Organic-inorganic Aquion®/silica hybrid solid acid for catalytic etherification and dehydration reactions

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Abstract: Amphiphilic Aquion® perfluorosulfonic acid resin (PFSA) was used as both acidic and template agent for synthesis of amorphous mesoporous silica immobilized Aquion® hybrid solid acid which was found highly active and productive for catalytic etherification of glycerol with n-butanol and dehydration of D-fructose to 5-hydroxymethylfurfural (HMF), respectively. Aquion®/silica catalyst was reusable after centrifugation and ion-exchange. The enhanced catalytic performances can be attributed to the combined effect of the strong acid sites of Aquion® resin with high accessibility and the large porosity of silica with good transport effect of reagents.

Keywords: Heterogenized perfluorosulfonic acid resin, Etherification, Dehydration

1. Introduction

Sulfonated mesoporous silica as alternative to commercially available sulfonated polymers, e.g. PFSA, represents an important solid sulfonic acid. Harmer and co-workers at DuPont first developed an efficient sol-gel method for synthesis of Nafion® resin particles entrapped within a mesoporous silica network via alkaline hydrolysis of tetraethyl orthosilicate (TEOS) followed by acidic ion exchange. These catalysts showed high catalytic performance and robustness in a broad spectrum of acid-catalyzed reactions.

New-born Aquion® PFSA shows an acid strength comparable to that of pure H2SO4 and a higher thermal stability than Nafion®. Nevertheless the prominent swelling ability in solvents limits its commercial application. In our laboratory, advanced synthesis was developed for heterogenization of Aquion® PFSA by silica or carbon as novel solid acid aimed to fine chemical manufacture from acid-catalyzed processes. Herein we communicate an experimental effort to prepare organic-inorganic Aquion®/silica hybrid solid acid as efficient and reusable catalyst for catalytic etherification and dehydration reactions in biorefinery. The composition, structure, acidity and morphology of Aquion®/silica catalyst were characterized in-depth using TGA, acid-base titration, N2 adsorption-desorption, XRD, TEM, FTIR, Raman, CNHS microanalysis, CP-MS NMR and XPS.

2. Experimental

Mesoporous silica was prepared by sol-gel method using Aquion® D66-20BS water-dispersion as both acidic and template agent. Aquion®/silica catalyst was prepared by impregnation method in presence of ethanol-water (v/v = 3/7) medium. Etherification reaction was performed in a sealed microwave reactor under N2 at 150 °C for 16 h. Results were quantified by Agilent 7890 GC equipped with FID detector and DB-1 column. Dehydration reaction was performed in a flask under atmosphere at 90 °C for 2 h. Results were quantified by Agilent 1260 HPLC equipped with RI detector and Shodex SH-1011 sugar column.

3. Results and discussion

The amphiphilic structure of Aquion® resin, i.e. the hydrophobic tetrafluoroethylene backbone and the hydrophilic vinyl ether side chain bearing SO3H group, makes itself very suitable as the template for synthesizing porous silica material. The synthetic protocol as proposed in Scheme 1 is carried out using a sol-gel method in the absence of hydrochloric acid, where the sulfonic groups of Aquion resin realizes the
acidic hydrolysis and simultaneous polycondensation of TEOS. During that TEOS can self-assemble following the template provided Aquivion® resin. After removal of the template by air-calcination at high temperature, the high-surface porous silica material is obtained. The subsequent impregnation of silica to Aquivion® dispersion allows organosulfonic acid groups to be fixed to silica network via the formation of covalent bonds and/or electrostatic interactions. Such a protocol is effective and environmentally benign without addition of extra organic template or hydrochloric acid, leading to mesoporous Aquivion®/silica hybrid catalyst with highly accessible SO₃H acid sites to reactants.

Aquivion®/silica combines hybrid characteristics of Aquivion® PFSA and silica (Raman, IR, XRD and CP-MS NMR). It shows a higher stability after immobilization than the ‘naked’ polymer (TGA). The Aquivion® loading (TGA, CNHS microanalysis) is in good agreement with the derived acidity (acid-based titration), suggesting high accessibility of SO₃H sites to reactants. Aquivion®/silica is constituted by accumulation of small silica particles (ca. 10 nm), showing a typical amorphous morphology derived from an assembly of randomly distributed interparticle mesopores (TEM, XRD, N₂ isotherms).

The Aquivion®/silica hybrid solid acid shows superior yield and efficiency towards the target products as compared to the typical benchmark solid sulfonic acids (Table 1). No significant leaching of SO₃H groups is detected. The catalyst can be easily separated and reused through centrifugation and ion-exchange.

Table 1. Catalytic performances of Aquivion®/silica catalyst compared to typical benchmark solid sulfonic acids for model reactions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield_ab (%)</th>
<th>Activity (mol_{HMF/mol_{GLC}})</th>
<th>Catalyst</th>
<th>Yield_ab (%)</th>
<th>Productive (mol_{HMF/mol_{GLC}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquivion®/silica</td>
<td>45</td>
<td>31</td>
<td>Aquivion®/silica</td>
<td>85</td>
<td>43</td>
</tr>
<tr>
<td>Nafion NR50</td>
<td>29</td>
<td>27</td>
<td>Nafion/MCF</td>
<td>89</td>
<td>31</td>
</tr>
<tr>
<td>Amberlyst-45</td>
<td>28</td>
<td>25</td>
<td>KIT-6-Pr-SO₃H</td>
<td>84</td>
<td>10</td>
</tr>
</tbody>
</table>

4. Conclusions

Aquivion® PFSA was smartly used as acidic and template reagent for preparation of mesoporous silica by sol-gel method. The porosity of such silica was proved very effective to immobilize Aquivion® resin by impregnation method. The Brønsted acid sites provided by SO₃H groups within Aquivion® resin were easily accessible to the reactants. The Aquivion®/silica catalyst demonstrated a higher efficiency for acid-catalyzed biorefinery reactions as compared to many other reported typical heterogeneous solid acid benchmark catalysts. The enhanced activity can be attributed to the combined effects of the strong acid sites of Aquivion® resin with high accessibility and the large porosity of silica with good transport effect of reagents. These features were expected to lead consequently to a better distribution of acid sites and facilitate their accessibility. The Aquivion®/silica showed good stability and reusability.

References