Tuning the catalytic activity of metal-organic frameworks (UiO-66) through the linker: defects or functional group?

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UiO-66 is famous for its defects in its structure which are generated when organic linkers are missing without suffering from severe loss of stability. These defects have triggered great interests for researches in developing more applications, such as in gas sorption, catalysis and sensing by tuning MOFs’ physical-chemical properties. Therefore, at the presence of defects the Bronsted acidity of MOFs can be created via hydroxyl group or water molecule bound to Zr sites. Herein, the Bronsted acidity of UiO-66 was investigated via functionalization by different linkers to create different number of defects, which was further employed as the catalyst for fructose dehydration to produce hydroxymethylfurfural (HMF).

Five different samples of (Zr)UiO-66 with different number of mixed linkers (H$_2$BDC-NH$_2$ and H$_2$BDC-NO$_2$) were prepared to study the effect of the linker composition on their catalytic activity. The defects on MOFs were calculated by thermal gravimetric analysis (TGA). Based on the TGA results, none of these samples is fully connected to 12 linkers. Instead, the result is indicative that more defects can be created by more -NH$_2$ group incorporated. Therefore, the dehydration of fructose was evaluated as an industrially relevant catalytic reaction to produce HMF, which is an important platform molecule. The number of amino groups has a clear effect on their catalytic activity. With more defects in MOFs resulted from the increase of -NH$_2$ groups in MOFs, the yield of HMF was improved from 47% to 71. It was also found that coordinated H$_2$O plays a crucial role in MOFs’ catalytic activity. By dehydration of MOFs at high temperature, MOFs’ catalytic activity could be undermined, suggesting the importance of Bronsted acidity of MOFs created by coordinated H$_2$O, which is in agreement with previous report. More characterizations were done to confirm its Bronsted acidity, such as N$_2$ physisorption, pH of MOFs in water and test reactions.

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