DMM effect on ammonia oxidation

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Summary

This study evaluates how dimethoxymethane (DMM) 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

Ammonia (NH_3) combustion is emerged as a promising clean alternative to conventional fuels due to its carbon-free nature and its potential to be synthesized via renewable energy sources. Nevertheless, NH_3 presents several unfavorable thermochemical characteristics that limit its direct application as a fuel.

One potential strategy to overcome these limitations is the co-combustion of NH_3 with fuels with better thermochemical properties. Previous studies have demonstrated that dimethoxymethane (DMM) can considerably reduce ignition delay times and enhance the laminar burning velocity of ammonia by up to threefold through the formation of highly reactive radicals that accelerate NH_3 oxidation kinetics [1,2]. Furthermore, DMM has been reported to improve engine performance while reducing soot formation and NOx emissions compared with conventional fuels [3,4].

Experimental

A flow reactor setup is used to carry out these experiments. The reactor has an internal diameter 8.7 mm and 200 mm in length and is placed into an electric heated oven. A Type-K fine-wire thermocouple is employed to measure the isothermal conditions (±5 K). A detailed description of the setup is available elsewhere [5]. A total gas flow rate of 1000 mL·min-1 (STP) is used. Every gas reactant is added individually.

The excess oxygen ratio (λ) is defined as the fed oxygen divided by the O_2 necessary for complete oxidation. Temperature, excess oxygen ratio (λ), NH_3, and DMM concentrations have been varied in these experiments. Both ammonia and DMM initial concentrations are modified to cover different NH_3/DMM ratios. λ is changed for each experiment (0-3.2). Each experimental set was run in a range of temperatures between 875-1425 K.

A gas chromatograph Agilent 990 Micro GC equipped with thermal conductivity detectors (TCD) is used to measure CO, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2, NH_3, N_2O, H_2, N_2, O_2 and HCN. In addition, the outlet gas stream is analyzed using an Advance Optima AO2020 series continuous gas analyzer, which measures the concentration of NO.

A detailed kinetic model was used to study the behavior of the different identified species by means of a plug flow reactor (PFR) implemented in the CHEMKIN-Pro software.

Results and discussions

Figures 1A and 1C show the NH_3 profiles for different λ and NH_3/DMM ratios, respectively. NH_3 conversion is strongly affected by λ. Under fuel-lean conditions, NH_3 oxidation shifts to lower temperatures, with an approximate temperature shift of 100 K between fuel-lean and fuel-rich conditions. Under fuel-rich conditions, complete NH_3 conversion is not achieved, with approximately 16% of the initial NH_3 remaining unreacted.

DMM also has a significant influence on NH_3 conversion, provided that the initial DMM concentration does not exceed that of NH_3 (NH_3/DMM $\leq$ 1). However, under highly diluted DMM conditions (NH_3/DMM = 1), NH_3 conversion shifts to higher temperatures by approximately 150 K due to the lower radical availability. Concerning DMM, unlike NH_3, the conversion temperature range remains narrow as λ changes (Figure 1B), with temperature differences below 50 K. Its main consumption pathway is Hydrogen abstraction by CH_3 radicals, resulting in reduced competition for OH and O radicals, which play a key role in NH_3 conversion. DMM conversion is not significantly

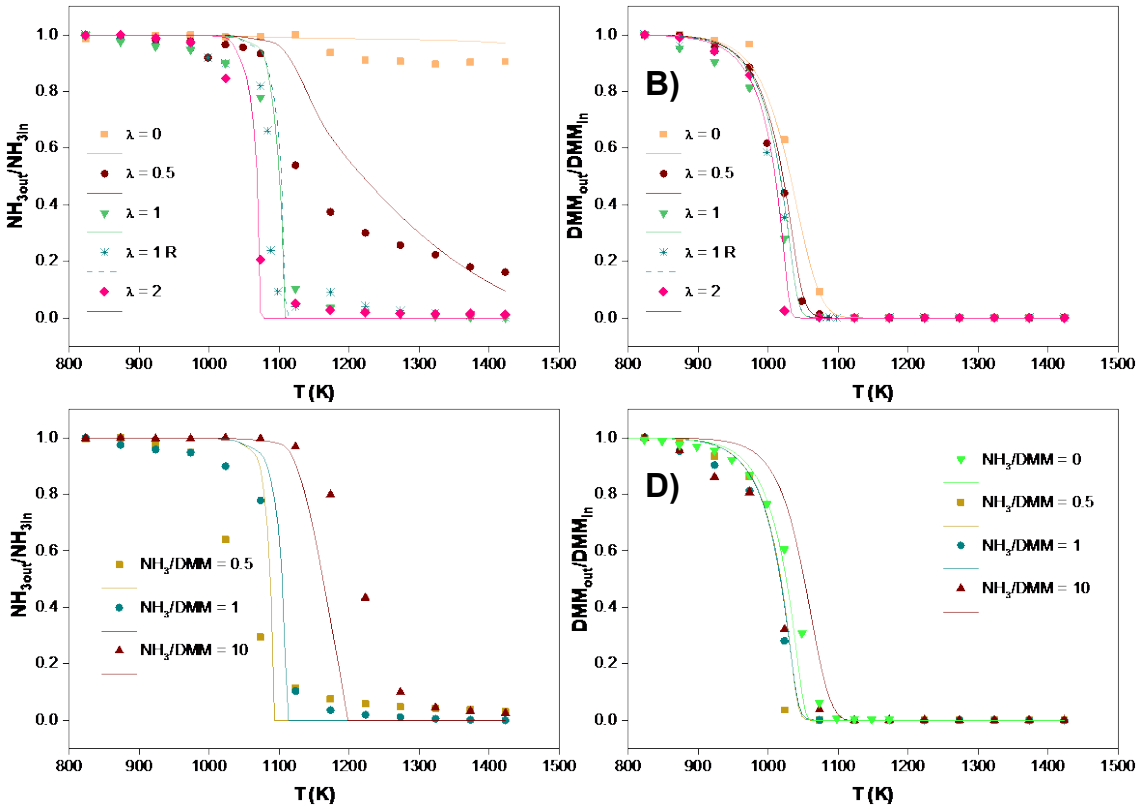

Figure 1. Fig. 1. A-B) Species profiles for NH_3 and DMM for different λ withNH_3/DMM mixture ratios similar to one. C-D) Species profiles for NH_3 and DMM for different NH_3/DMM mixture ratios at stoichiometric conditions

influenced by the initial NH_3 concentration, as the overall behaviour is similar to that observed for neat DMM oxidation (Figure 1D).

Conclusiones

The present study demonstrates that NH_3 conversion is highly dependent on oxygen availability, while DMM behaves as an effective combustion enhancer by promoting NH_3 oxidation without significantly competing for the main oxidizing radicals, namely OH and O.

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References

[1]. ELBAZ, A.M., GIRI, B.R., ISSAYEV, G., SHRESTHA, K.P., MAUSS, F., FAROOQ, A., et al. Experimental and Kinetic Modeling Study of Laminar Flame Speed of Dimethoxymethane and Ammonia Blends. Energy & Fuels. 2020, 34, pp. 14726-14740.

[2]. DAI, L., YUAN, Y., LIN, Q., LI, W., ZOU, C., LIU, J., et al. Shock tube and modeling study on the ignition delay times of ammonia/dimethoxymethane at high temperature. Combustion and Flame. 2023, 256, 112967.

[3]. MARRODÁN, L., MILLERA, Á., BILBAO, R. and ALZUETA, M.U. Experimental and Modeling Evaluation of Dimethoxymethane as an Additive for High-Pressure Acetylene Oxidation. The Journal of Physical Chemistry A. 2022, 126, pp. 6253-6263.

[4]. PAN, M., QIAN, W., WANG, Y., WU, C. and HUANG, H. Effect of dimethoxymethane (DMM) additive on combustion and emission characteristics under different working conditions in CI engines. Fuel. 2021, 284, 119304.

[5]. ABIÁN, M., BENÉS, M., GOÑI, A. de, MUÑOZ, B. and ALZUETA, M.U. Study of the oxidation of ammonia in a flow reactor. Experiments and kinetic modeling simulation. Fuel. 2021, 300, 120979.