A flow reactor study of NH_3/DEE oxidation

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Summary

This study evaluates how dimethyl ether (DEE) affects the oxidation of ammonia. This compound improves the reactivity of NH_3, reducing the temperature at which the chemical reaction begins. Likewise, a study is conducted on the different reaction routes that ammonia follows depending on various parameters.

Introduction

In light of the current energy crisis, driven by both the scarcity of conventional fuels and their associated harmful effects, the scientific community is intensifying its efforts to identify viable alternatives.

Ammonia combustion represents a promising clean alternative to conventional fuels use, owing to its potential for synthesis from renewable energy sources and its carbon-free composition. However, ammonia exhibits unfavourable thermochemical properties, including a low calorific value, low flame speed, and limited flammability. Furthermore, NH_3 combustion may result in NO_x emissions under certain conditions.

To overcome these problems, co-firing ammonia with other fuels with better thermochemical properties may be a solution. Other organic oxygenated compounds, such as methanol and DME, also show promising results. Preliminary studies of NH_3-DEE mixtures show an improvement in ignition delay times [1] or the explosion limit of ammonia with a small addition of DEE [2] compared to the combustion of net ammonia.

Experimental

The experiments were conducted using a quartz flow reactor. The reactor measures 8.7 mm in internal diameter and 200 mm in length. All reactions were carried out under isothermal conditions. To this end, the reactor was placed inside an electrically heated furnace equipped with three heating elements. A micro gas chromatograph (μGC) was used to quantify HCN, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2, NH_3, N_2O, H_2, N_2, O_2, CH_3OH, diethyl ether (DEE). In addition, due to the inability of the μGC to analyse NO, the outlet gas stream was monitored using a continuous analyser for NO concentration.

All experiments had a standardised flow rate of 1 $L\cdot min^{-1}$. The temperature range for the experiments was 875–1425 K. To cover the widest possible range of conditions, temperature, excess oxygen ratio (λ), and the NH_3/DEE ratio were controlled during each experimental run. The O_2 concentrations were calculated based on the following chemical reactions.

$$NH_3 + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O \qquad (r1)$$

$$(C_2H_5)_2O + 6\ O_2 \rightarrow 4\ CO_2 + 5\ H_2O \qquad (r2)$$

Additionally, calculations were carried out using Chemkin-Pro 2023 [3]. The kinetic model incorporates nitrogen chemistry from Glarborg et al. [4] and the DEE reaction subset from Tran et al. [5]. Thermodynamic parameters were taken from the respective sources.

Results and discussions

Figure 1A shows the behaviour of ammonia as a function of λ. It is shown that NH_3 oxidation occurs at lower temperatures with an increase in O_2 concentrations. Moreover, ammonia is not completely consumed under fuel-rich conditions. Calculations fit the experimental results obtained reasonably well.

According to calculations, ammonia oxidation takes place mostly due to its interaction with OH and O radicals, $NH_3 + OH \rightleftharpoons NH_2 + H_2O$ (r3) and $NH_3 + O \rightleftharpoons NH_2 + OH$ (r4). In addition, the reactions that directly affect the production of these radicals, either $H + O_2 \rightleftharpoons O + OH$ (r5) or $CH_3 + HO_2 \rightleftharpoons CH_3O + OH$ (r6), are the reactions that most positively affect NH_3 consumption. The significance of reaction (r6) indicates that the presence of DEE promotes an increase in radical concentration within the radical pool.

The study carried out on the NH_3/DEE ratio in the mixture (Figure 1B) further confirms the positive effect of DEE on ammonia conversion. This is attributed to the significant temperature differences (up to 250 K) observed between the most extreme cases in which complete NH_3 oxidation is achieved. These results suggest that DEE is a major contributor to the radical pool, particularly through reactions such as (r6), whose importance is reduced when DEE is present at lower concentrations.

Conclusions

Adding DEE to ammonia enhances NH_3 oxidation, favouring its conversion at lower temperatures as the proportion of DEE in the NH_3/DEE mixture increases. OH and O radicals are the principal drivers of NH_3 reactivity. An increase in λ shifts the oxidation temperature regime of both fuels to lower temperatures. The same reactions govern the reactivity of NH_3 even when a higher concentration of DEE is added.

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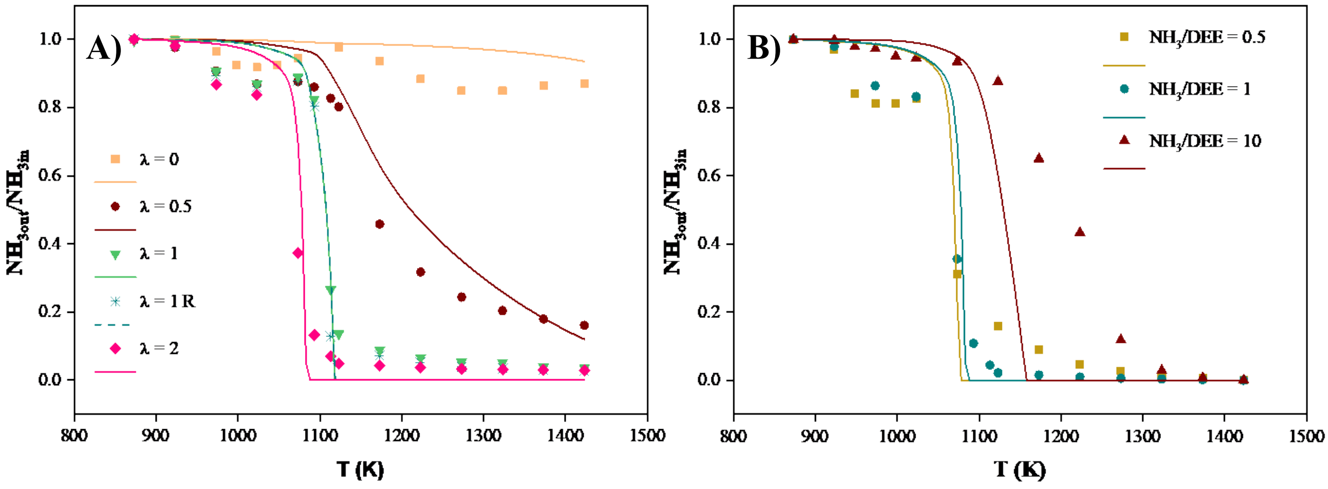

Figure 1. Ammonia profile comparisons for A) λ and B) NH_3/DEE mixture ratio.