

Revealing the Nitrogen Reaction Pathway for the Catalytic Oxidative Denitrification of Fuels

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Abstract : Aside from the desulfurisation, the denitrogenation of fuels is of great importance to minimize the environmental impact of transport emissions. The oxidative reaction pathway of organic nitrogen in the catalytic oxidative denitrogenation could be successfully elucidated. This is the first time such a pathway could be traced in detail in non-microbial systems. It was found that the organic nitrogen is first oxidized to nitrate, which is subsequently reduced to molecular nitrogen via nitrous oxide. Hereby, the organic substrate serves as a reducing agent. The discovery of this pathway is an important milestone for the further development of fuel denitrogenation technologies. The United Nations aims to counteract global warming with Net Zero Emissions (NZE) commitments; however, it is not yet foreseeable when crude oil-based fuels will become obsolete. In 2021, more than 50 million barrels per day (mb/d) were consumed for the transport sector alone. Above all, heteroatoms such as sulfur or nitrogen produce SO₂ and NO_x during combustion in the engines, which is not only harmful to the climate but also to health. Therefore, in refineries, these heteroatoms are removed by hydrotreating to produce clean fuels. However, this catalytic reaction is inhibited by the basic, nitrogenous reactants (e.g., quinoline) as well as by NH₃. The ion pair of the nitrogen atom forms strong pi-bonds to the active sites of the hydrotreating catalyst, which diminishes its activity. To maximize the desulfurization and denitrogenation effectiveness in comparison to just extraction and adsorption, selective oxidation is typically combined with either extraction or selective adsorption. The selective oxidation produces more polar compounds that can be removed from the non-polar oil in a separate step. The extraction step can also be carried out in parallel to the oxidation reaction, as a result of in situ separation of the oxidation products (ECODS; extractive catalytic oxidative desulfurization). In this process, H₈PV₅Mo₇O₄₀ (HPA-5) is employed as a homogeneous polyoxometalate (POM) catalyst in an aqueous phase, whereas the sulfur containing fuel components are oxidized after diffusion from the organic fuel phase into the aqueous catalyst phase, to form highly polar products such as H₂SO₄ and carboxylic acids, which are thereby extracted from the organic fuel phase and accumulate in the aqueous phase. In contrast to the inhibiting properties of the basic nitrogen compounds in hydrotreating, the oxidative desulfurization improves with simultaneous denitrification in this system (ECODN; extractive catalytic oxidative denitrogenation). The reaction pathway of ECODS has already been well studied. In contrast, the oxidation of nitrogen compounds in ECODN is not yet well understood and requires more detailed investigations.

Keywords : oxidative reaction pathway, denitrogenation of fuels, molecular catalysis, polyoxometalate

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