Application of Defect-Engineered Metal–Organic Frameworks for Aldol Condensation toward Aviation Fuel Precursors Synthesis

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Highlights

- UiO-66 MOFs synthesized with controlled HCl modulation.
- Modulator content induced defects without loss of crystallinity.
- Defect-engineered UiO-66 showed enhanced FF–CP aldol activity.
- 77% FC yield achieved with UiO-66 (H_2O/Zr = 40, HCl/Zr = 2.7).

1. Introduction

The aviation sector's move toward sustainability requires fuel production methods compatible with existing engines. Aldol condensation offers an efficient way to convert biomass-derived compounds into higher-carbon molecules, providing promising precursors for sustainable aviation fuels. Metal–organic frameworks (MOFs) have previously shown promise as catalysts for aldol condensation reactions[1]. In this work, metal-organic frameworks are introduced as a novel catalytic platform for the aldol condensation of furfural (FF) and cyclopentanone (CP). By tailoring the MOF structure through controlled synthesis parameters, including defect engineering via formic acid modulation, a clear relationship between structural properties and catalytic performance was established. Physicochemical characterization showed that the acidity and textural properties of the MOFs control conversion and selectivity, highlighting their potential for upgrading biomass to aviation fuel precursors.

2. Methods

UiO-66 samples were synthesized solvothermally from $ZrCl_4$ and terephthalic acid in DMF using H_2O and HCl as modulators. The H_2O/Zr ratio was kept constant at 40, while the HCl/Zr ratio varied from 11 to 0. These ratios define the sample notation UiO-66 (H_2O/Zr, HCl/Zr). Powder X-ray diffraction confirmed the successful synthesis of UiO-66 with varying modulator amounts, maintaining its framework structure. Higher HCl modulator content likely introduced structural defects without affecting crystallinity. Catalysts were dried at 110 °C overnight. Aldol condensation reactions were performed in a 300 mL stirred batch reactor under Ar (5 bar) at 130 °C for 6 h using FF:CP = 1:15, with furfural as the limiting reagent. Reaction conditions were selected based on previous work showing no significant mass-transfer limitations. Samples taken at regular time intervals were analyzed by gas chromatography (GC) to determine conversion as well as the yield and selectivity, while identification of products was done by GC coupled to mass-spectrometry (GC-MS). Additionally, the catalysts were characterized with a range of physico-chemical methods to correlate catalysts performance with the structure.

3. Results and discussion

Powder X-ray diffraction (XRD) patterns of the synthesized UiO-66 samples (Fig. 1a) confirm the successful formation of the characteristic UiO-66 framework for all modulator ratios. The diffraction peaks appear at the expected positions, and no additional crystalline phases are detected, indicating that varying the HCl modulator amount does not alter the overall crystal structure. However, changes in peak intensity suggest differences in defect density, with higher modulator content likely introducing structural defects while maintaining crystallinity.

The catalytic performance of the materials in the aldol condensation of FF with CP is shown in Fig. 1b. The activity strongly depends on the modulator content used during synthesis. The non-modulated UiO-

66 (40,0) exhibited negligible catalytic activity, showing almost no conversion over the reaction time. In contrast, defect-engineered UiO-66 samples displayed significantly enhanced catalytic performance.

Samples synthesized with moderate modulator amounts showed the highest activity. In particular, UiO-66 (40, 2.7) achieved nearly complete FF conversion within 2 h and provided the highest yield of the desired condensation product FC (77%). UiO-66 (40, 5.5) and UiO-66 (40, 8.3) also showed high conversions, although slightly lower than the optimal sample, while UiO-66 (40, 11) exhibited slower reaction rates. These results indicate that the introduction of defects improves catalytic performance by increasing the number of accessible active sites, but excessive modulation may reduce activity due to changes in structural or surface properties.

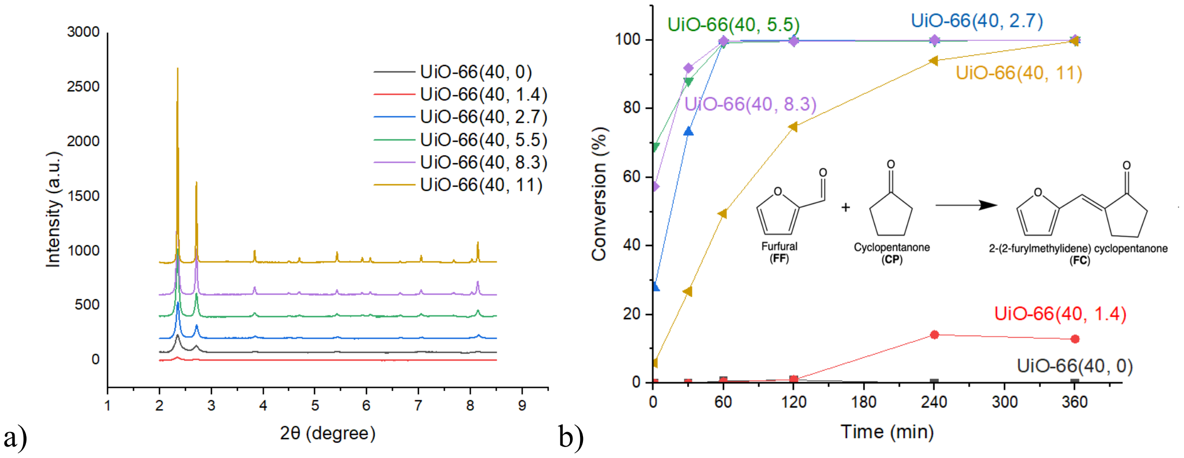

Figure 1. a) XRD patterns and b) catalytic performance of UiO-66 catalysts with varying defect densities in aldol condensation reaction of furfural with cyclopentanone. Conditions: mass ratio FF:cat = 10:1, molar ratio CP:FF = 15:1, reaction T = 130 °C, stirring speed = 900 rpm.

4. Conclusions

Defect-engineered UiO-66 MOFs were successfully synthesized and applied as catalysts for the aldol condensation of furfural and cyclopentanone. The results demonstrate that synthesis parameters, particularly modulator content, influence the structural properties and catalytic performance of the materials. Enhanced activity observed for defect-engineered samples highlights the role of textural properties in controlling conversion and selectivity. These findings confirm the potential of tailored MOF catalysts for biomass upgrading toward sustainable aviation fuel precursors.

References

[1] D. de la Flor, C. Lopez-Aguado, M. Paniagua, G. Morales, R. Mariscal, J. A. Melero, J. Catal. 2021, 401, 27-39.

Keywords
Aviation fuel precursors; Aldol condensation; UiO-66 MOFs; Defect engineering.