High-pressure study of ammonia/dimethyl-ether conversion in a flow reactor

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Objective:
• Extending the knowledge of NH₃/DME oxidation at high pressure under different operating conditions.
• Development of a detailed reaction kinetic model.

Methodology

Experimental Conditions:
Pressure: 1, 10, 20, 40 bar
Temperature: 350 – 1225 K; λ = 0.7, 1 and 3
[NH₃] = 1000 ppm, [DME] = 0.5, 50 and 300 ppm
[O₂] = 1000, 900, and 6600 ppm
Quartz tubular reactor: 153.8 cm long, inner diameter of 0.6 cm. As a gas bath reactor Simulation software: Chemkin pro

Residence time:

\[ \tau = \frac{V}{Q_{\text{total}}} \]

Oxygen excess ratio, Lambda:

\[ \lambda = \frac{O_2}{O_2_{\text{stoichiometric}}} \]

NH₃ + \frac{1}{2}O_2 = \frac{2}{3}N_2 + \frac{1}{3}H_2O \quad r1

CH₃(CH₂) + 3O₂ = 2CO₂ + 3H₂O \quad r2

Experimental Results

Figure 1 to 5: DME concentration as a function of temperature at 1, 10, 20 and 40 bar of pressure, for DME/NH₃ mixture oxidation and λ=0.7, 1 and 3 respectively.

Figure 6 to 10: NH₃ concentration as a function of temperature at 1, 10, 20 and 40 bar of pressure, for DME/NH₃ mixture oxidation and λ=0.7, 1 and 3 respectively.

Figure 11 and 12: DME and NH₃ reaction pathway in pre-, during and post-NTC behaviour at 40 bar of pressure, for DME/NH₃ = 0.3 and λ=1.

Conclusions

- NH₃ Reaction onset occurs at a lower temperature as pressure increases.
- DME addition (50 and 300 ppm) enhances the NH₃ conversion respectively (up to 250 K and 600 K) compared to pure NH₃ at 40 bar.
- Oxygen availability is a key variable: NH₃ and DME conversion occurs at lower temperatures under oxidizing conditions, slightly more remarkable for NH₃ than for DME.
- A negative temperature coefficient (NTC) is observed for NH₃ and DME conversion with higher DME/NH₃ ratios.
- CH₄O is an important intermediate product of the DME/NH₃ combustion and is involved in the NTC behavior.
- NH₃/DME oxidation produces NOₓ in significant quantities under almost all conditions and NO only under certain conditions, while pure NH₃ combustion does not produce NO and N₂O₂, CO, CO₂ and CH₄ (monochromatic basis) were found as carbon species in significant amounts.
- Calculations show good reproducibility and do follow the same trends as observed experimentally.

References:

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