Inorganic Chemistry
COMMUNICATION
pubs.acs.org/IC

Metal–Organic Frameworks of Vanadium as Catalysts for Conversion of Methane to Acetic Acid

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Supporting Information

ABSTRACT: A catalytic system combining the high activity of homogeneous catalysts and the ease of use of heterogeneous catalysts for methane activation is reported. The vanadium-containing metal–organic frameworks (MOFs) MIL-47 and MOF-48 are found to have high catalytic activity and chemical stability. They convert methane selectively to acetic acid with 70% yield (490 TON) based on $K_2S_2O_8$ as an oxidant. Isotopic labeling experiments showed that two methane molecules are converted to the produced acetic acid. The MOF catalysts are reusable and remain catalytically active for several recycling steps without losing their crystalline structures.

Methane is the main constituent of natural gas, which represents almost two-thirds of fossil fuels on earth. A long-standing challenge has been to find catalysts for conversion of methane to useful feedstock chemicals such as acetic acid (AA). Currently, the production of AA on an industrial scale involves multiple steps, uses expensive homogeneous metal (Rh or Ir) catalysts, and requires high temperatures (up to 250 °C).[1] Thus, efforts are ongoing to identify catalysts for the direct aerobic oxidation of methane to AA and that can operate at lower temperatures. Reported heterogeneous catalysts show activity in the direct oxidation of methane to AA but give low product yields and have lower selectivity than homogeneous systems.[2−5] Recently reported homogeneous catalyst systems using $K_2S_2O_8$ as an oxidant are based on vanadium(IV) complexes with an oxygen-dominated coordination sphere and give improved conversions at 80 °C.[6] It is desirable to develop a catalyst system that combines the high activity of homogeneous catalysts and the ease of use of heterogeneous catalysts. Metal–organic frameworks (MOFs) are promising materials for this application because of their high porosity and the flexibility with which the metal centers and the organic struts can be varied and functionalized. In this report, we show that a MOF (MIL-47), constructed from vanadium centers in an oxygen-dominated coordination sphere, can catalyze the oxidation of methane directly to AA with 70% yield using $K_2S_2O_8$ as an oxidant (yields based on $K_2S_2O_8$), 175 TON, and 80% selectivity at 80 °C. This performance was enhanced by functionalizing the pore with methyl groups, by which a new MOF (MOF-48) was synthesized. Also, adding CO to the reaction mixture increased the activity to 490 TON and the selectivity to 100% at 80 °C. We determined, under the same catalytic conditions, using ^{13}C-labeled methane, that methane is entirely incorporated into the AA product (100% from the methyl carbon and 90% for the carbonyl carbon). These MOF catalysts are easily separated and reused. They remain catalytically active for several recycling steps. Their overall performance rivals that of homogeneous vanadium catalysts and exceeds that of the heterogeneous systems.

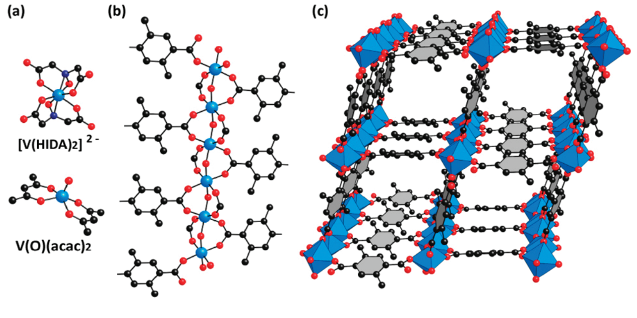

Figure 1. Ball-and-stick representations of (a) an amavadin-type complex, 2,2′-(hydroxyimino)diacetic acid (HIDA; top) and vanadyl acetylacetonate [V(O)(acac)$_2$; bottom], (b) a rodlike SBU of MOF-48 (chains of corner-sharing VO_6 octahedra), and (c) MOF-48 with 1D pores comprising protruding methyl groups (VO_6 are shown in blue polyhedra). Color code: V, blue; O, red; N, dark blue; C, gray. Hydrogen atoms omitted for clarity.

Scheme 1. Tentative Stoichiometric Catalytic Reactions for Conversion of Methane to AA in the (a) Absence and (b) Presence of CO[a]

$$\text{(a) } 2CH_4 + 2H_2O + 4\,K_2S_2O_8 \xrightarrow[\text{MOFs}]{\text{TFA, 80 °C, 20h}} CH_3COOH + 8KHSO_4$$

$$\text{(b) } CH_4 + CO + H_2O + K_2S_2O_8 \xrightarrow[\text{MOFs}]{\text{TFA, 80 °C, 20h}} CH_3COOH + 2KHSO_4$$

[a] See the SI for the proposed source and calculation of water and the proposed stoichiometric reaction of MTFA (reaction 1S in the SI, section S9).

Our strategy is to use a MOF whose secondary building unit (SBU) is a vanadium center having an oxygen-dominated

Received: June 29, 2011
Published: July 18, 2011

dx.doi.org/10.1021/ic201396m | Inorg. Chem. 2011, 50, 7388–7390

Table 1. Catalytic Activity of Heterogeneous MOF Catalysts in the Conversion of Methane to AA in the Absence of CO

catalyst[a]	CH_3CO_2H (AA) (mM)	$CF_3CO_2CH_3$ (MFTA) (mM)	yield of AA (%) [b]	yield of AA (%) [c]	MFTA [d]selectivity (%)	TON of AA[e]
MOF-48-as syn.	0.36	0.07	36	13	17	89
MOF-48–100	0.38	0.30	38	14	29	95
MOF-48–180	0.48	0.30	48	18	38	121
MIL-47-as syn.	0.38	0.08	38	14	18	94
MIL-47–350	0.60	0.08	60	22	11	150
MIL-47–480	0.70	0.07	70	26	9	175

[a] Reaction conditions: $p(CH_4)$ = 10 bar (25 °C), 4 mmol of $K_2S_2O_8$, 7.5 mL of TFA, 20 h at 80 °C. [b] The CH_3CO_2H yield was calculated as $\{(4[CH_3CO_2H])/[K_2S_2O_8]$, Scheme 1a$\}$ because $K_2S_2O_8$ is the limiting reagent (excluding gaseous products). [c] Yields based on methane; the CH_3CO_2H yield was calculated as $\{(2[CH_3CO_2H])/[CH_4]$, Scheme 1a$\}$ (excluding gaseous products; see the SI, section S9). [d] The $CF_3CO_2CH_3$ selectivity was calculated as the molar ratio of $CF_3CO_2CH_3$ to the total molar yield of products excluding gaseous products. [e] TON was calculated as the molar ratio of CH_3CO_2H to the metal content.

Table 2. Catalytic Activity of Heterogeneous MOF Catalysts in the Conversion of Methane to AA in the Presence of CO with 100% Selectivity

catalyst[a]	CH_3CO_2H (AA) (mM)	total yield [b] (%)	total yield [c] (%)	TON of AA[d]
MOF-48-as syn.	1.36	34	25	340
MOF-48–100	1.75	44	32	440
MOF-48–180	1.95	49	36	490
MIL-47-as syn.	0.95	24	18	240
MIL-47–350	1.16	29	21	290
MIL-47–480	1.32	33	24	330
$VOSO_4$	0.8	21	15	210

[a] Reaction conditions: $p(CH_4)$ = 10 bar (25 °C), $p(CO)$ = 10 bar (25 °C), 4 mmol of $K_2S_2O_8$, 7.5 mL of TFA, 20 h at 80 °C. [b] The total yield was calculated as $([CH_3CO_2H]/[K_2S_2O_8]$, Scheme 1b) because $K_2S_2O_8$ is the limiting reagent (excluding gaseous products). [c] Yields based on methane; the CH_3CO_2H yield was calculated as $\{[CH_3CO_2H])/[CH_4]$, Scheme 1b$\}$ (excluding gaseous products; see the SI, section S9). [d] TON was calculated as the molar ratio of CH_3CO_2H to the metal content.

coordination sphere. This structural motif is found in molecular complexes known as homogeneous catalysts (Figure 1a), specifically amavadin and vanadyl acetylacetonate.[6] In MIL-47,[7] the VO_6 octahedra are sharing opposite corners to make infinite SBUs that are linked together by terepthalate moieties to form a hexagonal arrangement of 1D channels. In the present work, we studied the conversion of methane to AA using MIL-47, $VO(BDC)\cdot(H_2BDC)_{0.75}$ (BDC = 1,4-benzenedicarboxylate), and we contrast its performance with the new methyl-functionalized analogue MOF-48, $VO(DMBDC)\cdot(H_2DMBDC)_{0.4}$ (DMBDC = 2,5-dimethylbenzenedicarboxylate; Figure 1b,c).

MIL-47 was synthesized according to the literature procedure.[7] For the new MOF-48, a different procedure was used. MOF-48 was obtained as light-yellow needlelike crystals, similar to other previously reported vanadium(IV) MOFs,[7] unlike the usual blue or greenish color exhibited for vanadium(IV) compounds,[8] together with green solid impurities [see the Supporting Information (SI), section S2].[9] The structure of MOF-48 was analyzed by single-crystal X-ray diffraction[10] and found to be isoreticular to that of MIL-47. The methyl functionalities in MOF-48 point toward the center of the channels (Figure 1c), where uncoordinated H_2DMBDC guest molecules were also observed (Figures 1S and 2S in the SI). The bulk purity of MOF-48 was confirmed by coincidence of the observed powder X-ray diffraction (PXRD) patterns with the calculated one from the single-crystal X-ray diffraction data (Figure 3S in the SI).

Both MIL-47 and MOF-48 were activated (removal of guest molecules from the pores) by calcination of the as-synthesized samples at 350 °C in air for 8 h.[7] MIL-47 and MOF-48 are thermally stable up to 425 °C (Figure 4S in the SI). N_2 adsorption isotherm measurements at 77 K showed a type I behavior consistent with the presence of a permanent porosity in these MOFs (Figure 5S in the SI). From these data, the Brunauer–Emmett–Teller (BET) surface areas were calculated and found to be 480 m^2/g (MIL-47) and 180 m^2/g (MOF-48). We also prepared an additional two samples for catalytic studies for which the pores were partially evacuated and had BET surface areas of 350 m^2/g (MIL-47) and 100 m^2/g (MOF-48).

The catalytic reactions (Scheme 1) were carried out using a mixture of trifluoroacetic acid (TFA; 7.5 mL), potassium peroxydisulfate ($K_2S_2O_8$; 4 mmol), and MOF (4 μmol) in a 21 mL high-pressure vessel. The vessel was flushed with N2 three times, pressurized with methane (10 bar) and CO (10 bar, if required) then stirred for 20 h at 80 °C. The reaction mixture was filtered, and the products were quantified by ^1H NMR (see the SI, section S8). The results are summarized in Tables 1 and 2 in the absence and presence of CO, respectively.

In the absence of CO, the major product is AA and the minor product is methyl trifluoroacetate (MTFA).[6] The MIL-47 and MOF-48 catalysts with the highest surface areas gave the best yield (70% and 48%) for AA and the best selectivity (38%) for MTFA (Table 1). The higher yields are associated with more open pores, while the higher selectivity is associated with the more hydrophobic pores of MOF-48.

To reduce the amount of oxidant consumed and enhance the amount of AA, we carried out the reaction in the presence of CO. Under the same conditions, the amount of AA produced increases significantly from 0.48 to 1.95 mmol, and TON increases from 121 to 490 for MOF-48 and a similar increase of lower magnitude is observed for MIL-47 (Table 2). This suggests that CO is a carbonylating agent, which is in accordance with other reports.[6] Indeed, in the presence of CO, the reaction gives 100% selectivity for AA (in the liquid phase) for both MOFs (Table 2).

To confirm the origin of the carbon atoms in the AA product, we examined the reaction both with and without CO using >99% ^{13}C isotopically enriched methane under the same catalytic conditions. We found that, without CO, 90% of the AA has both carbon atoms derived from methane molecules. This was evidenced

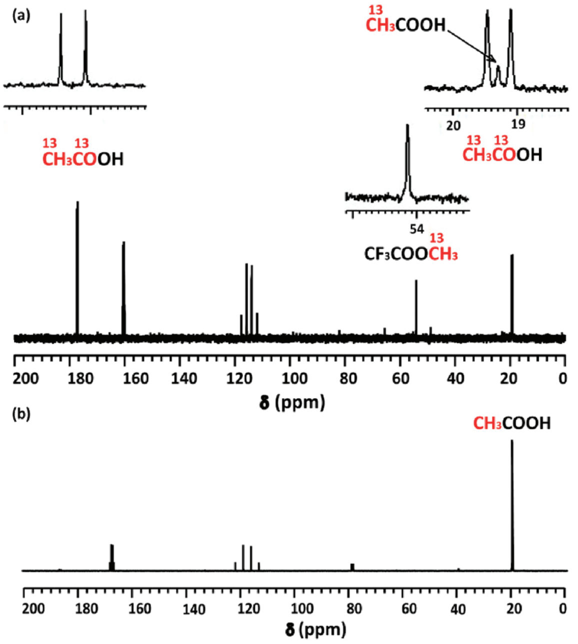

Figure 2. $^{13}C\{^1H\}$ NMR of the reaction mixture of $^{13}CH_4$ (a) in the absence of CO and (b) in the presence of CO.

by the $^{13}C\{^1H\}$ NMR spectrum of the crude reaction mixture from the reaction of $^{13}CH_4$ in the presence of the MOF catalyst. Doublets are found at $\delta = 19.5$ ppm ($^{13}CH_3-$), ^1J (^{13}C,^{13}C) = 57.2 Hz and $\delta = 177.5$ ppm ($-^{13}CO_2$), ^1J (^{13}C,^{13}C) = 57.2 Hz (Figure 2a).[1] Additionally, the spectrum shows a singlet at $\delta = 19.3$ ppm attributed to the remaining 10% of the AA, with only one carbon atom from methane and the other from TFA, which is known to act as a carbonylating agent.[6] For the homogeneous vanadium catalysts, it was found that, in the absence of CO, only the methyl group of the AA product is derived from methane and the carbonyl carbon comes from TFA.[6]

In the presence of CO, the majority of the AA has the methyl group derived from methane and the carbonyl group from CO, in agreement with previously reported results.[6] The $^{13}C\{^1H\}$ NMR spectrum of the crude mixture of this reaction shows a singlet at $\delta = 20.0$ ppm, which is assigned to the methyl group of AA ($^{13}CH_3-$; Figure 2b). This was further confirmed by using >99% ^{13}C isotopically enriched CO under the same catalytic conditions (Figure 6S in the SI).[6]

The heterogeneous nature of the catalytic reaction was confirmed by filtration. After the initial catalyst run, the MOF was removed and fresh $K_2S_2O_8$ and TFA were added to the filtrate. The reaction was performed under the same conditions as those of the initial experiment using the filtrate; no catalytic conversion was observed. To check that indeed the MOF is the catalyst and the reaction requires an oxidant, the reaction was performed without the MOF and/or an oxidant; these conditions showed no activity.

The MOF catalysts are reusable and maintain their structural stability and order even after the reaction, as evidenced by PXRD (Figure S8 in the SI). Recycling experiments were performed by adding more methane, $K_2S_2O_8$, and TFA to a previous reaction mixture after an aliquot was taken out for ^1H NMR analysis. TON (>250) remains nearly constant during the last three recycling steps (Figure 7S in the SI). In addition, the MOF catalysts maintain their structural integrity during the recycling, as evidenced by the close correspondence of the PXRD patterns of fresh and recycled catalysts (Figure S8 in the SI).

This preliminary study shows promising evidence that MOFs are active heterogeneous catalysts for the conversion of methane to AA and that their performance exceeds that of other such catalysts. We anticipate further elaboration of these studies because MOFs are easily functionalized and varied.

■ ASSOCIATED CONTENT

S **Supporting Information.** Detailed experimental, analytical, catalytic, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by BASF SE (Ludwigshafen, Germany). We thank Dr. Siddhartha Das and Dr. Hiroyasu Furukawa for valuable discussions. O.M.Y. was also supported by the WCU program (R-31-2008-000-10055-0). F.G. acknowledges funding by the Spanish Ministry of Education through the "Programa de Movilidad de Recursos Humanos del Plan Nacional de I-D+i 2008-2011".

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(9) Elem anal. Calcd for MOF-48 [$C_{14}H_{12}O_{6.6}V$]: C, 49.93; H, 3.59; V, 15.13. Found: C, 48.40; H, 3.34; V, 12.61.

(10) Crystal data for MOF-48: space group *Pnma*, $a = 6.7507(10)$ Å, $b = 16.9798(13)$ Å, $c = 12.9232(7)$ Å. All obtained crystals were found to be twinned. The best data were obtained with a crystal composed of three twin components. The small size of the crystals limited the maximum reached resolution. These factors account for the alerts present in the corresponding CIF file. Full crystal and refinement data and structure solution details can be found in the SI, section S4.