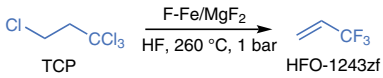
FLUORINATION CATALYSIS

An alternative to Chromium

Catal. Sci. Technol. https://go.nature.com/2HFYccL (2019).



Hydrofluoroolefins (HFOs) are a recent generation of refrigerants, considered to be a safer alternative to hydrofluorocarbons (HFCs) due to their reduced impact on global warming, as well as their zero-ozone depletion potential. The synthesis of HFOs requires the construction of C–F bonds, which is usually achieved via gas phase fluorination with hydrogen fluoride (HF) in the presence of chromium based catalysts. However, in addition to safety concerns associated with the use of HF, the toxicity of chromium and the related pollution hazards connected with its large scale utilization exacerbate the environmental impact of such processes. Now, Wei Mao, Jian Lu, Erhard Kemnitz and colleagues report that iron supported on hollow nano-MgF_2 particles (Fe/MgF_2) outperforms Cr systems as a catalyst for the gas-phase fluorination of 1,1,1,3-tetrachloropropane (TCP) with HF, and may potentially lead to their replacement.

The authors studied the stability of Fe/MgF_2 following HF treatment at 350 °C, and observed that the morphology of the system remained essentially unchanged, as confirmed by X-ray diffraction, microscopy and gas sorption analyses. In turn, surface techniques showed a moderate fluorination enhancement, which was ascribed to the partial conversion of iron oxides into iron fluorides. Such species increase the acidic strength of Fe/MgF_2. Interestingly, compared to a traditional Cr-based fluorination catalyst — that is, fluorinated Cr_2O_3 — the fluorinated iron catalyst ($F\text{-}Fe/MgF_2$) features a similar distribution of weak and medium acidic sites, but a smaller amount of strongly acidic sites, according to temperature programmed ammonia desorption. The acidic properties, as well as the stability under severe reaction environments, make $F\text{-}Fe/MgF_2$ a very competitive system for the fluorination of TCP (pictured). Remarkably, time on stream experiments revealed that the catalyst can sustain full TCP conversion for approximately 100 hours, reaching values of 85% in over 200 hours. As a comparison, the conversion for the benchmark fluorinated Cr_2O_3 drops to 77% in just 72 hours on stream. The selectivity of $F\text{-}Fe/MgF_2$ towards 3,3,3-trifluoropropene (HFO-1243zf) remains constantly above 92%, making this new catalyst attractive for industrial applications. Analysis of the spent catalyst indicates the lack of strong acidic sites as one of the possible reasons for the superior stability of $F\text{-}Fe/MgF_2$, possibly by limiting coke deposits formation in proximity of the catalytic sites.

Considering its catalytic properties, $F\text{-}Fe/MgF_2$ could become a potential replacement for the traditional Cr catalysts commonly employed for hydrofluorination reactions, thereby contributing to the reduction of the environmental risks associated with the synthesis of greener refrigerants, such as HFO-1243zf.

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Published online: 13 June 2019
https://doi.org/10.1038/s41929-019-0315-6