

Structure, dynamics, and reactivity of Fe sites in a metal organic framework for alkane oxidation

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Introduction

Metal Organic Frameworks (MOFs) with controlled nuclearity and porosity have the potential for use as biomimetic catalysts engendering the activation of light alkanes, opening new pathways for the enhancement of underutilized chemical feedstocks [1]. We report the use of the MOF MIL-100(Fe) [2] for the conversion of light alkanes using an atomic oxygen donor (N₂O) and stepped reaction scheme. The kinetics of the reaction are deduced by varying reactant concentration, temperature, and using chemical titration experiments to enumerate active surface species. Mechanistic pathways for dehydrogenation, hydroxylation, and over-oxidation products were obtained by examining changes in product selectivity with conversion and the introduction of co-reactants.

Materials and Methods

MIL-100(Fe) was synthesized according to a procedure detailed in the literature [3] and characterized by N₂ adsorption, X-ray diffraction, and vibrational spectroscopy. The reaction operates stoichiometrically using a stepped reaction scheme involving separate activation (250°C, *in vacuo*), reaction (75-120°C), and *ex-situ* extraction (25°C, H₂O_(l)) steps. Reaction rates were obtained utilizing a recirculating batch reactor containing a fixed bed of MIL-100(Fe) (30-60 mg), initially charged with He (20-90 kPa), Ar (10 kPa), propane (1-50 kPa), N₂O (1-50 kPa), and other co-reactants. Transmission IR spectroscopy was used to enumerate surface iron species using a custom IR cell connected to a vacuum manifold capable of dosing calibrated amounts of gaseous titrant (NO).

Results and Discussion

High temperature pretreatment *in vacuo* converts a fraction of Fe(III) sites in the nodes of MIL-100(Fe) to Fe(II), which we have confirmed and quantified by adsorbing calibrated doses of NO (Figure 1a). Subsequent exposure of the catalyst to N₂O and propane produces propylene in sub-stoichiometric amounts, indicating that propane derived compounds remain adsorbed onto the surface. *Ex-situ* extraction, performed by washing the catalyst post-reaction with water, induces the desorption of isopropanol and acetone (Figure 1b). The stability of the material exposed to these different treatment procedures (Figure 1c) is confirmed through the retention of crystallinity and surface area determined using X-ray diffraction and N₂ adsorption, respectively.

Operating in a batch reactor, kinetic studies were conducted varying experimental conditions and observing changes in the initial rates of reaction. Initial N₂ and propylene formation rates are first order in N₂O (Figure 1d) and zero order in propane, consistent with the rate limiting formation of an Fe(IV)=O species from the reaction of Fe(II) with N₂O. This supports cluster calculations using Kohn Sham density functional theory (DFT) methods that show the energy barrier for Fe(IV)=O formation being higher than the C-H activation and

subsequent steps in a proposed rebound mechanism. These observations in conjunction with on-going X-ray absorption studies and co-feed experiments demonstrate the ability of the MOF MIL-100(Fe) to activate light alkanes and further explicate the kinetics and mechanistic pathways to product formation.

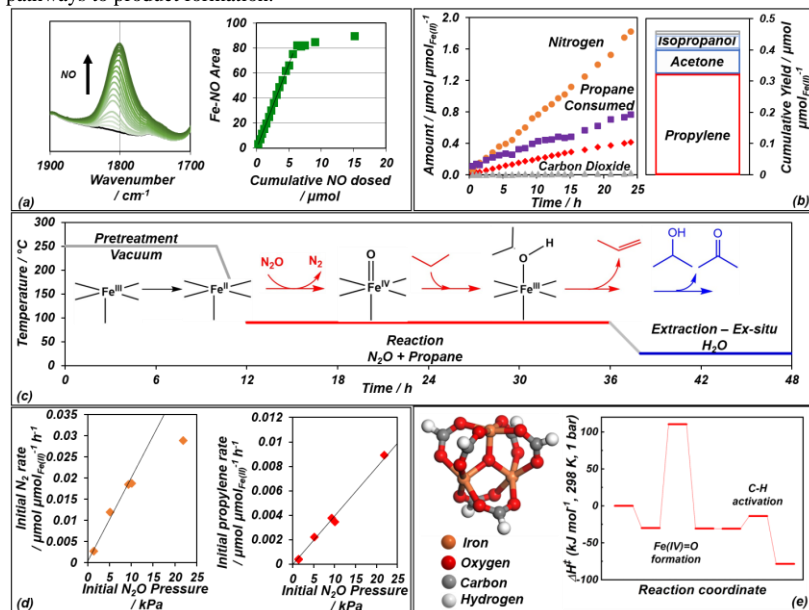


Figure 1. (a) IR bands of NO-Fe(II) adducts. (b) Reaction data from recirculating batch reactor and final yield including products desorbed by extraction. (c) Stepped reaction scheme. (d) Dependence of initial N₂ and propylene production rates on initial N₂O pressure. (e) Reaction profile obtained from DFT calculations for oxidation of propane to isopropanol.

Significance

Our work elucidates the catalytic function for a site isolated Fe-framework based MOF, materials that represent an emerging class of materials for low temperature alkane activation.

References

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