ACS central science

FIRST REACTIONS

Oxidative Dehydrogenation of Propane in the Realm of Metal–Organic Frameworks

Maciej Damian Korzyński and Mircea Dincă

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States

Propylene (propene) is one of the most important feedstocks in the chemical industry. It is a starting material for the synthesis of a wide variety of commodity chemicals ranging from small molecules (cumene, isopropanol, acrylonitrile, acrylic acid, propylene oxide, and butyraldehyde) to polymers (most notably, polypropylene). In 2013, approximately 85 million tons of propylene were processed worldwide—14 million in the United States alone.[1,2] Traditionally, propylene is produced along with other light olefins by steam cracking or fluid catalytic cracking of higher hydrocarbons.[3] These methods are not ideal as the costs of the starting materials escalate and due to poor selectivity increasing production, purification, and energetic costs.

An intriguing alternative is to develop and utilize "on-purpose" methods, in which propylene is the intended end product and is produced with high selectivity (as opposed to a range of light olefins).[4] One of the most promising processes in this regard is propane dehydrogenation (PDH), which ideally produces just propylene and hydrogen. Although some industrial processes such as Catofin and Oleflex already take advantage of this transformation, they satisfy only a small percentage of the propylene demand currently. As we excavate more shale gas and shift from naphtha to ethane steam cracking, a favorable price difference between propane and propene emerges. In addition, as the demand for propylene increases, the role of PDH in propene production will continue to gain importance; however, the classical PDH process still faces several challenges. Most importantly, the formation of propylene and hydrogen is endothermic. Reasonable conversions thus require high temperature, which also leads to significant coking and gradual catalyst deactivation.

One exergonic alternative to PDH is the oxidative dehydrogenation (ODH) of propane, where addition of O_2 to the propane feed ideally produces propene and water.

Metal–organic framework-based catalytic formation of propene holds promise for low temperature sustainable production of this important feedstock.

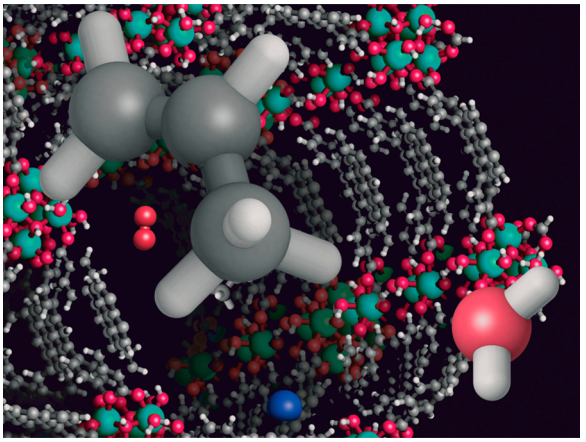

Figure 1. MOF-immobilized cobalt species are robust low temperature ODH catalysts. Credit: Kiley Schmidt.

One exergonic alternative to PDH is the oxidative dehydrogenation (ODH) of propane, where addition of O_2 to the propane feed ideally produces propene and water.[5] Here, the challenge is to avoid further oxidation of propylene and formation of CO_2, which is favorable thermodynamically and often drastically reduces overall selectivity for propene. Typical catalysts for ODH are supported vanadium, molybdenum, and chromium oxides. They still require quite high operating temperatures in the 300–650 °C range. Because the identity and morphology of the support and the active species are obviously key in defining catalyst performance, improvements in ODH catalysts are largely empirical. The ability to control these variables is thus attractive for generating new catalysts.

In their recent report, Li et al. introduce the ODH of propane into the realm of metal–organic frameworks (MOFs) (Figure 1).[6] These already well-established materials built from

Published: January 17, 2017

DOI: 10.1021/acscentsci.7b00013
ACS Cent. Sci. 2017, 3, 10–12

This concept takes advantage of all of the defining characteristics of MOFs: high surface areas, well-defined crystalline structure facilitating investigation of the nature of active species, as well as site isolation preventing deleterious self-destruction of the active species.

inorganic nodes and organic linkers form extended periodic structures with well-defined, high porosity. Many approaches to immobilization of catalytically active species have been utilized so far. In the highlighted report, the authors explore whether MOFs can compete with classical solid supports such as zirconia, alumina, silica, and others for ODH catalysis. This concept takes advantage of all of the defining characteristics of MOFs: high surface areas, well-defined crystalline structure facilitating investigation of the nature of active species, as well as site isolation preventing deleterious self-destruction of the active species. The particular system that the report focuses on is the well-characterized and robust platform NU-1000, made from zirconium nodes and aromatic carboxylic acid linkers.[7] Inspired by previous reports of catalytic ODH of propane by nanocrystalline Co_3O_4 under ambient conditions,[8] the authors immobilize cobalt(II) precursors with two methods and demonstrate the activity of cobalt for ODH.

They investigate two different methods to prepare the catalysts: solvothermally (SIM) and through atomic layer deposition (AIM) yielding Co-SIM + NU-1000 and Co-AIM + NU-1000, respectively. Both materials have an onset of ODH activity around 200 °C, remarkably milder than the conditions necessary for typical ODH catalysts. Impressively, the catalyst's activity remains almost unchanged after even 20 h on stream. At the upper end of the catalyst's thermal stability (230 °C), the turnover frequency (TOF) reached 1 per hour, significantly surpassing dispersed cobalt on zirconia. The only identifiable side product during the catalysis is carbon dioxide, which can be essentially eliminated by decreasing the temperature. At 180 °C, selectivity for propene is all the way up to 100%, although the cost there is activity, falling to just 1% conversion. The elimination of the deleterious combustion of propene is noteworthy, and the high selectivity for propene is assigned to the higher rate of propane dehydrogenation versus propene combustion.

To understand the structural basis for the observed catalytic activity as well as the differences between the two materials, the authors take a combined experimental and computational approach. Visualization of the regions of increased electron density associated with incorporated cobalt species using difference envelope densities confirms that the Co deposits form in close proximity to the nodes. Probing of the activated catalyst by combined XANES/EXAFS analysis reveals that the coordination environment of cobalt in Co-AIM + NU-1000 is highly reminiscent of the Co_3O_4 active sites observed for classical ODH catalysts. By contrast, the Co-SIM + NU-1000 shows no significant presence of Co−Co interactions, suggesting only one immobilized cobalt ion per isolated face of the MOF node. This proposed mononuclear Co is used to model a plausible catalytic cycle with density functional theory (DFT) calculations, which for the investigated theoretical model, at

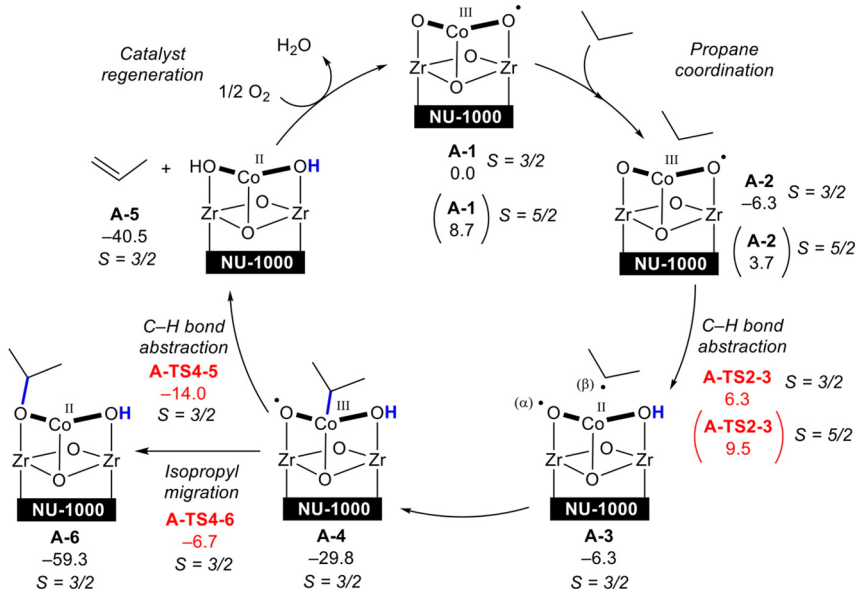

Figure 2. A combination of experimental and computational approaches were used to propose a catalytic cycle. Reprinted with permission from ref 6.

DOI: 10.1021/acscentsci.7b00013
ACS Cent. Sci. 2017, 3, 10−12

least, confirm a kinetic preference for the formation of propene (Figure 2).

The contribution by Li et al. provides the first example of propane oxidative dehydrogenation in MOFs, underscoring the potential of MOFs as competent supports for catalytic species. The retention of reactivity at lower temperatures should spur future investigations of MOFs as platforms for ODH of propane. Of particular interest are the mechanistic investigations of the Co-AIM + NU-1000 as well as attempts to minimize any undesired side reactivity that may be associated with the Lewis acidity of the MOF itself. Screening other metals for their activity in ODH is an attractive opportunity given the already demonstrated versatility of the NU-1000 platform for the isolation of catalytic moieties with controlled nuclearity.[9,10]

Author Information

E-mail: mdinca@mit.edu.

ORCID

Mircea Dincă: 0000-0002-1262-1264

REFERENCES

(1) Ceresana. Market Study: Propylene (2nd ed.); http://www.ceresana.com/en/market-studies/chemicals/propylene/ceresana-propylene-market-study.html (accessed December 18, 2016).

(2) Ceresana. Market Study: Propylene - USA; http://www.ceresana.com/en/market-studies/chemicals/propylene-usa/ (accessed December 18, 2016).

(3) Buonomo, F.; Sanfilippo, D.; Trifiro, F. Dehydrogenation of Alkanes: Section 4.3.1. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1997.

(4) Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. Catalytic dehydrogenation of light alkanes on metals and metal oxides. *Chem. Rev.* **2014**, *114* (20), 10613−10653.

(5) Cavani, F.; Ballarini, N.; Cericola, A. Oxidative dehydrogenation of ethane and propane: How far from commercial implementation? *Catal. Today* **2007**, *127* (1−4), 113−131.

(6) Li, Z.; Peters, A. W.; Bernales, V.; Ortuño, M. A.; Schweitzer, N. M.; DeStefano, M. R.; Gallington, L. C.; Platero-Prats, A. E.; Chapman, K. W.; Cramer, C. J.; Gagliardi, L.; Hupp, J. T.; Farha, O. K. Metal−Organic Framework Supported Cobalt Catalysts for the Oxidative Dehydrogenation of Propane at Low Temperature. *ACS Cent. Sci.* **2016**, DOI: 10.1021/acscentsci.6b00290

(7) Wang, T. C.; Vermeulen, N. A.; Kim, I. S.; Martinson, A. B. F.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. Scalable synthesis and post-modification of a mesoporous metal-organic framework called NU-1000. *Nat. Protoc.* **2015**, *11* (1), 149−162.

(8) Davies, T. E.; García, T.; Solsona, B.; Taylor, S. H. Nanocrystalline cobalt oxide: a catalyst for selective alkane oxidation under ambient conditions. *Chem. Commun. (Cambridge, U. K.)* **2006**, *32*, 3417−3419.

(9) Yang, D.; Odoh, S. O.; Wang, T. C.; Farha, O. K.; Hupp, J. T.; Cramer, C. J.; Gagliardi, L.; Gates, B. C. Metal-Organic Framework Nodes as Nearly Ideal Supports for Molecular Catalysts: NU-1000- and UiO-66-Supported Iridium Complexes. *J. Am. Chem. Soc.* **2015**, *137* (23), 7391−7396.

(10) Li, Z.; Schweitzer, N. M.; League, A. B.; Bernales, V.; Peters, A. W.; Getsoian, A. B.; Wang, T. C.; Miller, J. T.; Vjunov, A.; Fulton, J. L.; et al. Sintering-Resistant Single-Site Nickel Catalyst Supported by Metal-Organic Framework. *J. Am. Chem. Soc.* **2016**, *138* (6), 1977−1982.

DOI: 10.1021/acscentsci.7b00013
ACS Cent. Sci. 2017, 3, 10−12