

Stability investigation of hybrid dimethyl ether catalyst

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Highlights

- Analysis by microprobe line scan and SEM showed impeded interphase migration of Zn.
- Activity test according to constant conversion principle minimized kinetics dependency.
- Lower degree of Zn intrusion in the post run coarse particle pellets explains stability.

1. Introduction

Dimethyl ether (DME) is known as an environmentally benign chemical with good LPG and diesel substitute characteristics. In specific process configurations, e.g. wherein synthesis gas is supplied from gasification based front-ends, the optimal feed gas composition for the DME synthesis via methanol has a module fulfilling $(\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2) = 1$.

For such layouts the coexistence of activity in both methanol synthesis (R1), water gas shift (R2) and methanol dehydration to DME (R3) is especially beneficial, in that the product water formed (R1 and R3) is efficiently consumed by the WGS (R2), creating a powerful reaction synergy [1].

The combination of methanol/WGS active material with DME active material, i.e. the full set of catalytic functions needed for direct DME synthesis, may be obtained e.g. in a hybrid catalyst of co-pelleted particles in domain proximity. Hybrid catalysts are known to be challenged by stability issues [2], but are seen as attractive due to their easier handling, and their potentially higher reactivity at low water concentration. Select process conditions and alternative active phases may provide improved catalyst behavior.

2. Methods

Two variants of a hybrid catalyst, pelletized from a combination of Cu/ZnO/Al₂O₃ (CuZnAl domain) particles (active in (R1) and (R2)) silica-alumina (SiAl domain) particles (active in (R3)), respectively, of distinctly different particle sizes, were kinetically tested on a module = 1 synthesis gas for 800 h.

The principle for catalyst testing was 1) [deactivation] longer term exposure of catalyst to feed gas under full conversion and preferred industrial conditions, yielding low approaches to equilibrium for all three reactions, interrupted by 2) [activity test] short lasting intermittent changes to low temperature and low flow rate conditions securing significant approaches to equilibrium for all three reactions involved. The test was conducted with repeated switches between these two conditions, 1) and 2), ensuring that the exit CO₂ as indicator of degree of conversion was held as constant as possible under the activity testing, managed by a feed flow rate adjustment, minimizing the dependency of the relative activity evaluation on accurate kinetics.

The fine (catalyst A) and the coarse (catalyst B) samples were characterized by light microscopy, microprobe line scan and scanning electron microscopy before and after testing.

3. Results and discussion

The pellets (catalyst A) made from finer 50-100 μm particles showed lower stability than pellets (catalyst B) made from the coarser 600-1000 μm particles. Characterization by a combination of scanning electron microscopy and microprobe line scans of fresh and spent catalyst showed that migration of both Zn from the CuZnAl domains 10-15 μm into the SiAl domains and, conversely, the migration of Si from the SiAl domains particles hundreds of μm into the CuZnAl domains, took place across the particle interphases.

Customized and carefully conducted kinetic testing and data analysis, establishing the relative activity developments, showed that the DME active domain (SiAl) of the fine particle variant of the hybrid catalyst (catalyst A) deactivated significantly faster than the coarse particle variant (catalyst B), while the relative deactivation rate of the methanol active CuZnAl domain was almost unaffected.

Suggesting that Zn may deactivate the SiAl domains, the scale of the Zn migrant intrusion depths found by characterization (see Figure 1 to the right, ►) is consistent with the higher degree of reciprocal contamination of the more closely co-existing domains in the fine particle pellets of catalyst A, being expressed through a lower catalyst DME stability: The relative DME activity of the coarser particle catalyst B leveled out after 400h, while it continued decreasing for catalyst A after 800 h (see Figure 2, left, below, ▼). Furthermore, in conjunction with the easy interphase migration of Si, the methanol activity evolution of catalyst A and B remained parallel (see Figure 2, right, below, ▼).

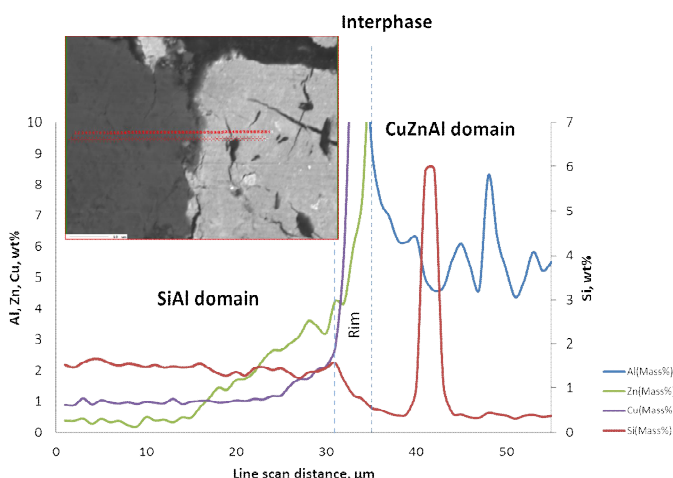


Figure 1. SEM and microprobe line scan shows impeded intrusion of Zn in the SiAl domain. Si migrates easily into the CuZnAl domain.

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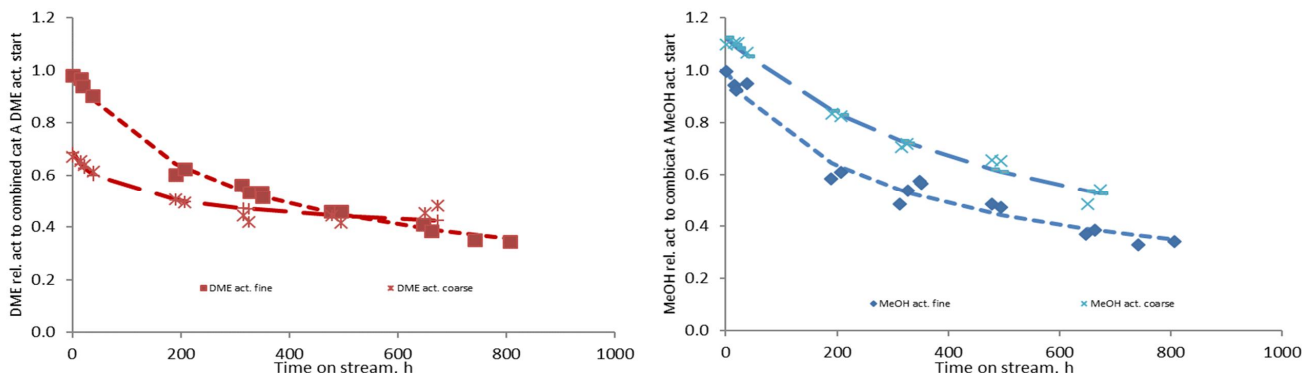


Figure 2. Left: DME (R2) activity vs time (■ (red squares): fine particle catalyst A; * (red asterisk): coarse particle catalyst B). Right: Methanol and WGS (R1 and R3) activity vs time (◆ (blue diamond): fine particle catalyst A; × (light blue cross): coarse particle catalyst B).

4. Conclusions

Activity testing of several simultaneous catalyzed functions requires a customized test plan.

The impeded Zn migration explains the comparatively more stalled deactivation of the SiAl particle domains, active in dimethyl ether formation, in the coarser hybrid B. The CuZnAl domain particles, active in methanol synthesis and the water gas shift reactions, deactivated equally fast in hybrids A and B.

Hybrid catalysts must be carefully designed to obtain proper catalyst stability.

References

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- [2] García-Trenco, A., A. Martínez, The influence of zeolite surface-aluminium species on the deactivation of Cu/ZnAl/zeolite hybrid catalysts for the direct DME synthesis. *Catalysis Today*, 2014. 227: pp. 144-153.

Keywords

Hybrid dimethyl ether catalyst; deactivation; test method; migration.