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Exploring the Brønsted Acidity of UiO-66 (Zr, Ce, Hf) Metal-**Organic Frameworks for Efficient Solketal Synthesis from Glycerol** Acetalization

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Vasudeva Rao Bakuru,^{a,b,#} Sathyapal R. Churipard,^{a,#} Sanjeev P. Maradur,^a and Suresh Babu Kalidindi a*

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Zr, Ce, Hf-based isostructural UIO-66 MOFs exhibited varying degree of Brønsted acidity (UiO-66(Hf)>UiO-66(Ce)>UiO-66(Zr)) ontheir secondary building units owing to their differnces in their oxophilities. UIO-66(Hf) showed remarkable catalytic activity for solketal synthesis with turnover frequency as high as 13,886 h⁻¹ which is 90 times higher than UiO-66(Zr) and several order higher when compared to H₂SO₄ or Zeolites.

Metal-organic frameworks (MOFs) are crystalline materials constructed by the co-ordination linkage between secondary building unit (SBU)/ metal cluster and bi- or multipodal organic linkers.¹The interesting properties of MOFs include well defined pores, high tunable pore surfaces, flexible nature, and rational design of their structures.² MOFs have been designed to their advantage, in many areas like gas separation/storage,³ energy storage,⁴ sensing,⁵ biomedical and catalysis applications.⁶ "MOFs for heterogeneous catalysis"7 is particularly an attractive prospect, because the well defined pore surface chemistry of MOFs allows much desired structure-activity relation to be established which is very difficult to achieve in many of the traditional heterogeneous catalysts.8 Especially, with the development of MOFs with excellent thermal/chemical stabilities⁹ MOFs have been explored for various catalytic applications in recent times.¹⁰

M(IV) (M=Zr, Hf and Ce) based UiO-66 family of MOFs {M₆O₄ $(OH)_4[(O_2C)-C_6H_4-(CO_2)]_6\}$ are attractive for catalysis not only because of their robustness but also due to their interesting structural features.¹¹ This family of MOFs has large window size, high surface area and decent pore volume which play vital role in the diffusion of reactants and products. The SBU $[M_6O_4 (OH)_4]$ of UiO-66 contains μ_3 -OH and μ_3 -O groups that alternatively bind to M₆-octahedral cluster and the SBU is connected to twelve 1, 4benzenedicarboxylate (BDC) linker via edge sharing to give UIO-66 framework with fcu-topology(Scheme1). The μ_3 -OH groups present



Increase in Bronsted acidity with increase in oxophilicity

Scheme1. a) UiO-66 MOF framework {M₆O₄ (OH) ₄[(O₂C)-C₆H₄-(CO₂)]₆}, b) Octahedral cage of UiO-66 MOF, and c) Secondary building units (SBU) corresponding to UiO-66(Zr), UiO-66(Ce), and UiO-66(Hf) MOF respectively, the µ3-OH sites (Bronsted acidic) represented in cyan colour.

on SBUs of UiO-66(Zr), ^{11(a)} UiO-66(Hf) ^{11(b)} and UiO-66(Ce) ^{11(c)} are worth exploring for systematic tuning of Brønsted acidity as three metal ions have different degree of oxophilicity.¹² The trend is Hf(IV)>Ce(IV)>Zr(IV) based on their M-O bond dissociation energies which are 801 kJ/mol, 790 kJ/mol, and 766 kJ/mol, respectively.¹² Higher oxophilicity should impart greater Brønsted acidic character to μ_3 -OH groups (pK_a<3.5) present on SBU.^{13,7e} Also, missing linker defects present in UiO-66 family MOFs also could impart some weak Brønsted acidity (pKa>5.5). Each missing linker site is generally charge compensated by either modulator (such as acetate ion) or –OH and H_2O depending on the synthesis conditions. UiO-66(Hf) MOF is has been used as solid acid catalyst for reactions such as epoxides ring opening, ^{13(b)} fructose dehydration. ¹⁴ However, systematic study that explores the Brønsted acidity of UiO-66 family of MOFs is yet to be reported.

a. Materials Science Division, Poornaprajna Institute of Scientific Research, Devanahalli, Bangalore Rural- 562164, India. Email:

sureshk@poornaprajna.org/ksureshu@gmail.com

^{b.} Manipal Academy of Higher Education, Manipal-576104, India.

[#] both authors contributed equally to this manuscript

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Figure 1. a) Powder-XRD patterns and b) Nitrogen isotherms(at 77K) of UiO-66(Zr), UiO-66 (Ce) and UiO-66(Hf) materials, closed symbols represent the adsorption and open symbols desorption.

Alkyl levulinates and solketal are very versatile compounds and finds several applications in the formulation of gasoline, diesel and biodesel, in pharmaceutical synthesis as a solvent, and also in cosmetic products as well.¹⁵ Esterification of levulinic acid with alcohols is being reported with several solid acid catalysts. But there are only few reports on using MOFs as catalysts for this reaction.¹⁶ Solketal was previously synthesized by the acetalization of glycerol with acetone using homogeneous catalysts such as H₂SO₄,¹⁷ SnCl₂, ¹⁸ iron(III), ¹⁹ Brønsted Acidic Ionic Liquids (BAIL) ²⁰ p-toluenesulfonic acid²¹ and recently many heterogeneous catalysts such 15(b) 22(a,b,c) as zeolites, heteropolyacids,^{23(a,b)} mesoporous silicas, ^{24(a,b)} mesoporous polymers²⁵ titanate nanotubes with metals ²⁶ and mesoporous cellular foam (MCF) 27 have been reported. Despite the everescalating number of MOF structures, there is only one report using MIL-47(V) and MIL-100(V) MOFs as catalysts for glycerol condensation with acetone to solketal synthesis.²⁸ However, achieving high conversions of glycerol with good selectivity towards solketal at room temperature is highly sought after. Herein, we explored the intrinsic acidic nature of SBUs of UiO-66 MOFs in the esterification of Levulinic acid (LA) with alcohols and for the synthesis of solketal by the acetalization of biomass derived platform molecule glycerol.

We synthesized UiO-66(Zr), UiO-66(Ce) and UiO-66(Hf) catalysts using solvothermal methods reported in literature.¹¹ The crystalline nature of all materials was confirmed by powder x-ray diffraction (XRD) analysis (Figure 1a). Confirming the formation of phase pure materials, the patterns matched very well with simulated powder patterns from single crystal data. N₂ sorption analysis (at 77K) showed Type-I curves for three MOFs confirming their microporosity (Figure 1b). The surface area and pore volume of UiO-66(Zr), UiO-66(Ce), UiO-66(Hf), were measured to be 1161 m^2/g and 0.62 cm³/g; 1084 m²/g and 0.53 cm³/g; and 950 m²/g and $0.6 \text{ cm}^3/\text{g}$, respectively. These are consistent with reported values. The scanning electron microscopy (SEM) images of three MOFs are shown Figure S1. The morphology and particle size of UiO-66(Zr), UiO-66(Ce) and UiO-66(Hf) are nearly spherical and 50-200 nm, deformed octahedral and 100-270 nm, nearly spherical and 50-220 nm, respectively. Potentiometric acid-base titrations were performed for all the three isostruictural UIO-66 MOFs according to previously reported procedures to identify the number of missing linker defects as this method proved to be more accurate compared thermo gravimetric analysis.^{13(a,c),29} From the titration curves (Figure S2 to S4) the number of missing linker sites per SBU were calculated to be 1.0, 1.4, and 1.6 for UiO-66(Hf), UiO-66(Ce), and UiO-66(Zr) respectively(Table S2 to S5).

The three MOFs were soaked in $NaNO_3$ solution for 18 h to exchange acidic protons in MOFs with $Na^{\scriptscriptstyle +}.$ After overnight



Figure2: a) Scheme of Levulinic acid (LA) esterification reaction, and b) Plot of yield (%) versus catalysts. Reaction conditions: Levulunic acid (1 mmol), alcohol (15 mmol), catalyst amount 20 mg and reaction carried for 4h at 80 °C

exchange, the pH values of the solutions were measured to be 3.5, 4.6 and 5.8 for UiO-66(Hf), UiO-66(Ce), and UiO-66(Zr) respectively (table S2). These pH values suggest that UIO-66(Hf) has stronger acidic sites compared to other two MOFs. Further the total released H⁺ ions were determined to be (Table S1) 0.25 mmol/g, 0.82 mmol/g and 1.26 mmol/g for UiO-66(Zr), UiO-66(Ce), and UiO-66(Hf) respectively by the acid base titrations. The higher labile nature of UiO-66(Hf) protons is ascribed to greater oxophilicity of Hf(IV) metal ion.

Esterification of alcohols is one of the basic reactions catalyzed by acidic sites. Levulinic acid esterification was performed with isostructural UIO-66 MOFs in order to further establish the acidity present in three MOFs (figure 2a). The effect of metal ion present in SBUs of MOFs on the catalytic activities is clearly evident from Figure 2. UiO-66(Hf) showed the highest catalytic activity followed by UiO-66(Ce) and UiO-66(Zr). This order is consistent with the acidity order suggested by acid-base titrations.

This proven varying degree of acidity present in UiO-66 family MOFs is explored for the acetalization reaction between glycerol and acetone. This reaction furnishes five-membered solketal and six-membered acetal products (figure 3a) over acid catalysts. Since, selectivity of the reaction depends on the type and strength of acidic center it would be interesting to explore UiO-66 (Zr Ce, Hf) MOFs as catalysts. UiO-66 family of MOFs have tetrahedral (7.5 Å) and octahedral pores (12 Å) with window openings of ~7 Å which is large enough to allow glycerol and acetone into the pores of MOF (Scheme S1). Glycerol acetalization reactions were carried out in a batch reactor at room temperature. The comparison between the catalytic performances of UiO-66(Zr), UiO-66 (Ce) and UiO-66(Hf) is shown in Figure 3b. UiO-66(Hf) outperformed other two catalysts owing to its higher degree of acidity. UiO-66(Hf) catalyst showed a glycerol conversion of 94.5 % and a solketal selectivity of 97.2 % at room temperature. On the other hand, at the same reaction conditions, UiO-66(Zr), UiO-66(Ce) showed glycerol conversions of 1.5 %, 70.1 % and the solketal selectivities of 73.2 % and 90.1 %, respectively. Therefore order of catalytic performance is UiO-66(Hf)> UiO-66(Ce)> UiO-66(Zr). This order is again coinciding with aforementioned acidity order of these MOFs. Higher the Brønsted acidity of MOF, higher was the glycerol conversion and solketal selectivity. UiO-66(Hf) MOF possessing relatively strong protic µ3-OH groups on its SBU exhibited highest catalytic activity.

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a) H₂O Glycerol Acetone Solketal Acetal b) Conv.(%) & sel.(%) 70.1 90 UiO-66(Hf) Glucose UiO-66(Ce) Solketa UiO-66(Zr) Acetal 13866.9 c) 15000 10000 TOF(h⁻¹) 3801.0 5000 150.0 0 UiO-66(Zr) UiO-66(Ce) UiO-66(Hf)

Figure 3: a) Scheme of glycerol acetalization reaction, b) Plot of conversion and selectivity versus isostructural UiO-66 MOFs, and c) Activity (TOF) of UiO-66(Zr), UiO-66(Ce) and UiO-66(Hf) catalysts in the solketal synthesis. Reaction conditions: Glycerol = 1.0 g, Acetone = 2.52g, Glycerol: acetone = 1:4, catalyst = 10.0 wt% (referred to glycerol weight), reaction carried at room temperature for 1h.

Further, we have calculated the turnover frequencies of three catalysts by carrying out reactions for at room temperature for 5 min using 0.25 wt % catalyst (referred to glycerol) with 1:4 molar ratio of glycerol to acetone. The comparison of TOFs is shown in figure 3c. The UiO-66(Hf) catalyst exhibited a very high TOF of 13886 h⁻¹ which is 90.7 folds and 3.6 folds more than UiO-66(Zr) TOF and UiO-66(Ce) TOF, respectively (Figure 2b). We have compared our results with various solid acid catalysts such as zeolites, silica, MIL-53(V) etc (Table S7). It is very clear from the Table S7 that UiO-66(Hf) performance is one of the best. It is interesting to note that UiO-66(Hf) outperformed zeolites (H-ZSM-5 and H-Beta) and even homogeneous H₂SO₄.

Since glycerol acetalization with acetone is a reversible reaction, using higher mole ratio of one of the reactant will push the equilibrium towards products. To evaluate this, we studied the effect of mole ratio by varying the mole ratio between glycerol to acetone from 1:1 to 1:5 (Figure S5). As expected, the increase in acetone amount favoured high glycerol conversion up to 1:4 mole ratios, but further increase in mole ratio of glycerol to acetone (1:5) did not show much improvement. This is possibly due to the dilution effect where the probability for the reactants to find an active site reduces upon dilution. Also, there was significant improvement in solketal yield upon increase in catalyst amount from 0.25 wt% to 2.5 wt% (Figure S6). However, further increase in catalyst concentration to 5 wt% and 10 wt% did not improve the solketal yield significantly.

The mechanism of acid catalyzed solketal synthesis from glycerol and acetone is reasonably well established in the literature.³⁰ The mechanism of Brønsted acid catalyzed solketal synthesis involves formation of glycerol-acetone adduct in the first step. This adduct turns into a tertiary alcohol. Brønsted acid sites (present on the SBU of MOFs) interact with this intermediate to



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Scheme 2. Plausible reaction mechanism for glycerol acetalization with acetone over Brønsted acidic present in UIO-66 MOFs

generate a carbocation upon dehydration as shown in the scheme



Figure 4: a) Recyclability of UiO-66(Hf) catalysts, b) PXRD patterns and N_2 isotherm (77 K) plots of fresh and used UiO-66(Hf) catalysts.

2. The secondary or terminal hydroxyl group of glycerol can attack this carbocation to generate five membered and six membered products, respectively with the elimination of a water molecule in the last step.

Recyclability and leaching tests were carried out in order to confirm the stability and heterogeneity of UiO-66(Hf) material (Figure 4a). In recyclability tests, around ~ 7% of conversion was decreased in the first cycle. Probably, due to the residual reactants or products were slightly trapped within the pores or strongly adhered with active sites of UiO-66(Hf). Nevertheless, after first cycle to fourth cycle no significant change in the glycerol conversion was observed. Further, we characterized spent catalyst using x-ray diffraction and N₂ sorption (Figure 4b). UiO-66(Hf) retained its crystallinity even after four cycles and the surface area and pore volume of used catalyst is 968 m^2/g and 0.58 cm^3/g , respectively. In addition, leaching test was performed in order to check the nature of catalysis. After removing the catalysts from reaction medium after 5 min there was almost no change in the glycerol conversion up to 1h reaction time (Figure S7). Further, inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis of supernatants after the reaction did not show any detectable amounts (<1 ppm) of respective metal ions. These observations confirm that the UiO-66(Hf) MOF retained its structure after 4 cycles and the catalysis is heterogeneous in nature.

Conclusions

Tuning the acidic sites is highly desired to achieve superior catalytic performance and the results discussed here show how oxophilicty of metal ions effects the acidity of SBUs $(M_6O_4(OH)_4)$ present in UiO-66 MOFs. Isostructural UIO-66 MOFs (Hf, Zr, Ce) exhibited varying degree of acidity on their SBUs. The acidity order is found to be UiO-66(Hf)>UiO-66(Ce) > UiO-66(Zr) in accordance with their oxophilicity order. The varying degree of acidity present in this class of MOFs has been evaluated for the synthesis of alkyl levulinate and solketal. UiO-66(Hf) exhibited one of the higher activities for solketal synthesis from glycerol acetalization reported to date with turnover frequency as high as 13,886 h⁻¹ which is 90 times higher than its isostructural UiO-66(Zf). Overall, the studies reported here sheds light upon the versatile acidity present on the

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 $\ensuremath{\mathsf{SBUs}}$ of UiO-66 family and can simulate further studies in this direction.

Conflicts of interest

"There are no conflicts to declare".

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Notes and references

‡ Experimental details, additional characterization of catalysts, details of defects calculation from acid-base titrations are given in supporting information.

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