Effect of the Brønsted acid site strength on ionone isomer distribution during pseudoionone cyclization on solid catalysts

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Introduction
Ionones (α,β,γ) are valuable chemicals widely used in pharmaceutical and cosmetic industries. Ionones are commercially produced using strong and corrosive liquid acid catalysts such as H₂SO₄, and therefore, attempts have been made recently to replace this technology by solid acid. However, the most valuable isomer, β-ionone, has not been produced by heterogeneous catalysis. In this work we present silica-supported catalysts containing tungstophosphoric (HPA) and triflic (TFA) acids and an Amberlyst resin for ionone synthesis. Our goal was to investigate how the strength of the Brønsted acid surface species affects the activity and mainly, the ionone isomer distribution.

Materials and Methods
HPA/SiO₂ (HPAS) and TFA/SiO₂ (TFAS) catalysts with acid contents of 58.5 wt% and 8.2 wt%, respectively, were prepared by incipient wetness impregnation method using aqueous solutions of HPA and TFA. Commercial Amberlyst 35W resin was pretreated at 373K. The Lewis (L) or Brønsted (B) acid nature of the surface sites of TFAS and HPAS was determined by Infrared Spectroscopy (FTIR) of adsorbed pyridine. Pseudoionone, PS (Fluka, > 95%) cyclization was performed at 353 K under autogenous pressure in a batch Parr reactor, using dehydrated toluene as a solvent with typically a Toluene/PS = 71 molar ratio and a catalyst/PS = 28-56 wt% ratio.

Results and Discussion
The HPA structure in HPAS sample was confirmed by XRD. Triflic acid on TFAS sample was essentially Brønsted catalysts with a Brønsted site.

Table 1. Acidic properties and catalytic results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>5g Total acid</th>
<th>Acid site</th>
<th>XIONONE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m²/g)</td>
<td>number</td>
<td>nature</td>
</tr>
<tr>
<td>TFAS</td>
<td>245</td>
<td>540°</td>
<td>222°</td>
</tr>
<tr>
<td>Amberlyst</td>
<td>39</td>
<td>5200°</td>
<td>--</td>
</tr>
<tr>
<td>HPAS</td>
<td>144</td>
<td>610°</td>
<td>450°</td>
</tr>
</tbody>
</table>

Table 1. Acidic properties and catalytic results

by acid-base titration; e from manufacturer information; pyridine evacuation at 353 K, pyridine evacuation at 373 K.

Significance
TFAS, HPAS and Amberlyst 35W catalysts convert efficiently PS into ionones. Catalyst activity and selectivity toward the three ionones strongly depend on the surface acid site strength. Thus, α isomer is favored at high reaction times on Amberlyst resin while the stronger TFAS shifts the isomer distribution toward the β isomer.

Figure 1. Ionone yield as a function of time at 353 K

Figure 2. Ionone isomer distribution as a function of time.

contribution B/(B+L) ≥ 90% (Table 1). Figure 1 shows the time evolution of ionone yields per H⁺ calculated from the total acid site number, for HPAS, TFAS and Amberlyst 35W catalysts. From these curves, the initial ionone formation rates (rIONONE) were determined by calculating the slope at t = 0, Table 1. Results in Table 1 reveal that the ionone initial activity order is: TFAS >> HPAS > Amberlyst 35W. The catalytic activity results of the three catalysts reflect not only differences in the Brønsted site activity but also in the proton site strength. In fact, protons on TFA present the strongest acidity on a Hammett acidity function basis (Hα = -14.6), in contrast to -13.2 on HPAS and -2.65 on Amberlyst 35W.