

Article

Oligomerization of light olefins catalyzed by Brønsted-acidic Metal-Organic Framework-808

Ping Liu, Evgeniy Redekop, Xiang Gao, Wen-Chi Liu, Unni Olsbye, and Gabor A. Somorjai J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.9b03867 • Publication Date (Web): 02 Jul 2019 Downloaded from http://pubs.acs.org on July 2, 2019

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Oligomerization of light olefins catalyzed by Brønsted-acidic Metal-Organic Framework-808

Ping Liu,^{†,‡,*,#} Evgeniy Redekop,^{I,#} Xiang Gao,^{†,⊥,#} Wen-Chi Liu,^{†,⊥} Unni Olsbye,^I and Gabor A. Somorjai ^{†,⊥,*}

[†] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

[‡] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou, Jiangsu 213164, China

¹ Centre for Materials Science and Nanotechnology (SMN), Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

¹ Department of Chemistry, Kavli Energy NanoSciences Institute at Berkeley, and Berkeley Global Science Institute, University of California-Berkeley, Berkeley, California 94720, United States

KEYWORDS: Light olefins, Isobutene, Oligomerization, Dimerization, Metal-Organic Framework-808

ABSTRACT: Sulfated Metal-Organic Framework-808 (S-MOF-808) exhibits strong Brønsted-acidic character which makes it a potential candidate for the heterogeneous acid catalysis. Here, we report the isomerization and oligomerization reactions of light olefins (C₃-C₆) over S-MOF-808 at relatively low temperatures and ambient pressure. Different products (dimers, isomers and heavier oligomers) were obtained for different olefins, and effective C-C coupling was observed between isobutene and isopentene. Among the substrates investigated, facile oligomerization occurred very specifically for the structures with an α -double bond and two substituents at the second carbon atom of the main carbon chain. The possible oligomerization mechanism of light olefins was discussed based on the reactivity and selectivity trends. Moreover, the deactivation and regeneration of S-MOF-808 were investigated. The catalyst deactivates *via* two mechanisms which predominance depends on the substrate and reaction conditions. Above 110 °C, a loss of acidic sites was observed due to water desorption, and the deactivated catalyst could be regenerated by a simple treatment with water vapor. For C₅ substrates and unsaturated ethers, the oligomers with increased molecular weight caused deactivation *via* blocking of the active sites, which could not be readily reversed. These findings offer the first systematic report on carbocation-mediated olefin coupling within MOFs in which the Brønsted acidity is associated with the secondary building units of the MOF itself and is not related to any guest substance hosted within its pore system.

Introduction

Metal-Organic Frameworks (MOFs) are emerging as a promising class of heterogeneous catalysts due to their unique physical and chemical properties including high surface area, adjustable pore structure, tunable element composition and the potential for surface modification.¹⁻⁶ Importantly, their well-defined molecular structure and chemical environment may contribute to a more detailed mechanistic understanding of catalytic reactions, thereby enabling the development of "bespoke" catalysts.⁷⁻¹² In recent years, acidic MOFs have attracted significant research interest because of their potential application in a large class of acid-catalyzed reactions, including isomerization^{13,14}, cyclization¹⁵, biomass transformation^{16,17}, benzylation¹⁸ and alkylation¹⁹.

The sulfated MOF-808 obtained by treating Zr-based MOF-808 with sulfuric acid was reported to have strong acidity.¹⁵ Subsequently, the strong Brønsted acid site in the sulfated MOF-808 was identified as a water molecule co-adsorbed in an equatorial plane of a zirconia cluster with a bidentate sulfate group that is chelated to a single zirconium atom. The adsorbed water participates in hydrogen bonding with the sulfate, giving rise to a labile proton.²⁰ Preliminary screening of catalytic properties showed that the sulfated MOF-808 was active and selective in the dimerization of isobutene.

ACS Paragon Plus Environment

Oligomerization of light olefins (C3-C6) to heavier, more valuable products (gasoline, diesel, jet fuel, or synthetic lube oils) has been commercially used for over 80 years.²¹⁻²⁴ Numerous studies demonstrated that different olefins reacted according to different oligomerization mechanisms, depending on the type of catalyst (acidity, structure) and reaction conditions (temperature, pressure).²⁵⁻³⁰ Solid acids catalyze the oligomerization reactions via a carbocation-mediated mechanism which has been extensively characterized in zeolites^{28,31}, phosphoric acid³², sulfated polymers²³ and heteropolyacids³³. However, the majority of research on applications of MOFs for the oligomerization of light olefins has so far been focused on ethylene dimerization on metal centers and not Brønsted sites.³⁴⁻³⁷ Moreover, cross-coupling of different olefins can provide an efficient route for C-C bond formation, however, it has rarely been reported.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55 56

57 58 59

60

The purpose of this study was to investigate the reaction of different olefins (C3-C6) over sulfated MOF-808 in order to fulfill a significant gap in the literature concerning carbocation chemistry in MOFs and to explore the potential of this catalyst for technologically-relevant olefin transformations. Unsaturated (vinyl) ethers were also employed as reactants to better understand the reaction mechanism, since alkoxy groups can contribute significantly to carbocation stabilization. The results demonstrated that olefins (isobutene, 2-methyl-1-butene, and 2methoxypropene) with very similar structure resulted in drastically different products distributions (dimers vs. isomers vs. heavier oligomers). Additionally it was demonstrated that sulfated MOF-808 can effectively catalyze the coupling of isobutene and isopentene. The deactivation and regeneration of sulfated MOF-808 were also studied, and the deactivated catalyst in the isobutene reaction could be completely regenerated by water vapor treatment.

Results and discussion

On the origin of catalytic activity

S-MOF-808 was prepared according to the established procedure¹⁵ by first synthesizing pristine MOF-808 (Figure 1a), $Zr_6O_5(OH)_3(BTC)_2(HCOO)_5(OH_2)_2$, and then exchanging a sulfate ligand onto zirconia clusters (see Supporting information, Section S1). In MOF-808, each 6connected (6-c) zirconia cluster is linked to six 1,3,5benzenetricarboxylate (BTC) linkers to form a 3D porous framework which contains two different types of pores. The smaller tetrahedral pores are isolated from each other, while the larger adamantane pores are interconnected to form continuous channels. Sulfate substitution occurs at the larger continuous channels in MOF backbones to afford S-MOF-808, $[Zr_6O_4(OH)_{5,6}(C_9H_3O_6)_2(HCOO)_{9,18}(SO_4)_{2,1}](H_2O)_2$ (Figure 1b). X-ray diffraction analysis of S-MOF-808 showed that sulfate ligands coordinate to zirconia clusters in a bidentate fashion with two crystallographically different sites: i) bridging mode to two zirconium atoms when in solution

and ii) chelating mode to a single zirconium atom following activation by heating under dynamic vacuum (Figure 1c).²⁰ The Brønsted acidity of S-MOF-808 originates from the water molecules adjacent to chelating sulfate ligands. As-synthesized S-MOF-808 has nearly identical crystal structure as that of pristine MOF-808, as confirmed by PXRD, N₂ adsorption, SEM and TEM (Figures S2-6).



Figure 1. The structure of (a) pristine MOF-808, (b) sulfated S-MOF-808, and (c) schematic representation of the two modes of sulfate ligands coordinated to zirconia clusters.

A series of catalysts including pristine MOF-808, Cl-MOF-808 (PXRD in Figure S7), S-MOF-808, and S-MOF808-Hf (PXRD in Figure S8) were compared in the dimerization of isobutene in order to unambiguously assign the oligomerization activity to sulfated metal-oxide clusters within MOF frameworks. Cl-MOF-808 was synthesized by submerging pristine MOF-808 in HCl aqueous solution instead of H_2SO_4 , and S-MOF-808-Hf was obtained similarly to S-MOF-808-Zr, but with Hf atoms taking place of Zr atoms. Preliminary reaction tests (Table S1) showed that MOF-808 and Cl-MOF-808 were almost inactive in the dimerization of isobutene, while S-MOF-808 and S-MOF-808-Hf gave much better conversion and selectivity to dimers at 101.325kPa, 100 °C. These data establish that olefin activation occurs on the active sites associated with sulfate-substituted metal-oxide clusters, with the nature of the metal playing only a secondary role in the active site formation. Moreover, the conversion increased with the increase of sulfate groups (Figure S9). It is assumed that the amount of sulfate groups represents the number of active sites. Based on the similar activities of S-MOF-808 with 2.1 and 2.5 SO₄ per Zr secondary building unit (SBU), the remaining experiments focused on the reaction studies of S-MOF-808 with 2.1 SO₄ per Zr SBU which consumed less sulfuric acid.

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55 56

57

Table 1 Reactions of different olefins over S-MOF-808 catalysts

		STY _{iso} ^a	CTV -	S _{oligom} (%)			
Entry	Reactant	[mmol/g _{cat} /h] (X, %)	$[\text{mmol/g}_{cat}/h]$ (X, %)	Dimers	Trimers	Tetramers	
1	H ₃ C ^C CH ₂	/	<0.05 (<0.1)	/	/	/	
2	H ₃ CH ₃	/	6.28 (15.7)	72.5	23.7	3.6	
3	H ₃ C ^{CH} 2	1.03 (2.57)	0.05 (0.13)	/	48.9	51.0	
4	H ₃ C CH ₂	45.3 (75.5)	2.69 (4.48)	8.93	3.57	/	
5	H ₃ C CH ₃ CH ₃	7.4 (12.3)	0.58 (0.97)	35.6	9.59	/	
6	\bigcirc	/	<0.10 (<1)	100	/	/	
7	H ₂ C CH ₃	12.9 (21.6)	0.85 (1.40)	33.9	/	/	

Reaction conditions: 4 mmol/h reactant (gas) (entry 1-3), ca. 6 mmol/h reactant (liquid) (entry 4-7), 53 mmol/h He, o.1 g catalyst, 101.325 kPa, 100 °C, Time on stream (TOS) 5h. ^a STY_{iso} and STY_{oligom}: Site-time-yield of isomerization and oligomerization, respectively; Isomer (double-bond isomerization): 2-butene (entry 3), 2-methyl-2-butene (entry 4), 2-methyl-1-butene (entry 5), 3-methyl-2-pentene (entry 7).

Reactions of light C₃-C₆ olefins

The reactions of different olefins (C3-C6) were investigated over S-MOF-808 under ambient pressure flow conditions. As shown in Table 1, different activities and product distributions were observed for different light olefins. Almost no reaction occurred for propene. Isobutene and cyclopentene mainly produced dimers, albeit with drastically different activities, while other olefins (1-butene, 2methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1pentene) preferred isomerization.

Over S-MOF-808 with Brønsted acidic site, the C-C coupling of olefins most likely proceeds as cationic polymerization, i.e. via the formation of a carbocation by olefin protonation and the subsequent attack of the second olefin molecule by this carbocation, followed by the product deprotonation and desorption.³⁸ The C-C coupling pathway competes with the monomolecular isomerization pathway, where the carbocation deprotonates to release a more thermodynamically-stable isomer of the original olefin. Bimolecular isomerization via dimerization and cracking is unlikely at such low temperatures. The primary factors that govern Gibbs free energies of various processes and, therefore, control the outcome of the competing reactions are: (1) charge stabilization in the carbocation, (2) steric considerations during microporous diffusion and adsorption of olefins, and (3) local structural factors affecting the transition state of the C-C coupling Before relating the observed reactivireaction. ty/selectivity trends to the reaction mechanism, it is useful to point out the key structural features by which various substrates can be distinguished. Propene, isobutene, and cyclopentene are not capable of forming isomers. The methyl shift and the ring-opening steps that would be required to isomerize isobutene and cyclopentene, respectively, are highly activated and, thus, precluded in this temperature range. The most stable carbocations that can be formed from propene, linear butene, and cyclopentene by protonation and double-bond shift are secondary, while the rest of the reactants can form more stable tertiary cations. Finally, only isobutene and 2-methyl-1-butene contain a structural motif in which an α -double bond has two substituents in the second position.

Electron-donating substituents typically facilitate the rate of cationic oligomerization because they stabilize the reaction intermediates-carbenium ions.^{38,39} Therefore, a reasonable starting hypothesis to understand the reactivity of S-MOF-808 towards different substrates is that electron-donating substituents and carbocation stabilization determine which molecules are more likely to form oligomers. For propene, the ability of one methyl group to donate electrons is insufficient to generate a stable secondary carbenium ion, making propene oligomerization problematic. In comparison, two methyl groups in isobutene increase the electron density on the double bond and stabilize tertiary carbocation, facilitating the C-C coupling reactivity for isobutene. The most stable carbocation that the next olefin - 1-butene - can form is secondary, and, in line with the carbocation stability hypothesis, it forms nearly no oligomers. Surprisingly, it also exhibits very low

isomerization rate despite a strong thermodynamic driving force for the 1-butene to 2-butene transformation.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55 56

57 58 59

60

The next two substrates in the table - 2-methyl-1butene and 2-methyl-2-butene - can form a stable tertiary carbocation from which a more thermodynamically stable 2-methyl-2-butene isomer emerges after desorption⁴⁰, consistently with the thermodynamic equilibrium distribution of pentene reported by Mäurer et al.⁴¹. The isomerization rates for these olefins fall in line with thermodynamic expectations (Table 1, entries 4 and 5). It would be expected by the analogy with isobutene, which also produces a tertiary carbocation, that 2-methyl-butenes would additionally produce a significant amount of oligomers, as exemplified for 2-methyl-1-butene in Scheme S1. As seen from Table 1, 2-methyl-1-butene does oligomerize five times faster than 2-methyl-2-butene. However, both structural isomers of pentene exhibited relatively low oligomerization activity. For cyclopentene reaction, the conversion to oligomers was very low (<1%) although the selectivity to dimers reached 100%. Finally, 3-methyl-1pentene mostly isomerized according to the stability of the carbocation and reacted to some degree into a dimer.

Taken together, the aforementioned observations suggest that the propensity of olefins for C-C coupling is governed by a combination of two factors – the presence of a terminal double bond in the α -position and the ability to produce a stable tertiary carbocation upon protonation. Isobutene offers both features and, uniquely among other olefins, does not engage in a side isomerization reaction into β -olefin that could lower the yield of oligomers. 2methyl-1-butene also satisfies these criteria, but it can also isomerize by shifting the double bond into the β -position and, therefore, mostly yields the isomer. Several peculiarities in Table 1 remain unexplained within this general trend, e.g. low isomerization activity of 1-butene.

Additionally, comparison with other solid acid catalysts (Table S2) in the isobutene oligomerization reveals that although the activity of S-MOF-808 (under its applicable reaction temperature (Figures 4) and weight hourly space velocity (WHSV) (Figure S10) conditions) could not be favorably compared to non-MOF catalysts, it provides one of the highest dimer selectivities reported. The kinetic curves of the commercial resin - Amberlyst-15 and S-MOF-808 showed that Amberlyst-15 had a higher activity than S-MOF-808 at the same reaction conditions (Figure S11). However, Amberlyst-15 had more acid capacity than S-MOF-808 (4.70 vs. 1.54 mmol/g) (Table S3). Therefore, a higher TOF value of isobutene conversion was obtained over S-MOF-808. Moreover, S-MOF-808 exhibited more than two-fold TOF value of dimers formation than Amberlyst-15 due to its much higher selectivity to dimers (Table S₃). High selectivity and unique preference for isobutene motivates further research into carbocationmediated reactions in MOFs which will provide a valuable extension of their catalytic repertoire.

Temporal Analysis of Products (TAP) study

Steady-state data at atmospheric flow conditions were complemented by pulse-response TAP experiments at the low pressure regime, which provide unique insight into the mode of interaction between a probe molecule and a catalyst in the limit of zero coverage.⁴² In a typical TAP experiment (see Supporting information, Section S₂), the exit-flow rate curves of different gases directly reflect the differences in their residence times within the catalyst and, therefore, TAP data can be used to evaluate the relative strength of interactions between olefins and S-MOF-808 in the absence of inter-molecular interactions and the effects of pore crowding. Figure 2A depicts a set of isobutene responses over an inert material, non-acidic pristine MOF-808, and sulfated S-MOF-808. We note that the parent MOF interacts slightly with the olefin, resulting in a noticeable delay with respect to the inert standard. This weak interaction is attributed to electrostatic forces between the probe molecule and the framework rather than diffusional hindrance, since isobutene molecules are much smaller than the pore diameter. S-MOF-808 delays the olefin to a much greater extent due to the presence of acidic sites. When comparing the responses of different olefins in Figure 2B, their residence times correlate positively with the total length of the carbon chain, but are nearly insensitive to the isomer structure. These data definitively rule out the effects of adsorption strength and/or diffusional limitations on the relative activities of isobutene and 1-butene, strongly suggesting that it is the increased charge stabilization and the unique steric arrangement of the oligomerization transition state that are implicated in the superior activity of isobutene in the C-C coupling.



Figure 2. TAP exit-flow rate transients at 100 °C. (A) Isobutene over inert material representing bed-scale diffusion, non-acidic MOF-808, and acidic S-MOF-808; (B) Propene, isobutene (IB), 1-butene (1B), 2-methyl-1-butene (2M1B), and 2-methyl-2-butene (2M2B) over S-MOF-808. All curves were height-normalized and scaled in time to match the diffusion rate of inert standard (neon) in order to facilitate data comparison.

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60

Table 2 Co-reactions of two different olefins over S-MOF-808 catalysts

Entw	Desistants	Commission /0/	Selectivity ^a /%						
Entry	Reactants	Conversion/ %	Isomers	C8	C9	C10	C12	C13	C15-16
1	$H_{3}C \xrightarrow{CH_{3}} H_{3}C \xrightarrow{+} CH_{2} H_{3}C \xrightarrow{+} CH_{2} CH_{3}$	9.1(IB) 82.5(2M1B)	93·5	31.0	12.1	3.5	13.4	5.3	33.6
2	H_3C H_3C H_3C H_3C H_3C CH_3 CH_3 CH_3 CH_3	7.8(IB) 11.3(2M2B)	81.9	41.7	15.2	2.1	22.6	7.4	9.6
3	$H_{3}C \xrightarrow{CH_{3}} H_{3}C \xrightarrow{+} H_{2}C \xrightarrow{+} CH_{3}$	10.1(IB) 16.5(3M1P)	92.7	43.8	/	1.9	37.8	1.3 ^b	13.9

Reaction conditions: 4 mmol/h isobutene (IB) (gas), 2.7 mmol/h liquid reactant (2-methyl-1-butene (2M1B), 2-methyl-2-butene (2M2B) or 3-methyl-1-pentene (3M1P)), 53 mmol/h He, o.1 g catalyst, 101.325 kPa, 100 °C, TOS 5h. ^a Selectivity to isomer: calculated based on the converted 2-methyl-1-butene, 2-methyl-2-butene and 3-methyl-1-pentene, respectively. Isomer: 2-methyl-2-butene (entry 1), 2-methyl-1-butene (entry 2), 2-methyl-2-pentene (entry 3). Selectivity to C8-C16: calculated based on both of the converted reactants subtracting the isomers. ^b The selectivity to C14.

Cross-coupling reactions

Table 2 shows the co-reactions of isobutene and another olefin including 2-methyl-1-butene, 2-methyl-2butene and 3-methyl-1-pentene. Isobutene was selected as the fixed reactant because of its superior activity and selectivity to dimers. C-C coupling reactions between isobutene and another olefin were observed for all of the three entries. As shown in entries 1 and 2, a considerable amount of co-reaction products (C9 and C13) were obtained, indicating efficient C-C coupling between different olefins over S-MOF-808. It is worth noting that the isomerization selectivity of 2-methyl-2-butene (entry 2) in co-reaction case was lower than that in single reaction case (entry 5 in Table 1) (81.9% vs. 92.7%) at close conversion levels. It suggests that the carbenium ions formed from isobutene is most likely to be the initiator of the coreaction between isobutene and 2-methyl-2-butene. The possible co-reaction path is depicted in Scheme 1.

$$\begin{array}{c}
CH_{3} \\
H_{3}C \\
CH_{2} \\
H_{3}C \\
\end{array}^{+} H^{+} \\
H_{3}C \\
\end{array}^{+} CH_{3} \\
(1)$$

$$\begin{array}{c} CH_{3}\\ H_{3}C^{+}+CH_{3} \end{array}^{+} H_{3}C \underbrace{CH_{3}}_{CH_{3}} \end{array} \xrightarrow{H_{3}C} \underbrace{CH_{3}}_{H_{3}C} CH_{3} CH_{3} \\ H_{3}C \underbrace{CH_{3}}_{CH_{3}} CH_{3} + \underbrace{H_{3}C}_{H_{3}C} CH_{3} CH_{3} \\ H_{3}C \underbrace{CH_{3}}_{H_{3}C} CH_{3} \\ H_{3}C \underbrace{CH_{3}} CH_{3}$$

Scheme 1. The possible co-reaction path of isobutene and 2-methyl-2-butene over S-MOF-808

The effect of electron-donating substituents

Next, 2-methoxypropene and ethyl vinyl ether were employed as reactants to further substantiate the positive effect of electron-donating substituents, in this case ether oxygen, on the oligomerization reaction rate. As shown in Table 3, high initial activities (69.2 and 99.5%) were obtained for both ethers at TOS of 10 min. However after 40 min on stream, their conversions declined quickly to 3.2 and 12.4%, respectively. The products distribution showed that less than 30% selectivities to dimers were obtained, while most of the products were heavier oligo-(degree of polymerization: n=3-5 for mers methoxypropene; *n*=3-8 for ethyl vinyl ether). These heavier oligomers hardly desorb from the surface of the catalyst in accordance with their high boiling points, which can be confirmed by changes in the color of the catalyst before and after use. As shown in Figure S12, the color of the catalyst changed from white to yellow (for 2methoxypropene) or dark brown (for ethyl vinyl ether). The deactivation of the catalyst was attributed to the deposition of heavier oligomers.

The high initial oligomerization activities of vinyl ethers over S-MOF-808 reflect the overall electrondonating properties of their ether functionalities. Compared to isobutene and 1-butene, both 2-methoxypropene and ethyl vinyl ether have a similar structure, but additionally contain an oxygen atom in their molecules. The induction effect would reduce the electron density on the C-C double bond due to the greater electronegativity of oxygen. However, the p- π conjugation effect between C-C double bond and p orbital of oxygen atom effectively increase the electron density of C-C double bond. For vinyl ether, the p- π conjugation effect is dominant relative to induction effect.^{38,39} Therefore, oxygen substituent shows the strong ability of electron-donation, which is conducive to the formation of stable carbenium ion for cationic oligomerization. Additionally, vinyl ether has a resonance structure that makes the carbenium ion more stable by dispersing the positive charge (Scheme S2). In comparison, lower conversion of 2-methoxypropene than that of ethyl vinyl ether might be influenced by the molecular size. The oligomers of 2-methoxypropene have more branched chains, which may significantly impede their diffusion out of the pores of MOF-808.

Table 3 Reactions of vinyl ethers over S-MOF-808 catalysts

Reactant	Conve at differ	rsion/% cent TOS	Selectivity/% at 10 min		
icuctum	10 min	40 min	Dimers	Heavier oligomers	
	69.2	3.2	27.9	72.1 ^ª	
H ₂ C ^C O ^C H ₃	99.5	12.4	21.4	78.6 ^b	

Reaction conditions: 0.1 g catalyst, 6 mmol/h reactant, 53 mmol/h He, 101.325 kPa, 100 °C. Degree of polymerization of heavier oligomers (n): ^a 3-5, ^b 3-8, measured by mass spectroscopy.

Stability study

The stability behavior for the reactions of isobutene and 2-methyl-1-butene over S-MOF-808 is illustrated in Figure 3. The conversion of isobutene gradually increased in the first 5 h, and then remained stable at around 10% up to 22 h. The initial increase of conversion is related to the activation of the catalyst, that is, the transformation of adsorbed water to Brønsted acid sites. Unlike in the isobutene reaction, fast deactivation was observed in the reaction of 2-methyl-1-butene where the conversion dropped by approximately 45% within 12 h from its starting value of 88.4%. The PXRD and N₂ adsorption results showed that the spent catalysts maintained their crystallinity and pore structure (Figures S13-16). However, the spent catalyst after 2-methyl-1-butene reaction had less pore volume than the spent catalyst after isobutene reaction (Figures S15-16). The TG analysis of spent catalysts (Figure S17) showed that the weight loss from the spent catalyst after isobutene reaction was similar to that from the fresh catalyst, suggesting that no additional heavier oligomers or carbon were deposited in the pores of S-MOF-808. The elemental analysis of the spent S-MOF-808 after isobutene reaction (Table S4) showed that the S content in the catalyst did not decrease obviously after 22 h of reaction, indicating that the sulfate groups was stable enough under this reaction conditions. The spent catalyst after 2-methyl-1-butene reaction had 32.4% weight surplus with respect to the fresh catalyst up to 250 °C. The IR

and NMR results (Figures S18, S19) verified that the accumulated heavier oligomers remained in the S-MOF-808 pores. It is worth noting that we could not quantify all products of the reaction of 2-methyl-1-butene because the sum of the selectivities to the products obtained with GC did not reach 100% (Table 1). We attribute this discrepancy of the mass balance to the heavier oligomers trapped within the catalyst framework and in the pipes connecting reactor and GC due to their higher boiling point. Similar behavior was observed in stability tests of other reactants.



Figure 3. The conversion of isobutene and 2-methyl-1-butene over S-MOF-808 as a function of TOS. Reaction conditions: 6 mmol/h isobutene, 6 mmol/h 2-methyl-1-butene, 53 mmol/h He, 0.1 g catalyst, 101.325 kPa , 100 °C.



Figure 4. The conversion and selectivity of isobutene reaction over S-MOF-808 as a function of reaction temperature. Reaction conditions: 0.1 g catalyst, 6 mmol/h isobutene, 53 mmol/h He, 101.325 kPa.

Temperature dependence of isobutene dimerization

The influence of the reaction temperature on the dimerization of isobutene over S-MOF-808 is shown in Figure 4. With increasing reaction temperature from 80 to 120 $^{\circ}$ C, the conversion rose up to first up to 110 $^{\circ}$ C and

1

2

3

4

5

6

7

8

9

10 11

12

13

14 15

16

17 18

19 20

21 22

23

24

25

26 27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55 56

57 58 59

60

then decreased. We attribute this behavior to the stability of active Brønsted-acidic sites. The acidic site originates from the adsorbed water participating in a hydrogen bond with sulfate that is chelated to one zirconium atom. At the higher temperature (>110 °C), the adsorbed water is removed easily from the surface of MOF-808, resulting in the decay of the acidic site, thus reducing the catalytic activity.³⁰ In general, the selectivity to dimers decreased and the selectivities to trimers and tetramers increased with increasing reaction temperature. At the lower reaction temperatures (≤90 °C), the selectivity to dimers remained at a high value (>85%), while it decreased at 100 °C due to increased conversion and continued to decrease with further increase in temperature.



Figure 5. The performance of regenerated S-MOF-808 in the isobutene reaction. (a)Fresh catalyst; (b) deactivated catalyst regenerated by adsorbing water in humid air at room temperature for one day, (c) deactivated catalyst regenerated by feeding water vapor (33 mmol/h H₂O gas with 30 mmol/h He) at 100 °C for 50 min. Reaction conditions: 0.1 g catalyst, 6 mmol/h isobutene, 53 mmol/h He, 101.325 kPa, 150 °C.

Catalyst regeneration

The regeneration of the catalyst is the most direct and effective way to confirm or reject its deactivation mechanism. According to the previous discussion, the deactivation of S-MOF-808 in the isobutene reaction was attributed to the desorption of terminal water from the clusters at high temperature. Hypothetically, the catalyst could be regenerated by returning water to its original position. Based on this idea, we conducted the isobutene reaction over S-MOF-808 at 150 °C to prepare a deactivated catalyst. The conversion of isobutene sharply dropped from 13.6 to 3.1% within 21 h (Figure 5a). First, the deactivated catalyst was placed in humid air to absorb water at room temperature. The weight of the catalyst increased by 25% after one day. However, activity did not regenerate significantly after this room temperature water adsorption (Figure 5b). Then, we treated the deactivated catalyst by feeding water vapor at 100 °C. Surprisingly, the activity of the catalyst was completely restored, and the

deactivation curve was nearly the same as that of the fresh catalyst (Figure 5c), indicating that the catalyst was completely regenerated by treating with water vapor.

The proposed mechanism of regeneration of S-MOF-808 is shown in Figure 6. During the preparation of S-MOF-808, the bridging mode of sulfate ligands coordinating to zirconia clusters changed into chelating mode by heating under dynamic vacuum, and then forms acid site by hydrogen bonding interaction with terminal water. At the high temperature (150 °C), the terminal water desorbed and the acid site was removed, resulting in the deactivated catalyst. When the deactivated catalyst was placed in humid air, the absorbed water could not reform hydrogen bonds with the sulfate at room temperature because the chelating mode of sulfate was likely to return to the bridging mode. Therefore, the Brønsted acid could not be restored by this method. It was worth noting that the conversion of isobutene had a slight increase within the first 3 h over the regenerated catalyst in humid air. At the high reaction temperature of 150 °C, both desorption of water and formation of acid site were occurring at the same time. The increase of activity could be caused by the formation of acid sites during the reaction process. However, the desorption of water at this elevated temperature eventually counteracted the formation of new acid sites. Therefore, the activity decreased subsequently after 3 h. When the deactivated catalyst was regenerated with water vapor at 100 °C, the water would be returned to the original state directly, recovering the catalytic activity completely.



Figure 6. Proposed mechanism of regeneration of S-MOF-808.

Conclusions

In summary, light olefins (C3-C6) oligomerization was studied over S-MOF-808 at low temperature (80-120 °C) and ambient pressure. Different products were achieved for different olefins at the same reaction conditions. Despite similarities of their molecular structures, isobutene, 2-methyl-1-butene and 2-methoxypropene, gave dimers, isomers and heavier oligomers, respectively. The for-

mation of stable carbenium ions and the presence of the double bond in the α -position are the key for oligomerization of olefins. The two methyl groups in isobutene and the p- π conjugation effect in vinyl ether both promoted the formation of stable carbenium ions. Additionally, efficient C-C coupling reactions between isobutene and isopentene occurred over S-MOF-808 with a possible carbenium ions initiator formed from isobutene. S-MOF-808 deactivated in isobutene reaction due to the desorption of water molecules from the catalyst surface at higher temperature (>110 °C), but feeding the water vapor was an effective method to achieve its complete regeneration. Overall, the reported results suggest that Brønsted acid sites in sulfated MOF-808 exhibit surprising oligomerization specificity towards α -olefins with double substitution at the second carbon atom, most likely due to a delicate balance between adsorption energetics and unique steric factors in the vicinity of the active site.

ASSOCIATED CONTENT

Supporting Information

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

56

57 58 59

60

Details of syntheses and characterization, PXRD patterns, SEM images, TEM images, N₂ gas adsorption isotherms, H/C NMR spectra, TGA isotherms, IR, elemental analysis and catalytic tests are available free of charge *via* the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*somorjai@berkeley.edu *pingliu@cczu.edu.cn

Author Contributions

[#]P. Liu, E. Redekop, and X. Gao equally contributed to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

P.L. acknowledges the financial support by Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, Changzhou University for the opportunity to visit Lawrence Berkeley National Laboratory. U.O. and E.A.R. acknowledge the support by the Peder Sather Foundation and the use of NICE - the Norwegian national research infrastructure – for TAP measurements. The authors thank Dr. Andrea Lazzarini (UiO) and Mr. Erlend Aunan (UiO) for their help with IR and NMR measurements of the deactivated sample, respectively.

REFERENCES

(1) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. Design and Synthesis of an Exceptionally Stable and Highly Porous Metal-Organic Framework. *Nature* **1999**, *402*, 276-279.

52 Organic Framework. *Nature* 1999, 402, 276-279.
53 (2) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular Synthesis and The Design of New Materials. *Nature* 2003, 423, 705-417. (3) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.

(4) Stock, N.; Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chem. Rev.* **2012**, *112*, 933-969.

(5) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. Introduction to Metal-Organic Frameworks. *Chem. Rev.* 2012, *112*, 673-674.

(6) Martell, J. D.; Porter-Zasada, L. B.; Forse, A. C.; Siegelman, R. L.; Gonzalez, M. I.; Oktawiec, J.; Runcevski, T.; Xu, J.; Srebro-Hooper, M.; Milner, P. J.; Colwell, K. A.; Autschbach, J.; Reimer, J. A.; Long, J. R. Enantioselective Recognition of Ammonium Carbamates in a Chiral Metal–Organic Framework. *J. Am. Chem. Soc.* **2017**, *139*, 16000-16012.

(7) Chughtai, A. H.; Ahmad, N.; Younus, H. A.; Laypkov, A.; Verpoort, F. Metal–Organic Frameworks: Versatile Heterogeneous Catalysts for Efficient Catalytic Organic Transformations. *Chem. Soc. Rev.* **2015**, *44*, 6804-6849.

(8) Zhang, X.; Vermeulen, N. A.; Huang, Z.; Cui, Y.; Liu, J.; Krzyaniak, M. D.; Li, Z.; Noh, H.; Wasielewski, M. R.; Delferro, M.; Farha, O. K. Effect of Redox "Non-Innocent" Linker on the Catalytic Activity of Copper-Catecholate-Decorated Metal-Organic Frameworks. *ACS Appl. Mater. Interfaces* **2018**, *10*, 635-641.

(9) Mondloch, J. E.; Katz, M. J.; Isley, W. C., III; Ghosh, P.; Liao, P.;Bury, W.; Wagner, G. W.; Hall, M. G.; DeCoste, J. B.; Peterson, G. W.; Snurr, R. Q.; Cramer, C. J.; Hupp, J. T.; Farha, O. K. Destruction of Chemical Warfare Agents Using Metal-Organic Frameworks. *Nat. Mater.* **2015**, *14*, 512-516.

(10) Li, X.; Zhang, B.; Fang, Y.; Sun, W.; Qi, Z.; Pei, Y.; Qi, S.; Yuan, P.; Luan, X.; Goh, T. W.; Huang, W. Metal-Organic-Framework-Derived Carbons: Applications as Solid-Base Catalyst and Support for Pd Nanoparticles in Tandem Catalysis. *Chem.* -*Eur. J.* **2017**, *23*, 4266-4270.

(11) Ji, P.; Sawano, T.; Lin, Z.; Urban, A.; Boures, D.; Lin, W. Cerium-Hydride Secondary Building Units in a Porous Metal-Organic Framework for Catalytic Hydroboration and Hydrophosphination. J. Am. Chem. Soc. **2016**, *138*, 14860-14863.

(12) Xiao, D. J.; Bloch, E. D.; Mason, J. a; Queen, W. L.; Hudson, M. R.; Planas, N.; Borycz, J.; Dzubak, A. L.; Verma, P.; Lee, K.; Bonino, F.; Crocellà, V.; Yano, J.; Bordiga, S.; Truhlar, D. G.; Gagliardi, L.; Brown, C. M.; Long, J. R. Oxidation of Ethane to Ethanol by N_2O in a Metal-Organic Framework with Coordinatively Unsaturated Iron(II) Sites. *Nat. Chem.* **2014**, *6*, 590-595.

(13) Alaerts, L.; Séguin, E.; Poelman, H.; Thibault-Starzyk, F.; Jacobs, P. A.; De Vos, D. E. Probing the Lewis Acidity and Catalytic Activity of the Metal-Organic Framework [Cu₃(btc)₂] (BTC=Benzene-1,3,5-Tricarboxylate). *Chem. - Eur. J.* **2006**, *12*, 7353-7363.

(14) Sabyrov, K.; Jiang J.; Yaghi O. M.; Somorjai G. A. Hydroisomerization of n-Hexane using Acidified Metal-Organic Framework and Platinum Nanoparticles. *J. Am. Chem. Soc.* 2017, 139, 12382-12385.

(15) Jiang, J.; Gándara, F.; Zhang, Y.-B.; Na, K.; Yaghi, O. M.; Klemperer, W. G. Superacidity in Sulfated Metal–Organic Framework-808. J. Am. Chem. Soc. **2014**, 136, 12844-12847.

(16) Zhang, Y.; Degirmenci, V.; Li, C.; Hensen, E. J. M. Phosphotungstic Acid Encapsulated in Metal–Organic Framework as Catalysts for Carbohydrate Dehydration to 5-Hydroxymethylfurfural. *ChemSusChem* **2011**, *4*, 59-64.

(17) Chen, J.; Wang, S.; Huang, J.; Chen, L.; Ma, L.; Huang, X. Conversion of Cellulose and Cellobiose into Sorbitol Catalyzed by Ruthenium Supported on a Polyoxometalate/Metal-Organic Framework Hybrid. *ChemSusChem* **2013**, *6*, 1545-1555.

- (18) Li, B.; Leng, K.; Zhang, Y.; Dynes, J. J.; Wang, J.; Hu, Y.; Ma,
 D.; Shi, Z.; Zhu, L.; Zhang, D.; Sun Y.; Chrzanowski, M.; Ma, S.
 Metal-Organic Framework Based upon the Synergy of a Brønsted
 Acid Framework and Lewis Acid Centers as a Highly Efficient
 Heterogeneous Catalyst for Fixed-Bed Reactions. J. Am. Chem.
 Soc. 2015, 137, 4243-4248.
 (10) Zheng, M.; Liu, Y.; Wang, C.; Liu, S.; Lin, W. Cavity, Induced
 - (19) Zheng, M.; Liu, Y.; Wang, C.; Liu, S.; Lin, W. Cavity-Induced
 Enantioselectivity Reversal in a Chiral Metal-Organic Framework
 Brønsted Acid Catalyst. *Chem. Sci.* 2012, 3, 2623-2627.
 - 8 (20) Trickett, C. A.; Popp, T. M. O.; Su, J.; Yan, C.; Weisberg, J.;
 - Huq, A.; Urban, P.; Jiang, J.; Kalmutzki, M. J.; Liu, Q.; Baek, J.;
 Head-Gordon, M. P.; Somorjai, G. A.; Reimer, J. A.; Yaghi, O. M.
 Identification of the Strong Brønsted Acid Site in a Metal-
 - Indefiniteation of the strong Divisited Acta Site in a Metal-Organic Framework Solid Acid Catalyst. Nat. Chem. 2019, 11, 170-176.
 Delley M F.: Prayeen C S.: Borosy A P.:Núñez-Zarur F.:
 - (21) Delley, M. F.; Praveen, C.S.; Borosy, A. P.;Núñez-Zarur F.;
 Comas-Vives, A.; Copéret, C. Olefin Polymerization on Cr(III)/SiO₂: Mechanistic Insights from the Differences in Reactivity between Ethene and Propene. *J. Catal.* 2017, 354, 223-230.
 - (22) Granollers, M.; Izquierdo, J.F.; Cunill, F. Effect of Macroreticular Acidic Ion-Exchange Resins on 2-Methyl-1-Butene and 2-Methyl-2-Butene Mixture Oligomerization. *Appl. Catal. A: Gen.*2012, 435-436, 163-171.
 - (23) Cruz, V.J.; Bringué, R.; Cunill, F.; Izquierdo, J.F.; Tejero, J.;
 Iborra, M.; Fité, C. Conversion, Selectivity and Kinetics of the
 Liquid-Phase Dimerisation of Isoamylenes in the Presence of C1
 to C5 Alcohols Catalysed by a Macroporous Ion-Exchange Resin. *J. Catal.* 2006, 238, 330-341.
 - 24 (24) Fehér, C.; Tomasek, S.; Hancsók, J.; Skoda-Földes, R. Oligomerization of Light Olefins in the Presence of a Supported
 26 Brønsted Acidic Ionic Liquid Catalyst. *Appl. Catal. B: Environ.*27 2018, 239, 52-60.

 - (26) Yoon, J. W.; Jhung, S. H.; Choo, D. H.; Lee, S. J.; Lee, K.-Y.;
 Chang, J.-S. Oligomerization of Isobutene over Dealuminated Y
 Zeolite Catalysts. *Appl. Catal. A: Gen.* 2008, 337, 73-77.
 - 33 (27) Granollers, M.; Izquierdo, J. F.; Fité, C.; Cunill F. Kinetic
 34 Study of Methyl-Butenes Dimerization and Trimerization in
 35 Liquid-Phase over a Macroreticular Acid Resin. *Chem. Eng. J.*26 2013, 234, 266-275.
 - 2013, 234, 200-275.
 (28)Corma, A.; Martínez, C.; Doskocil, E. Designing MFI-Based
 Catalysts with Improved Catalyst Life for C3 and C5 Oligomerization to High-Quality Liquid Fuels. *J. Catal.* 2013, 300, 183-196.
 - (29) Rabeah, J.; Radnik, J.; Briois, V.; Maschmeyer, D.; Stochniol,
 G.; Peitz, S.; Reeker, H.; La Fontaine, C.; Brückner, A. Tracing
 - 41 Active Sites in Supported Ni Catalysts during Butene Oligomeri-242 zation by Operando Spectroscopy under Pressure. *ACS Catal.* 2016, 6, 8224-8228.
 - 43 (30) Coelho, A.; Caeiro, G.; Lemos, M.A.N.D.A.; Lemos, F.;
 44 RamôaRibeiro, F. 1-Butene Oligomerization over ZSM-5 Zeolite:
 45 Part 1 Effect of Reaction Conditions. *Fuel* 2013, *111*, 449-460.
 - 46 (31) Yoon, J. W.; Chang, J.-S.; Lee, H.-D.; Kim, T.-J.; Jhung, S. H.
 47 Trimerization of Isobutene over a Zeolite Beta Catalyst. *J. Catal.*48 2007, 245, 253-256.
 - (32) Malaika, A.; Rechnia-Gorący, P.; Kot, M.; Kozłowski, M.
 Selective and Efficient Dimerization of Isobutene over H3PO4/Activated Carbon Catalysts. *Catal. Today* 2018, 301, 266-273.
 - 52 (33) Chen, G.; Li, J.; Yang, X.; Wu, Y. Surface-Appropriate Lipo53 phobicity—Application in Isobutene Oligomerization over Tef54 lon-Modified Silica-Supported 12-Silicotungstic Acid. *Appl. Catal.*55 *A: Gen.* 2006, 310, 16-23.

57 58 59

60

(34) Liu, J.; Ye, J.; Li, Z.; Otake, K.; Liao, Y.; Peters, A. W.; Noh, H.; Truhlar, D. G.; Gagliardi, L.; Cramer, C. J.; Farha, O. K.; Hupp, J. T. Beyond the Active Site: Tuning the Activity and Selectivity of a Metal-Organic Framework-Supported Ni Catalyst for Ethylene Dimerization. *J. Am. Chem. Soc.* **2018**, *140*, 1174-1178.

(35) Metzger, E. D.; Comito, R. J.; Hendon, C. H.; Dincă, M. Mechanism of Single-Site Molecule-Like Catalytic Ethylene Dimerization in Ni-MFU-41. J. Am. Chem. Soc. 2017, 139, 757-762.

(36) Canivet, J.; Aguado, S.; Schuurman, Y.; Farrusseng, D. MOF-Supported Selective Ethylene Dimerization Single-Site Catalysts through One-Pot Postsynthetic Modification. *J. Am. Chem. Soc.* **2013**, *135*, *4195-4198*.

(37) Liu, S.; Zhang, Y.; Han, Y.; Feng, G.; Gao, F.; Wang, H.; Qiu, P. Selective Ethylene Oligomerization with Chromium-Based Metal-Organic Framework MIL-100 Evacuated under Different Temperatures. *Organometallics* **2017**, *36*, 632-638.

(38) Sawamoto, M. Modern Cationic Vinyl Polymerization. Prog. Polym. Sci. 1991, 16, 111-172.

(39) Matyjaszewski, K. Cationic Polymerizations: Mechanisms, Synthesis, and Applications. **1996**, ISBN13: 9780824794637.

(40) Kim, Y. T.; Chada, J. P.; Xu, Z.; Pagan-Torres, Y. J.; Rosenfeld, D. C;Winniford, W. L.; Schmidt, E.; Huber G. W. Low-Temperature Oligomerization of 1-Butene with H-Ferrierite. *J. Catal.* **2015**, 323, 33-44.

(41) Mäurer, T.; Kraushaar-Czarnetzki B. Thermodynamic and Kinetic Reaction Regimes in the Isomerization of 1-Pentene over ZSM-5 Catalysts. *J. Catal.* **1999**, *187*, 202-208.

(42) Gleaves J. T.; YablonskyG.;Zheng, X.; FushimiR.; Mills P. L. Temporal Analysis of Products (TAP)—Recent Advances in Technology for Kinetic Analysis of Multi-Component Catalysts. *J. Mol. Catal. A.* **2010**, *315*, 108-134.

Graphical abstract

