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Stabilized Vanadium Catalyst for Olefin Polymerization by Site Isolation in a Metal-Organic Framework

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Abstract: Vanadium catalysts offer unique selectivity in olefin polymerization, yet are underutilized industrially owing to their poor stability and productivity. We report the immobilization of vanadium by cation exchange in MFU-4*l*, providing a metal-organic framework with vanadium in a molecule-like coordination environment. This material forms a single-site heterogeneous catalyst with methylaluminoxane, providing polyethylene with low polydispersity (PDI~3) and the highest activity (up to 148,000 hr^{-1}) reported for a MOF-based polymerization catalyst. Furthermore, polyethylene is obtained as a free-flowing powder as desired industrially. Finally, the catalyst shows good structural integrity and retains polymerization activity for over 24 hours, both promising attributes for the commercialization of vanadium-based polyolefins.

Vanadium catalysts have long been known to offer exceptional sequence and stereoselectivity in the polymerization of light olefins.[1] These features have made them indispensable to the manufacture of specialty elastomers.[2] Yet vanadium catalysts typically suffer from rapid deactivation under polymerization conditions.[3] Consequently, their low productivity limits the commercialization of vanadium catalysts toward other polyolefin products. This shortcoming has motivated extensive efforts to develop more stable and productive vanadium catalysts, with the majority of these studies using soluble metalloligand complexes.[1,3]

A classic strategy to stabilize organometallic catalysts involves immobilization onto a solid support, wherein site isolation minimizes deactivation through multimetallic pathways.[4] Furthermore, solid catalysts are often required for commercial olefin polymerization in order to control the morphology of the insoluble products, and thus to avoid reactor fouling on a large scale.[5] To realize this strategy with vanadium, a variety of immobilization strategies have been studied,[6] but structurally inhomogeneous supports often have a negative effect on activity and selectivity. Consequently, there are relatively few examples of single-site heterogeneous vanadium catalysts that are capable of reproducing the exquisite molecular selectivity of their soluble counterparts in the solid state.[7]

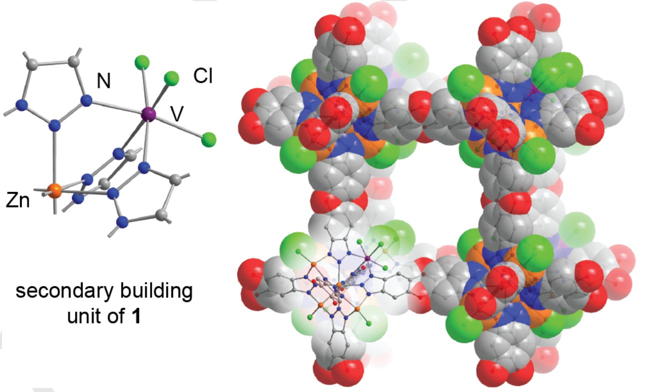

Figure 1. Proposed structure of V^{IV}-MFU-4*l* (**1**), a single-site vanadium catalyst for olefin polymerization.

Toward this end, metal-organic frameworks (MOFs) have emerged as a class of materials uniquely suited for single-site heterogeneous catalysis.[8] The molecular-level structural control[9] and modularity[10] possible with MOFs allow molecule-like catalyst design in the solid state. Although essentially all components of a MOF may be modified for catalysis, the inorganic nodes have attracted increasing attention as a structurally monodisperse and well-defined platform for transition metal catalysis.[11] In particular, these clusters or secondary building units (SBUs) often undergo cation exchange with structural retention,[12] offering a predictable strategy to incorporate transition metals for catalysis. Along these lines, our laboratory[13] and others[14] have developed effective single-site heterogeneous catalysts for olefin polymerization by postsynthetic modification of MOF SBUs.

With an interest in using MOF SBUs to stabilize vanadium catalysts for olefin polymerization, we targeted the material MFU-4*l* ($Zn_5Cl_4(BTDD)_3$, H_2BTDD = bis(1*H*-1,2,3-triazolo[4,5-*b*],[4',5'-i])dibenzo[1,4]dioxin).[15] The SBU of this triazole-based MOF features facial coordination of Zn^{2+} by three nitrogen atoms,[16] a scorpionate unit shown to structurally and functionally emulate the tris(pyrazolyl)borate[17] and tris(pyrazolyl)methane[18] ligands that provide effective vanadium catalysts for olefin polymerization. Based on this analogy between SBUs and small molecules, we anticipated that incorporation of vanadium into MFU-4*l* by cation exchange would provide an effective vanadium catalyst further benefitting from site isolation.

Encouragingly, cation exchange has been reported in MFU-4*l* with several transition metals,[19] although vanadium is absent from this series and rare for cation exchange in MOFs in general.[20] Typically, cation exchange with MFU-4*l* involves a large excess (~50 equivalents) of transition metal salt. However, treating MFU-4*l* with solutions containing 50 equivalents of

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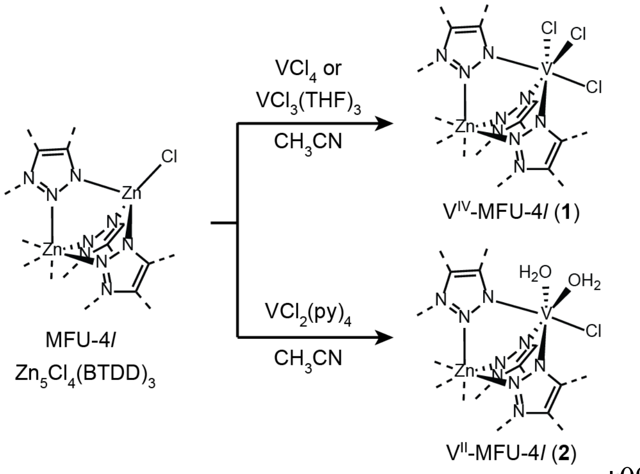
$VCl_2(py)_4$,[21] $VCl_3(THF)_3$, or VCl_4 decomposed the MOF in all cases. Nevertheless, vanadium incorporation was observed when each of these three precursors was used in a more modest excess (Table 1). The resulting materials showed good structural retention by powder X-ray diffraction and gas sorption analysis (section S3), consistent with the incorporation of vanadium into a structurally conserved framework. Furthermore, analysis of the supernatant indicated the release of zinc into solution consistent with cation exchange.

Table 1. Cation Exchange of vanadium into MFU-4*l*.



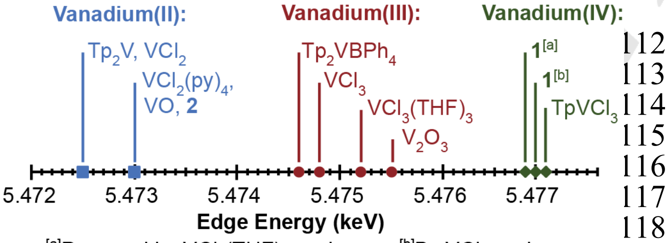
MFU-4*l*
$Zn_5Cl_4(BTDD)_3$

V^{IV}-MFU-4*l* (**1**)

V^{II}-MFU-4*l* (**2**)

Entry	Vanadium Source[a]	Product	Incorporation Ratio (V : Zn)[b]	Edge Energy[c]
1	VCl_4 (2 eq.)	**1**	0.64 : 4.36	5.4768
2	$VCl_3(THF)_3$ (1 eq.)	**1**	0.37 : 4.63	5.4769
3	$VCl_2(py)_4$ (5 eq.)	**2**	0.44 : 4.56	5.4730

[a]Conditions: CH_3CN, room temperature, 7-10 days. [b]Determined by ICP-MS. [c]From vanadium K-edge XAS in keV.



[a]Prepared by $VCl_3(THF)_3$ exchange. [b]By VCl_4 exchange.

Figure 2. Comparison of the edge energies obtained by vanadium K-edge XAS for exchanged MOFs and their standards.

To characterize the local structure of vanadium in the MOF, we next analyzed the resulting materials by vanadium K-edge XAS, with the tris(pyrazolyl)borate (Tp^-) complexes $TpVCl_3$, Tp_2VBPh_4, and Tp_2V serving as standards for V^{4+}, V^{3+}, and V^{2+} in MFU-4*l*. Unexpectedly, the materials exchanged with VCl_4 and with $VCl_3(THF)_3$ showed nearly identical edge energies and pre-edge features (Table 1, entries 1 and 2), both consistent with a vanadium(IV) oxidation state (Figure 2) and referred to hereafter as V^{IV}-MFU-4*l* (**1**). Presumably, disproportionation of $VCl_3(THF)_3$ accounts for the formation of **1**, a process previously reported for the ligation of $VCl_3(THF)_3$ with nitrogen-based ligands.[22] By contrast, the material exchanged with $VCl_2(py)_4$ exhibits an edge energy most consistent with vanadium(II), and is referred to hereafter as V^{II}-MFU-4*l* (**2**). Consistently, X-band EPR analysis resulted in nearly identical spectra for **1** prepared with either VCl_4 or $VCl_3(THF)_3$, with g and A tensor values consistent with a vanadium(IV) assignment, while **2** exhibited a distinct EPR spectrum (Section S10).

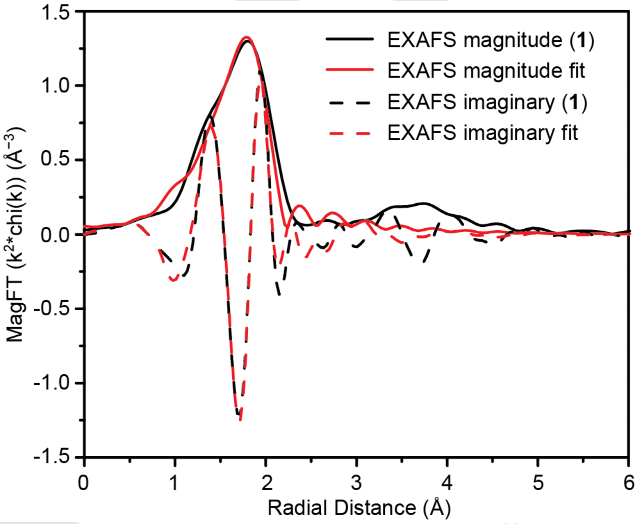


Figure 3. EXAFS analysis of **1** and its first-shell fit.[23]

Table 2. Quantitative results of the EXAFS fit.[a]

Sample	Scattering Pair	Coord. Number	Bond Length (Å)	S_0^2	ΔE_0 (eV)	σ^2 (Å^2)
Tp_2V	V−N	6	2.11	0.56	-3.6	0.002
VCl_2	V−Cl	6	2.49	0.50	0.5	0.003
1	V−N	3	2.07	0.50	-5.0	0.002
	V−Cl	3	2.31			0.002

[a]The average error in S_0^2 is 0.1, in bond length is 0.03 Å, in ΔE_0 is 2.9 eV and in $\Delta\sigma^2$ is 0.002 Å.

Furthermore, a pseudo-octahedral geometry could be assigned for both **1** and **2** based on analysis of the pre-edge feature, both displaying peaks of low to moderate intensity (Figures S6.4-5).[24] To fully describe the coordination environment of vanadium, we performed a first-shell fit of the extended X-ray absorption fine structure (EXAFS) data for **1**, prepared with VCl_4, obtaining good agreement between the experimental and modeled data (Figure 3, Table 2). This analysis resulted in a primary coordination sphere consisting of 3 N−V bonds (2.07 Å) and 3 Cl−V bonds (2.31 Å, Table 2), as anticipated for $TpVCl_3$-like structure proposed for **1** (Table 1). Models with different coordination numbers gave consistently worse fits. Although a suitable first-shell EXAFS fit was not obtained for **2**, we propose a six-coordinate V^{2+} involving two solvent molecules (Table 1) based on the results of edge energy, pre-edge analysis, IR and elemental analysis. Thus we provide a degree of structural characterization generally not possible with

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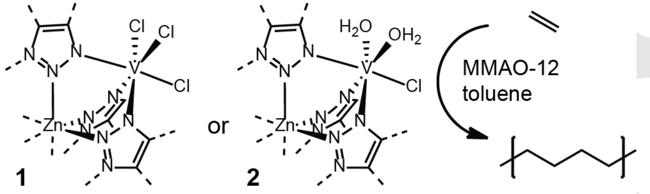
prior heterogeneous vanadium catalysts for olefin polymerization[6,7] which could greatly inform mechanistic analysis and catalyst optimization.

To evaluate ethylene polymerization, both **1** and **2** were treated with ethylene under slurry phase conditions with modified methylaluminoxane-12 (MMAO-12) as cocatalyst (Table 3). Indeed, with both materials we observed predominantly linear high-density polyethylene, all polymers showing a high peak melting temperature (T_M >130 °C) and moderate crystallinities (%C) as measured by differential scanning calorimetry (DSC). High-temperature gel permeation chromatography (HT-GPC) analysis of these polymers showed a high number-average molecular weight (M_N), with a weak dependence of M_N on ethylene pressure (entries 1 and 2). Furthermore, the generally low polydispersity indices (PDI) measured are consistent with single-site catalysts operating under the constraints of mass transport. Both **1** and **2** show a significant response to hydrogen, with around 100-fold decrease in number-average molecular weight (M_N) upon loading with a 1:1 mixture of ethylene and hydrogen (entries 3 and 6). Under comparable conditions, the M_N obtained with **1** is nearly half that obtained with **2**, whereas the M_N obtained for samples of **1** prepared using VCl_4 or $VCl_3(THF)_3$ were similar (entries 2, 4, and 5).

Table 3. Results of ethylene polymerization with **1** and **2**.

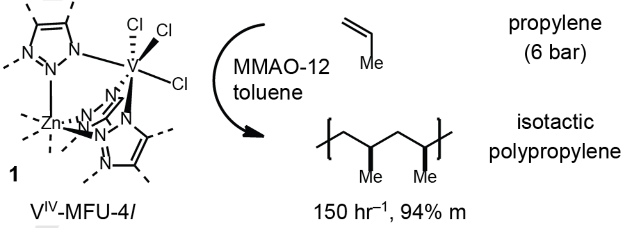


entry	MOF (w% V)	P_E[a] (bar)	P_{H2}[a] (bar)	TOF[b] (hr^{-1})	%C[c]	PDI[d]	M_N[d] ($/10^3$)
1	**1**[e] (1.5% V)	40	0	71,000	62%	3.4	650
2	**1**[e] (1.5% V)	10	0	51,000	62%	3.5	330
3	**1**[e] (1.5% V)	10	10	2,200	81%	36	3.8
4	**1**[f] (2.5% V)	10	0	7,500	59%	2.7	380
5	**2** (1.8% V)	10	0	6,400	66%	2.9	680
6	**2** (1.8% V)	10	10	900	70%	70	4.3

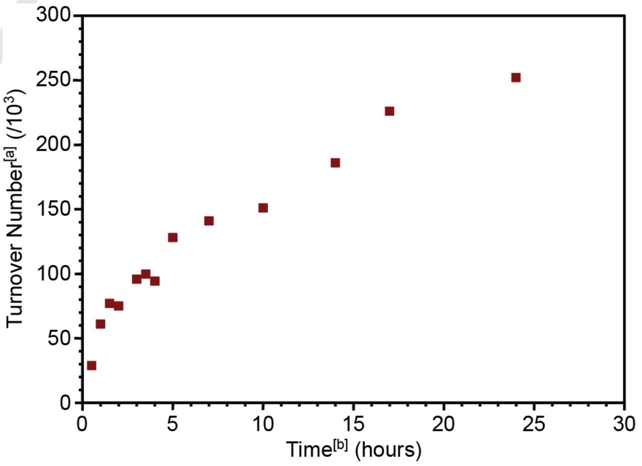
[a]Applied pressure of ethylene (E) and hydrogen (H2). [b]Turnover frequency in mol(ethylene)/mol(V) per hour. [c]Determined by DSC. [d]Determined by HT-GPC. [e]Prepared with $VCl_3(THF)_3$. [f]Prepared with VCl_4.

Under similar conditions, we found that **1**/MMAO-12 polymerizes propylene with moderate isotacticity (dyad count 94% m, Scheme 1). By contrast, Cr-MFU-4*l* shows negligible activity toward propylene while Ti-MFU-4*l* produces atactic polypropylene in low activity. Consistent with this result, soluble vanadium catalysts are often reported to give higher propylene tacticity than their chromium or titanium analogues.[1] To our knowledge, this is the first MOF-based catalyst and the first single-site heterogeneous vanadium catalyst reported to polymerize propylene stereoselectively.[25]

We next sought to optimize the activity of **1** by interrogating the catalyst composition and reaction conditions (section S7.6-8). First, we evaluated the Al : V ratio using a sample of **1** with a constant vanadium loading (prepared by $VCl_3(THF)_3$ exchange, Figure S7.2), finding 300 : 1 to be optimal. At this Al : V ratio, various alkylaluminums ($AlMe_3$, $AlEt_3$, $AliBu_3$, and $AlEt_2Cl$) give rise to active catalysts, although the combination of **1** and MMAO-12 was the most active for ethylene polymerization. Next we evaluated the effect of vanadium loading in **1**, at constant MMAO-12 concentration and a constant Al to V ratio of 300 : 1. Samples of **1** with lower vanadium concentration provided consistently higher activity. This loading effect accounts for the apparent differences in activity between samples of **1** prepared with $VCl_3(THF)_3$ and with VCl_4, featuring inequivalent vanadium loading (Table 3) Furthermore, this loading dependence is consistent with mass transport-limited activity at the surface of a heterogeneous catalyst. Along these lines, the combination of **1** and MMAO-12 shows an apparent first-order dependence of activity on ethylene pressure (Figure S7.3), with a maximum turnover of 148,000 hr^{-1} achieved at 50 bar. This activity, presumably underestimated due to the disproportional reactivity of surface-confined species, exceeds the reported activity of prior MOF catalysts for olefin polymerization.[13,14]



Scheme 1. Isoselective polymerization of propylene using **1** (VCl_4-exchange).



[a]Reported as mol(ethylene)/mol(V). [b]Run in separate batches.

Figure 4. Time study of ethylene polymerization with **1** ($VCl_3(THF)_3$ exchange).

Consistent with heterogeneous catalysis, polyethylene was predominantly obtained as a free-flowing powder using **1** and **2**, as desired for commercial polymerization. By contrast, the combination of $TpVCl_3$ or VCl_4 with MMAO-12 form homogeneous solutions in toluene, polymerizing ethylene as a solid mass firmly attached to the reactor wall (section S7.13).

Notably, both of these soluble catalysts are less active than **1** under comparable conditions. To confirm the heterogeneity of our MOF catalyst, a suspension containing **1** and MMAO-12 was stirred vigorously for 30 minutes and then separated under air-free conditions. PXRD analysis of the recovered catalyst showed retention of crystallinity (Figure S7.4). The supernatant showed a low propensity for vanadium leaching when analyzed by ICP-MS and low ethylene polymerization activity (section S7.10). Next, to further test the catalyst integrity, we studied the time course of ethylene polymerization out to 24 hours using **1**/MMAO-12 (Figure 4). The rate of ethylene polymerization indeed decreases over this 24-hour period, as would be expected even without catalyst deactivation due to the encapsulation of the catalyst in polymer. Nevertheless the continued activity after 24 hours affirms the long-term stability of this catalyst under polymerization conditions. Although single-site heterogeneous vanadium catalysts have been reported with higher initial ethylene polymerization activity than **1**/MMAO-12, generally these either suffer substantial deactivation within an hour, or their long-term stability has not been reported.[7]

In summary, we have shown that the incorporation of vanadium into MFU-4*l* by cation exchange is a promising strategy to achieve stable and productive vanadium catalysts for olefin polymerization. The resulting catalysts reproduce commercially relevant modes of polymer molecular control, including stereoselectivity and molecular weight control, while providing commercially desirable morphological control. These results will be relevant for the commercialization of advanced polyolefin products using vanadium catalysts, and the use of vanadium catalysts under more demanding conditions, such as multistage reactor processes.[26]

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Keywords: heterogeneous catalysis • metal-organic frameworks • organometallics • polymerization • X-ray absorption spectroscopy

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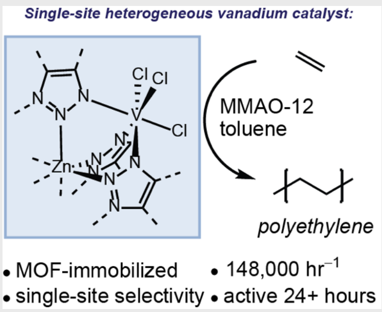
COMMUNICATION

Vanadium catalysts provide coveted selectivity in olefin polymerization, but suffer from poor stability and productivity. In this report incorporation of vanadium into a metal-organic framework provides a single-site heterogeneous catalyst with exceptional activity and stability for ethylene polymerization. X-ray absorption spectroscopy analysis provides evidence for a discrete, molecule-like coordination of V^{4+} cations in this material.



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Stabilized Vanadium Catalyst for Olefin Polymerization by Site Isolation in a Metal-Organic Framework