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Article

A Strategy to Improve Porous MOF Structural Stability for the Effective Removal of S/N Pollutants from (Bio)fuels

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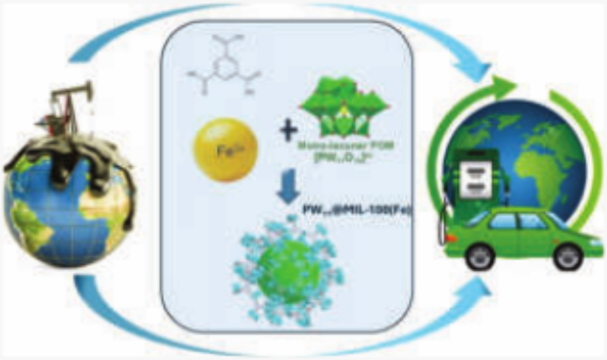
ABSTRACT: The need to mitigate environmental pollution drives the continuous quest for advanced desulfurization and denitrogenation methods in refineries. The presence of sulfur and nitrogen compounds in fossil fuels and biofuels contributes largely to atmospheric polllution. Oxidative catalysis presents a promising way for addressing these challenges, offering efficient and environmental friendly pathways. This work investigates the heterogeneous catalytic performance of the polyoxometalates, plenary Keggin PW_{12} structure and the derivative lacunary PW_{11} structure, supported on the porous MIL-100(Fe) metal−organic framework, for simultaneous oxidative desulfurization and denitrogenation. Both PW_{11}@MIL-100(Fe) and PW_{12}@MIL-100(Fe) catalysts demonstrated rapid and complete desulfurization within 60 min of reaction using a sustainable H_2O_2 oxidant. Remarkably, PW_{11}@MIL-100(Fe) exhibited higher catalytic efficiency and demonstrated high recycle capacity. In fact, notable results were attained to remove the most noxious pollutants in (bio)fuels, offering insights for the development of effective catalytic materials with high viability for the energy industry.



1. INTRODUCTION

The combustion of fossil fuels and biofuel blends leads to the emission of sulfur (S) and nitrogen (N) compounds, whose widespread presence impacts both environmental quality and human health through air pollution, acid rain, and respiratory disorders.[1] Despite the efficiency of current technologies, hydrodesulfurization and hydrodenitrogenation, in the removal of such impurities from fuels, these processes require high-pressure hydrogen and elevated temperatures, often resulting in low efficiency and significant operational costs.[2−4]

As the refining industry strives for more sustainable and cost-effective solutions, catalytic oxidative desulfurization (ODS) and denitrogenation (ODN) are emerging as promising alternatives toward the removal of S- and N-compounds.[5−10]

In extractive catalytic oxidative desulfurization (ECODS) and extractive catalytic oxidative denitrogenation (ECODN), extraction and catalytic oxidation occur simultaneously (Figure 1). Extraction solvents like ionic liquids (ILs) combine high extractive efficiency, catalytic compatibility, and high recycle capacity.[11] In a biphasic ECODS/ECODN system, S- and N-compounds are partially transferred to the higher polar extraction phase after oxidation. Although some initial extraction of these compounds can occur in the presence of a polar solvent, high desulfurization and complete denitrogenation are obtained only by performing catalytic oxidation simultaneously. The used catalyst needs to be able to activate the oxidant (usually H_2O_2 or O_2), where an oxygen donor is transferred to the heteroatom of the catalyst (Figure 1). This oxygen donor is then transferred to S- and N-compounds.[12] In the same way, the extraction solvent has a strong influence on mass transfer and oxidant accessibility to the catalyst.

During simultaneous S- and N-removal processes, S- and N-compounds compete with each other, which can significantly influence the reaction kinetics and selectivity. Typically, N-heterocycles (such as quinoline and indole) can coordinate better with acidic centers because of their higher basicity, inhibiting the adsorption or oxidation of S-compounds.[13] At the same time, the need for oxidants and the transport of S- and N-compounds into the extraction phase or catalyst pores lead to a trade-off. Since N-compounds dominate active-site occupancy, because they are extracted faster than S-compounds, they consume the oxidant more rapidly, and consequently, S-removal may slow down or not be completed.[14] Therefore, the

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