The Remarkable Catalytic Activity of the Saturated Metal Organic Framework V-MIL-47 in the Cyclohexene Oxidation

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Outline

- Introduction:
  - Definition: Metal Organic Framework (MOF)
  - Attractive features of MOFs

- Synthesis and characterisation of MIL-47

- Catalytic study: cyclohexene oxidation

- Regeneration capacity

- Hot filtration experiments

- Determination of the leached V

- Theoretical calculations: reaction pathway

- Conclusions
Definition: Metal Organic Framework

MOFs → Inorganic cluster (Metal Ion) + Organic Linker = Framework

MOF-5

Zn

Organic linker
Attractive features of MOFs

- Rigid structures
- High surface area (>3000m²/g)
- High metal loading
- Breathing

![Diagram of MOFs in different states: as, open, hydrated](image_url)
MIL-47

Vanadium containing MOF
Synthesis of MIL-47

Molar ratio: $\text{VCl}_3$/ terephthalic acid/ water$= 1/0.25/100$

Autoclave
Calcination, 21h30 min, 300°C

Characterisation of MIL-47

Surface area: 1200 m$^2$/g
Characterisation of MIL-47
Catalytic activity of MIL-47

Karen Leus, Ilke Muylael, Matthias Vandichel, Guy B Marin, Michel Waroquier, Veronique Van Speybroeck and Pascal Van Der Voort, *Chemical Communications*, **2010**, DOI:10.1039/C0CC01506G
Catalytic activity of VO(acac)$_2$
Regeneration capacity of MIL-47 (1)
Regeneration capacity of MIL-47 (2)
Second run experiment
Hot filtration experiments

- Cyclohexene conversion with catalyst
- Cyclohexene conversion without catalyst
Determination of the leached V

→ TGA of MIL-47 after catalysis
→ XRF (using Co as internal standard)

\[
y = 0.2208x
\]

→ 12.8% of the V leached after one hour
Hot filtration experiments

Graph showing the conversion of cyclohexene with and without a catalyst. The graph indicates an increase in conversion over time. The catalyst's effect is more pronounced, reaching higher conversion rates compared to the non-catalyst condition. The conversion of cyclohexene is also noted as 12.8% with catalyst.
Reaction pathway
Conclusions

- MIL-47 is catalytically active
- Good agreement with the homogeneous catalyst
- Catalysis occurs predominantly heterogeneous
- MIL-47 can be regenerated and reused
- Successful epoxidation is accompanied by a linker exchange with TBHP
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