>
<td>4.42</td>
<td>2.88</td>
<td>27.04</td>
<td>62.04</td>
</tr>
</tbody>
</table>

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