

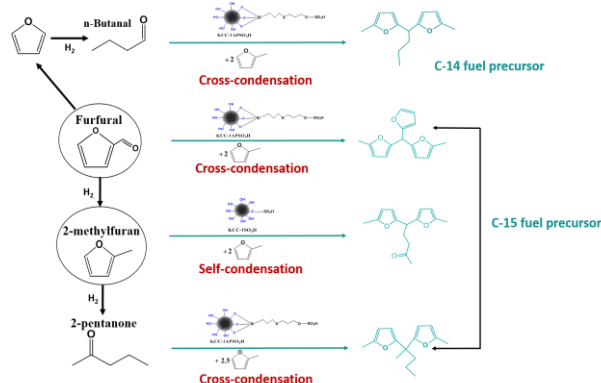
# A comprehensive investigation of condensation of furanic platform molecules to diesel precursors over sulfonic acid functionalized fibrous nano-silica (KCC-1)

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**Abstract:** 2-methylfuran is one of the most important derivatives of furfural. The hydrogenation of furfural to 2-methylfuran results in the formation of by-products (n-Butanal and 2-Pentanone). In this work, self-condensation reaction of 2-methylfuran, and its cross-condensation reactions with furfural, n-Butanal and 2-Pentanone have been implemented to produce C<sub>14</sub> and C<sub>15</sub> fuel precursors. Sulfonic acid catalysts were synthesized and investigated for these reactions. Among the synthesized catalyst, sulfonic acid-functionalized KCC-1 (KCC-1SO<sub>3</sub>H) and 3-((3-(Trimethoxysilyl) propyl) thio) propane -1-oxy-sulfonic acid-functionalized (KCC-1APSO<sub>3</sub>H) showed higher conversion and selectivity for the self-condensation and cross-condensation reactions respectively.



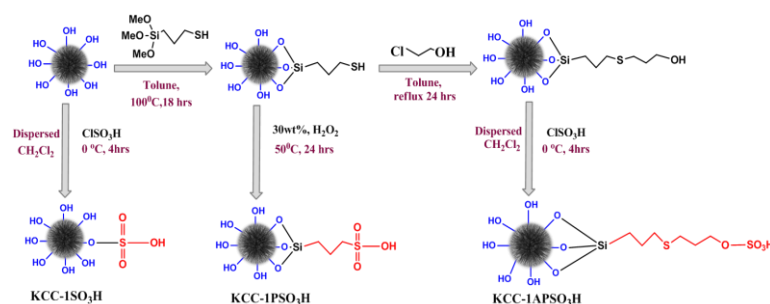
**Keywords:** Condensation reaction, Selectivity, Fibrous nano silica

## 1. Introduction

Furfural (FUR) has received attention as a potential platform for the production of biofuels and biochemicals. One of the derivatives chemicals of FUR is 2-methylfuran (2-MF). The nucleophilic aromatic ring of 2-MF provides remarkable chemical properties.<sup>[1]</sup> 2-MF can involve in hydroxyalkylation/alkylation with ketones and aldehydes or undergo trimerization itself to form a C<sub>15</sub> trimer.<sup>[2]</sup> Another method for the production of C<sub>15</sub> fuel precursors is the use of FUR and its hydrogenation by-products.<sup>[3]</sup> Here in, we have studied the self-condensation, and the cross-condensation reactions of 2-MF for the production of C<sub>14</sub> and C<sub>15</sub> fuel precursors over sulfonic acid functionalized fibrous nano-silica (KCC-1) catalysts. KCC-1, a new fibrous silica nanosphere, provides increased accessibility to the active sites.<sup>[4]</sup> Our objective was to develop catalyst with higher selectivity in the case of the self-condensation. As for the cross-condensation reactions, increased interaction with the hydrophobic reactants and stability over the in-situ formed water to enhance the formation of C<sub>15</sub> fuel precursors were the targets. Reaction time and temperature were optimized to achieve higher conversion of both 2-MF and co-reactants. The activity and selectivity of synthesized catalysts were compared with different commercial homogeneous and heterogeneous catalysts. The catalysts are recyclable for four consecutive rounds of reactions in each case.

## 2. Experimental

### 2.1 Catalysts synthesis



**Figure 1:** Schematic representation of the synthesis of KCC-1SO<sub>3</sub>H, KCC-1PSO<sub>3</sub>H, and KCC-1APSO<sub>3</sub>H. KCC-1 was synthesized based on the published procedure with some modification.<sup>[4]</sup> KCC-1SO<sub>3</sub>H, KCC-1PSO<sub>3</sub>H, and KCC-1APSO<sub>3</sub>H were synthesized by the post-grafting method and utilized for the self-condensation and cross-condensation reactions.

### 2.2 Condensation reaction

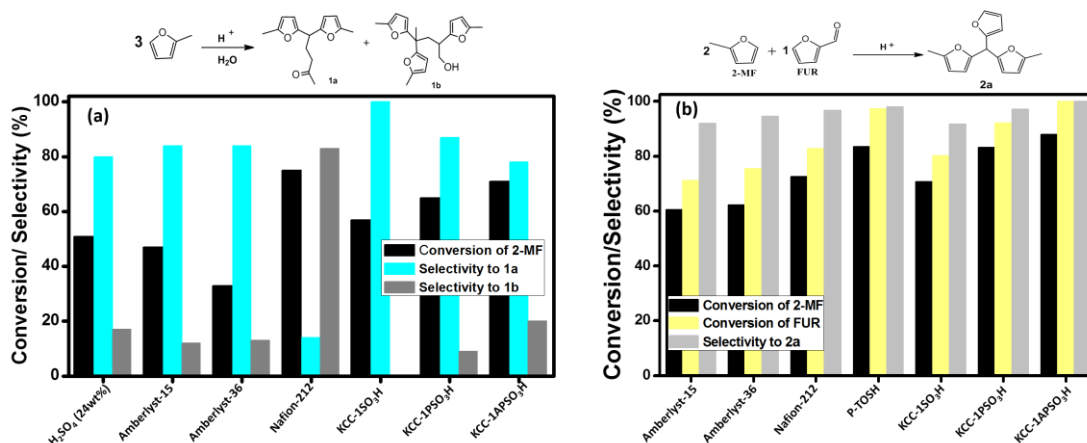
Self-condensation of 2-MF was carried out in a 100 mL round bottom flask. 2-MF (10 g, 0.12 mol), water (10 wt %), and catalyst (5 wt %) were mixed at room temperature. The reaction temperature was set at 85 °C and controlled by an oil bath. The mixture was refluxed for 48 h. In the cross-condensation reaction, 2-MF (3.69 g, 0.045 mol), FUR (1.93 g, 0.02 mol), and catalyst (5 wt % of 2-

MF) were mixed and refluxed at 70 °C for 2 h. After the reactions were completed, the catalysts were recovered by filtration. The obtained liquid reaction mixtures were analyzed by NMR (Bruker Advanced II + 400 MHz). The products were quantified by Waters high-performance liquid chromatography (HPLC).

### 3. Results and discussion

Scanning electron microscopy showed uniform spheres of ~400 nm diameter with fibrous structure for the bare support and functionalized catalysts. Observation of Transmission electron microscopy images of the material revealed the existence of dendrimeric fibers arranged to form the uniform spheres. The FT-IR spectra of KCC-1, KCC-1SO<sub>3</sub>H, KCC-1PSO<sub>3</sub>H, and KCC-1APSO<sub>3</sub>H showed the characteristic peaks corresponding to the organic moieties thus confirming the formation of the catalysts. All the synthesised materials show similar type IV isotherms and typical H1-hysteresis loops, indicating a mesoporous character. The thermal stability of KCC-1 was verified by conducting thermogravimetric analysis in the temperature range of 25 - 800 °C under nitrogen.

The reactions were conducted over different solid acid catalysts. Both Amberlyst-15 and Amberlyst-36 were active for this reactions but have lower conversion compared to Nafion-212. The higher activity of Nafion-212 over the Amberlyst resins is accredited to its structure. All the fibrous nano-silica supported catalysts showed higher conversion and selectivity. The activity sequence of these catalysts is found to be KCC-1APSO<sub>3</sub>H > KCC-1PSO<sub>3</sub>H > KCC-1SO<sub>3</sub>H in both self-condensation and cross-condensation reactions. 100% selectivity to the formation of 2-MF trimer was found in the self-condensation over KCC-1SO<sub>3</sub>H which can be accredited to the surface wettability and accessibility of the active sites. The highest selectivity in the case of all the cross-condensation reaction was obtained over KCC-1APSO<sub>3</sub>H. The highest activity and selectivity of KCC-1APSO<sub>3</sub>H can be accredited to the synergistic effect of increased hydrophobicity due to extended alkyl chain and increased acidic strength due to the electronic effect of additional S and O group.



**Figure 2:** Result of the self-condensation reaction (a) of 2-MF over various catalysts (reaction time = 48 hrs) with an addition of water (10 wt %) at 85 °C. The result of the cross-condensation (b) reaction of 2-MF and FUR over various catalysts for 2h at 70 °C.

### 4. Conclusions

In summary, we have demonstrated the synthesis of KCC-1 supported sulfonic acid catalysts by the post-grafting method and their application in the condensation of lignocellulosic furfural and its hydrogenation products. From the synthesized catalysts KCC-1SO<sub>3</sub>H showed excellent conversion of 57% for 2-MF and 100% selectivity to C<sub>15</sub> trimer in the self-condensation reaction of 2-MF due to its surface wettability in the presence of water and its high surface area. Among the most used commercial catalysts, Amberlyst-15 and Nafion-212 were found to be active yet with lower catalytic activities. KCC-1APSO<sub>3</sub>H presented the highest activity for all the cross-condensation reactions. (This work was supported by the Energy Efficiency & Resources (No. 20163010092210) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry & Energy.)

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