

Electronic modification and controlled defect introduction improve the catalytic activity of Zr-MOFs

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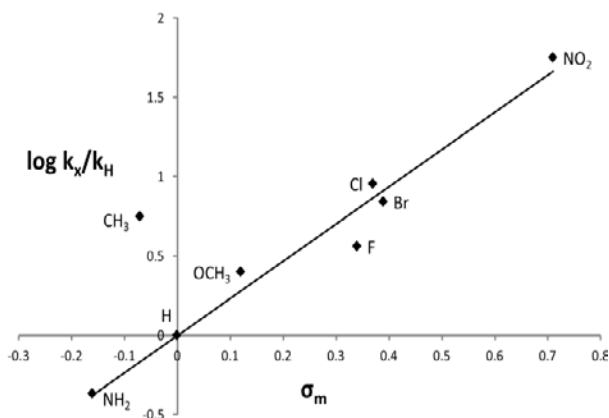
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This paper proposes two concepts for increasing the catalytic activity of MOFs. First, it is shown that functional groups in a MOF lattice can have a strongly promoting electronic effect on the catalysis at open sites. In a second strategy, the activity can be further boosted by using volatile monocarboxylate modulators.

Both strategies were implemented for Zr-terephthalates (UiO-66). The electronic influence of functional groups on the Lewis acidity was probed by using substituted UiO-66-X materials (X = substituent) as catalysts in the citronellal cyclization reaction. All UiO-66 materials are active in the cyclization, but the rate is dramatically enhanced with an electron-withdrawing group on the linker (F, Cl, Br, NO₂). The increase in reactivity can be correlated to the electronic nature of the ligand through a Hammett plot (figure 1).

The introduction of a nitro group results in a 56-fold rate increase, which clearly points to electronic active site modulation. Calculations evidenced that nitro-substitution increases the Lewis acidity, as reflected in a lower energy for the adsorbed reactant and a lower transition state.*



In another concept, monocipital ligands (e.g. acetic acid,...) were added as modulators during synthesis of UiO-66 type materials. These modulators not only improve the crystallinity; they are also incorporated inside the crystals and can create extra open Lewis acid sites upon mild thermal pretreatment, particularly if the corresponding acids are highly volatile, like formic acid or trifluoroacetic acid. This results in a much increased activity, without compromising framework stability.

* Vermoortele, De Vos et al., *Angewandte Chemie*, 2012, in the press.