

## SUPPORTING INFORMATION

### **Ethylene Oligomerization on Ni<sup>2+</sup> Single Sites within Lacunary Defects of Wells Dawson Polyoxometalate**

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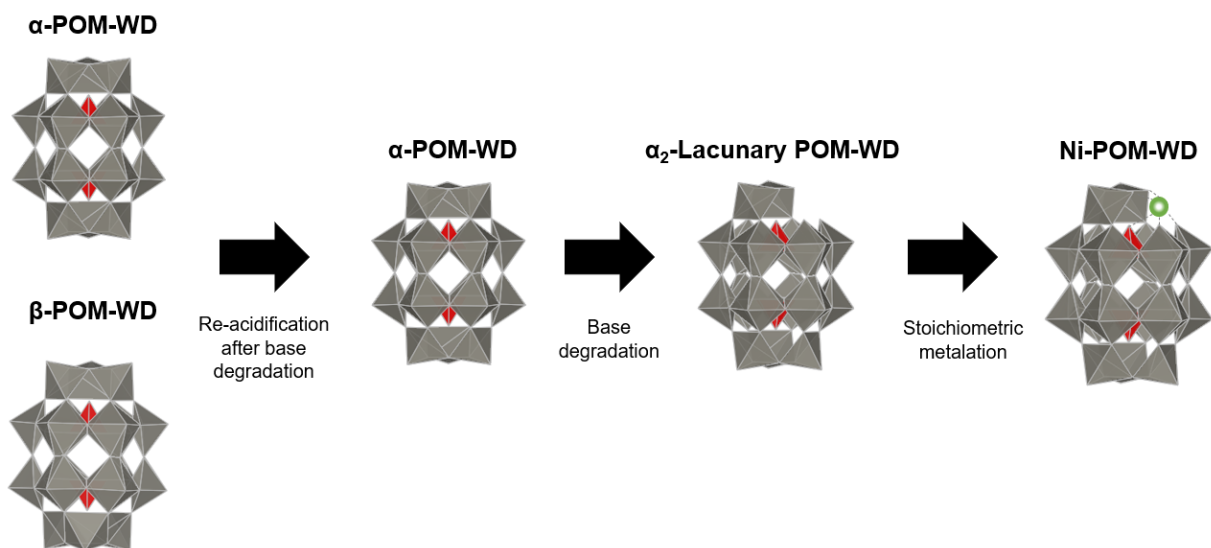
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## 1. Experimental Details

### 1.1 Material Synthesis

#### 1.1.1 Synthesis of Wells Dawson polyoxometalate and derivatives



**Figure S1.** Synthesis pathway of transition metal substituted Wells Dawson polyoxometalate

Isomeric mixture of  $\alpha/\beta$ -  $K_6P_2W_{17}O_{62}$  was prepared by following and slightly modifying the methods which were previously reported in literatures. The precursor solution was prepared by dissolving 100 g of  $Na_2WO_4$  (Alfa Aesar) in 350 mL of de-ionized water under reflux and stirring until the solution became clear. Then, 150 mL of phosphoric acid (Millipore Sigma) was added in dropwise over 30 min. The final solution was stirred under reflux for 24 h. The solution was then cooled to room temperature and 100 g of KCl (BDH Chemicals) was added to precipitate the crude product. Precipitates of the crude product were obtained by vacuum filtration via medium glass frits. For recrystallization, precipitates were dissolved in boiling de-ionized water and cooled at 2-3 °C overnight. The final product crystals were filtered under vacuum using a medium glass frit.

To obtain pure  $\alpha$ -  $K_6P_2W_{17}O_{62}$ , 52 g of as-synthesized  $\alpha/\beta$ -  $K_6P_2W_{18}O_{62}$  was dissolved in de-ionized water at 90 °C. Then 8 drops of bromine (ACROS) was added to remove heteropoly blue anions, which are non-fully oxidized side products. Immediately after the addition of bromine, 260 mL of 1 M  $KHCO_3$  (CHEM IMPLEX) solution was added dropwise. After stirring the mixed precursor solution for 30 min, 25 mL of 12 M HCl (Millipore Sigma) was added dropwise. Precipitates of the crude product were formed by adding 65 g of KCl (BDH Chemicals) and separated from solution by vacuum filtration using a medium frit. The precipitates were dissolved in boiling de-ionized water and cooled at 2-3°C overnight. The final product was filtered under vacuum using a medium glass frit.

For the synthesis of  $\alpha_2$  -  $K_{10}P_2W_{17}O_{61}$ , 33 g of as-synthesized  $\alpha$ -  $K_6P_2W_{17}O_{62}$  was dissolved in 73 mL of de-ionized water at 90 °C. After the dissolution, 122 mL of 1 M  $KHCO_3$  (CHEM

IMPLEX) solution was added dropwise over 30 min. Upon the base addition, milky precipitates were formed and collected by vacuum filtration using a coarse glass frit. The collected precipitates were dissolved in boiling de-ionized water and cooled at 2-3°C overnight. Crystals of final products were filtered under vacuum using a medium glass frit.

To substitute transition metal ions on lacunary sites, approximately a 1.1 multiple of the stoichiometric amount of the corresponding metal nitrate,  $\text{Ni}(\text{NO}_3)_2$  was used.  $\alpha_2 - \text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$  and metal nitrates were dissolved in boiling water and stirred for 30 min. Then, the crude products were precipitated by cooling at 2-3°C overnight. Precipitates were collected by vacuum filtration using a medium glass frit. Precipitates were re-dissolved in water and cooled at 2-3°C overnight for recrystallization. Final products were filtered under vacuum *via* medium glass frits.

### 1.1.2 Synthesis of SBA-15 and Immobilization of Ni-POM on SBA-15

A general synthesis procedure was followed what has been described in previously reported literatures.<sup>1</sup> EO-PO-EO block copolymer (18 g) was dissolved in a solution of 99.5 g of 12 M HCl and 561 g of de-ionized water. The prepared mixture was stirred at room temperature overnight. Then, 39.8 g of tetraethyl orthosilicate was added to the solution and stirred for 5 min. The prepared precursor solution was stirred at 35 °C for 20 h. Then, the precursor solution was aged at 80 °C for 24 h. Precipitated products were collected and washed with de-ionized water by vacuum filtration. Collected sample was then dried at 60 °C overnight. The dried sample was calcined by using the following temperature program: increasing temperature to 200 °C at a ramp rate of 1.2°C/min, holding the temperature at 200 °C for 1 h, increasing the temperature to 550 °C at the ramp rate of 1.2°C/min and holding the temperature at 550 °C for 6 h. The calcined sample was dried under vacuum at 200 °C for 3 h and stored under  $\text{N}_2$  atmosphere.

For immobilization, 10 wt. % of Ni-POM-WD was dissolved in 1.6 ml of water per gram of SBA-15. After dissolving Ni-POM-WD in water, the dispersion process was done via incipient wetness. Upon dispersion of the solution on SBA-15, the as-prepared material was dried at 100 °C for 12 h.

## 1.2. Characterization of Catalyst

### 1.2.1 FTIR

A Bruker Vertex 70 Fourier Transform Infrared Spectrometer equipped with an ATR cell (Pike Technologies GladiATR) was used to observe bonding features of synthesized Wells Dawson polyoxometalates and its derivatives. IR spectra were recorded from 400-4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  by using a mercury cadmium telluride MCT detector, which was cooled with liquid  $\text{N}_2$ .

### 1.2.2 $^{31}\text{P}$ NMR

$^{31}\text{P}$  NMR spectra of prepared Wells Dawson polyoxometalate and its derivatives were collected by a Bruker AVANCE III HD 400 MHz Nanobay. Samples were dissolved in a mixture of 90% water and 10%  $\text{D}_2\text{O}$  prior to the measurement.

### 1.2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra were obtained using a PHI 5000 VersaProbe II which has a monochromatic Al K<sub>α</sub> X-ray source (20 kV, 100 W) and an analyzer with a pass energy of 23.5 eV. Binding energy features were processed by using CASA XPS software. Obtained peaks were referenced to the adventitious C 1s at 284.5 eV.

### 1.2.4 <sup>31</sup>P MAS NMR

<sup>31</sup>P MAS NMR was measured using a JEOL ECX-300 with a CPMAS-300NB-HX-J3.2 two channel MAS NMR probe which was tuned for single pulse <sup>31</sup>P. Each sample was packed in a zirconia rotor and spun at 10 kHz during the data collection.

### 1.2.5 HAADF STEM – EDX

High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) and energy dispersive X-ray spectroscopy (EDX) were conducted using a Titan 80-300 transmission electron microscope operated at 300 kV. Samples were prepared by suspending the powder sample in acetone using sonication and then drop casting the resulting solution onto a carbon coated copper grid.

### 1.2.6 Inductively Coupled Plasma (ICP)

ICP experiments were performed to determine the nickel loadings of Ni-POM-WD based materials by using a Perkin Elmer Optima 8000 ICP-OES.

### 1.2.7 Pyridine Adsorption Diffusion Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Pyridine adsorption DRIFTS experiments were conducted with a Bruker Vertex 70 Fourier Transform Infrared Spectrometer equipped with a Harrick Praying Mantis cell with a high temperature ZnSe window. The sample was placed on top of the KBr bed inside the sample holder. The sample was pretreated at 300 °C for overnight prior to the experiment. The spectra were obtained 150°C with the appropriate background at 150°C. Spectra were collected while helium purging after the initial incorporation of pyridine at 25°C.

### 1.2.8 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was conducted by using a Mettler Toledo Star 1 instrument. The sample was heated from 30°C to 900°C at a ramp rate of 5°C /min under the flow of dry air.

### 1.2.9 Nitrogen Physisorption

Nitrogen physisorption data were collected with a Quantachrome 2200e unit. Samples were degassed at 150 °C under vacuum prior to the measurement. The actual measurement was carried out at 77K by cooling with liquid nitrogen.

### 1.3. Catalytic Ethylene Oligomerization

#### 1.3.1 Ethylene Oligomerization of TM-POM-WD

Catalytic ethylene oligomerization was performed with stainless steel flow reactor (0.64cm diameter). The reactor was packed with 200 mg of sieved (150-250 $\mu$ m) catalyst sample which was diluted by 200 mg of 60-100 mesh Davisil® silica gel on top of 25-30 mg of quartz wool. The packed catalyst bed was pre-treated at 300°C under flowing helium (Airgas) for 12 h to remove physisorbed water on polyoxometalate catalysts. After the pre-treatment, the reactor was cooled to 200°C and ethylene (Airgas, 99.9%) was introduced into the system at 15 mL/min. Temperature sweep experiments were done by cooling the reactor to (40.7, 51, 59 and 65°C) under the diluted ethylene ( $F_{\text{Helium}}= 25$  mL/min,  $F_{\text{ethylene}}= 5$  mL/min). Ethylene flow inside the reactor was pressurized to the desired setpoint (0.62 to 2 MPa) by using a back-pressure regulator. Then, the outlet stream of the reactor was fed into an SRI 8610C GC-FID for the quantitative analysis of products and analyzed at 35 min intervals.

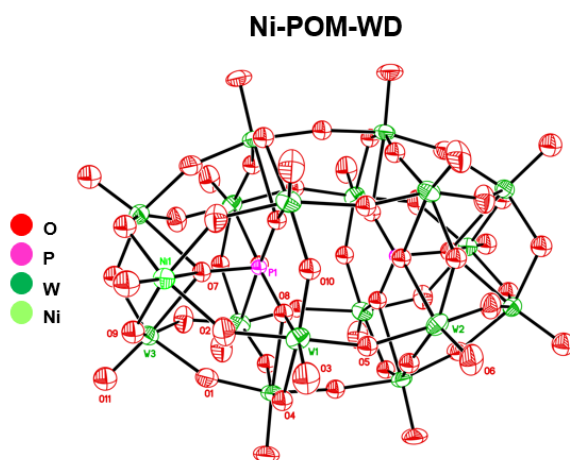
#### 1.3.2 Thermal Helium Catalyst Regeneration Experiment

Catalyst regeneration was done after the first cycle of ethylene oligomerization with fresh catalysts at 200 °C and 2MPa with the feed stream at  $F_{\text{feed}} = 7.5$  mL/min ( $F_{\text{Ethylene}} = 1.5$  mL/min,  $F_{\text{Helium}} = 6$  mL/min). Prior to the regeneration process, the reactor was purged under flowing helium (50mL/min) for 6 h. Then, the temperature was elevated to 300 °C while maintaining He flow for 12 h. The reactor was cooled and the next reaction cycle was started.

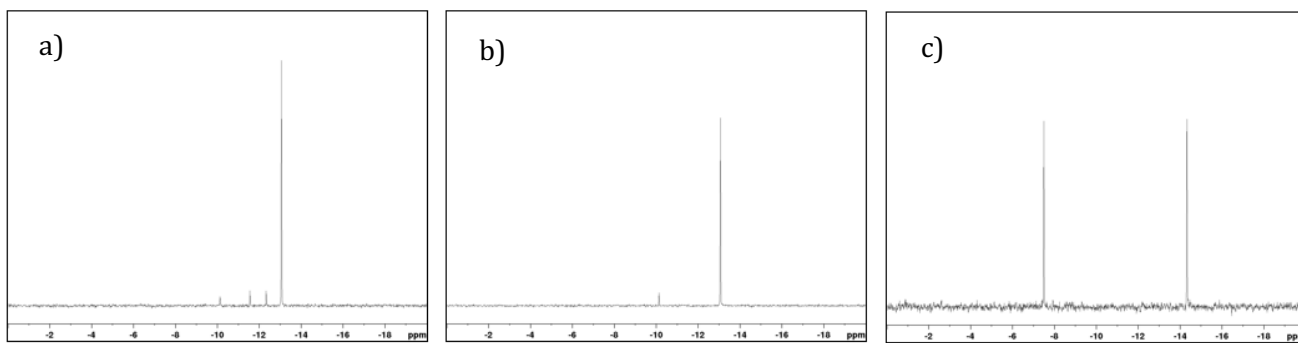
### 1.4 Reference

- 1 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548–552.

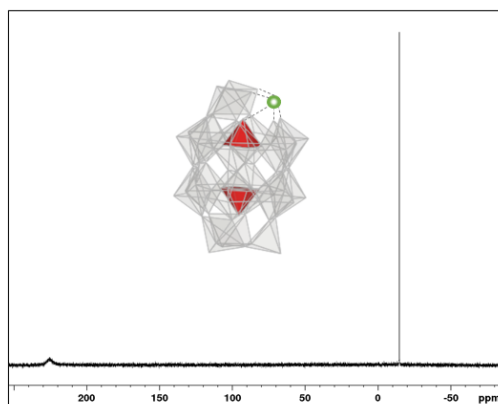
## 2. Supplementary Data and Figures



**Figure S2.** Solved anionic structure of Ni-POM-WD

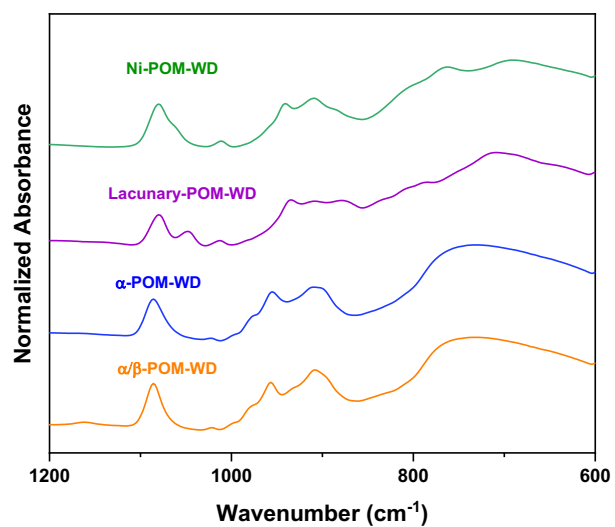


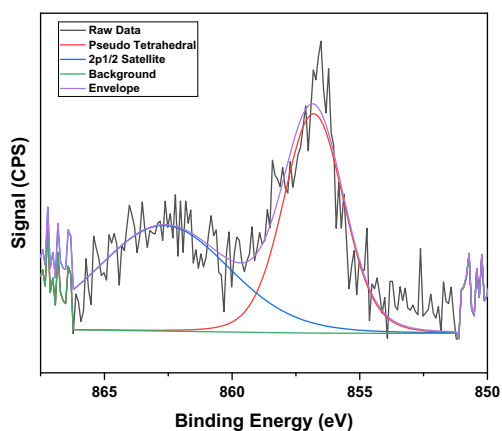
**Figure S3.**  $^{31}\text{P}$  NMR of  $\alpha/\beta$ -POM-WD (a),  $\alpha$ -POM-WD (b) and  $\alpha_2$ -Lacunary POM-WD (c)



**Figure S4.**  $^{31}\text{P}$  NMR of Ni-POM-WD

**Figure S5.** FTIR of synthesized Wells Dawson and derivative polyoxometalates





**Figure S6.** XPS of Ni $2p_{3/2}$  in Ni-POM-WD

	<b>BET Surface Area (m<sup>2</sup>/g)</b>	<b>BJH Adsorption Pore Size (Å)</b>	<b>Ni Loadings (wt. %)</b>
<b>SBA-15</b>	<b>802</b>	<b>68</b>	<b>N/A</b>
<b>Ni-POM-WD/SBA-15 10 wt%</b>	<b>518</b>	<b>67</b>	<b>0.11</b>
<b>Ni-POM-WD/SBA-15 1 wt%</b>	<b>564</b>	<b>68</b>	<b>0.011</b>
<b>Ni-POM-WD</b>	<b>N/A</b>	<b>N/A</b>	<b>1.1</b>

**Table S1.** Nitrogen Physisorption Pore Properties and Measured Ni Loadings

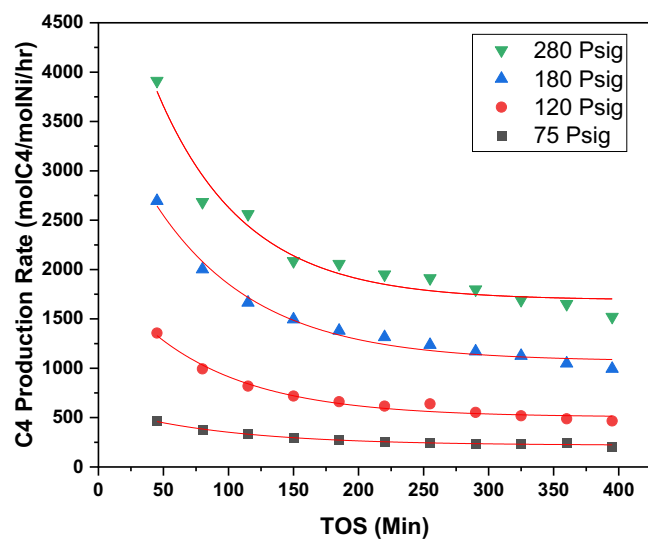


Figure S7. Ethylene oligomerization at four pressures and fitted first order deactivation curves

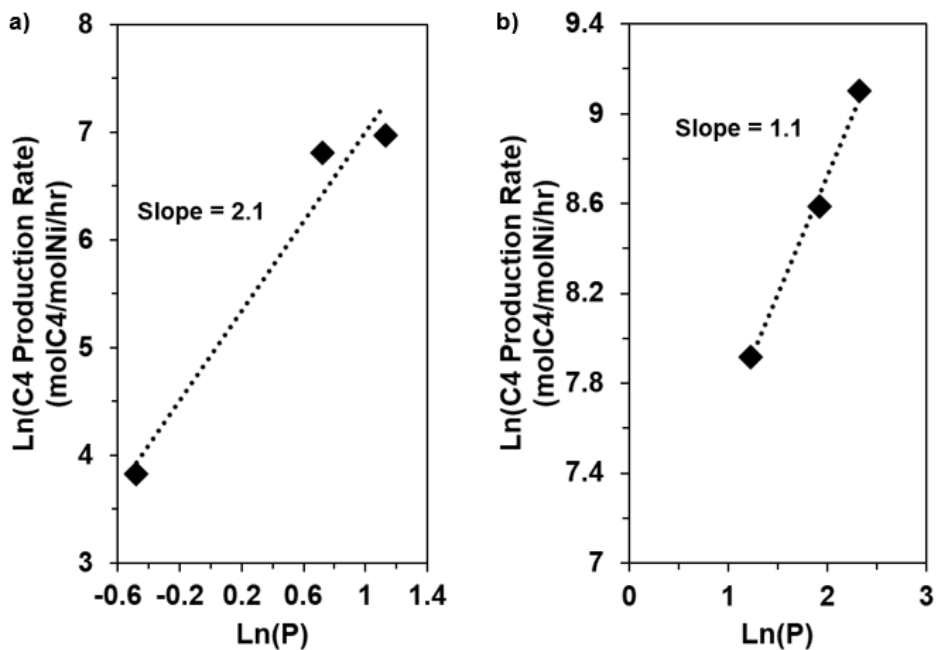
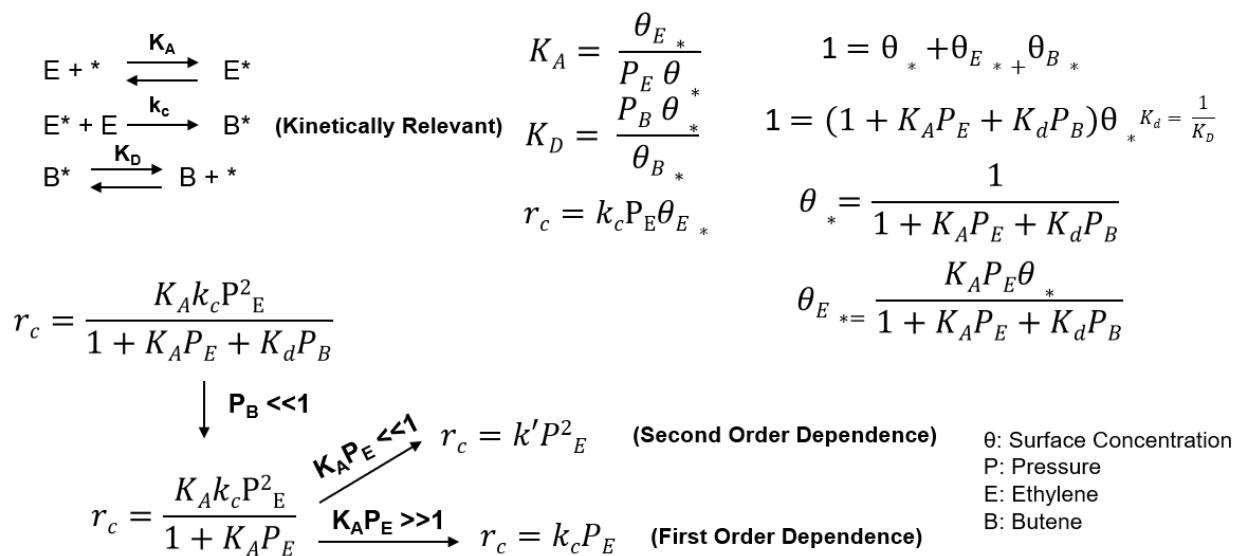
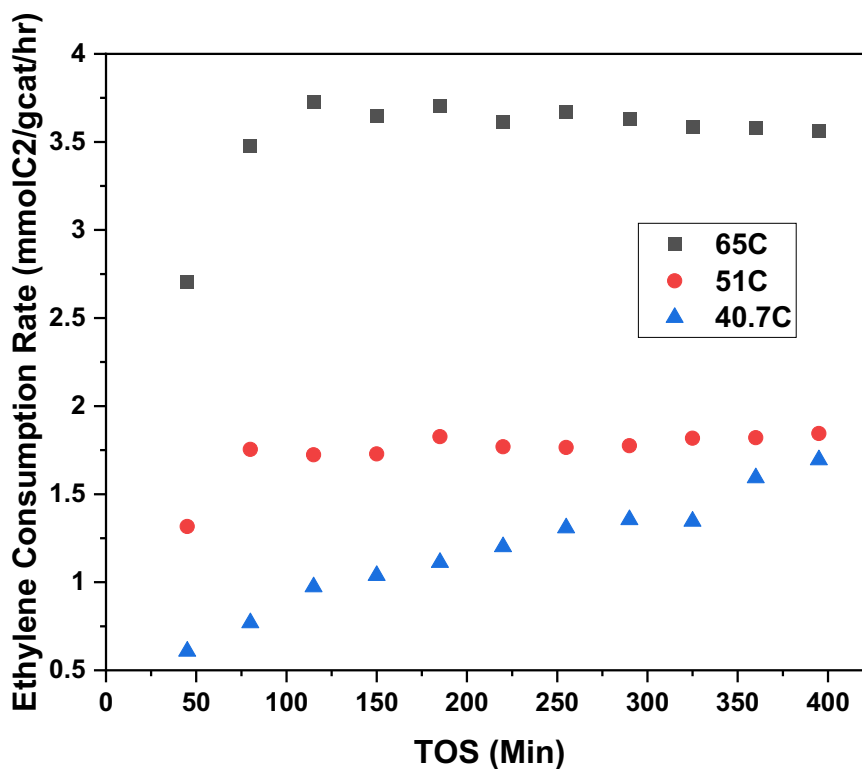


Figure S8. Ethylene Partial Pressure Dependence at 0.62 MPa and 2 MPa





**Scheme 1. Hypothesized Ethylene Dimerization Reaction Network**



**Figure S9. Variation in Temperature for Ethylene Oligomerization**

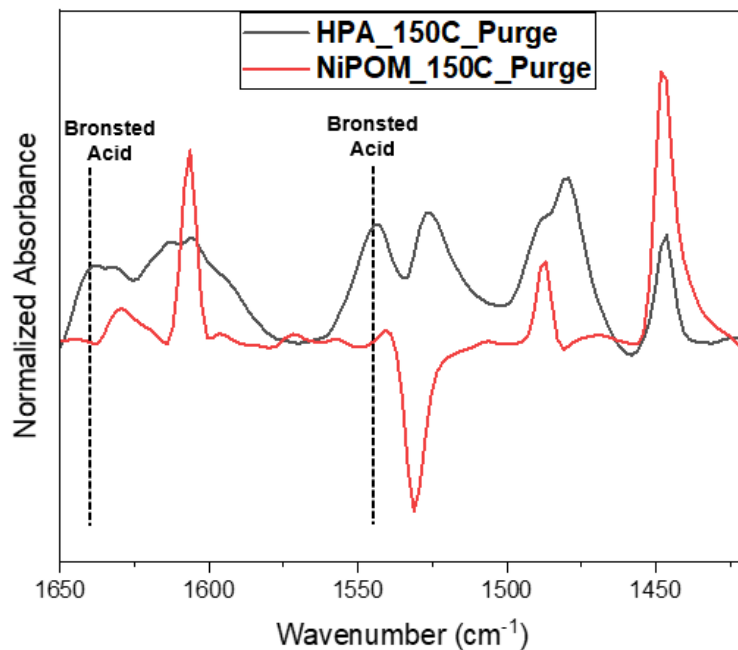


Figure S10. Pyridine Adsorption DRIFTS Spectra of Ni-POM-WD and Heteropolyacid (HPA)

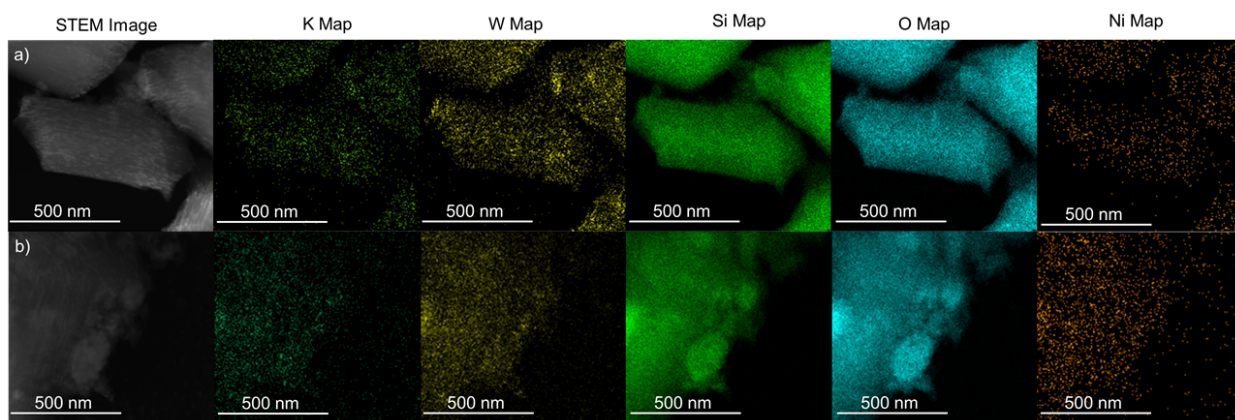
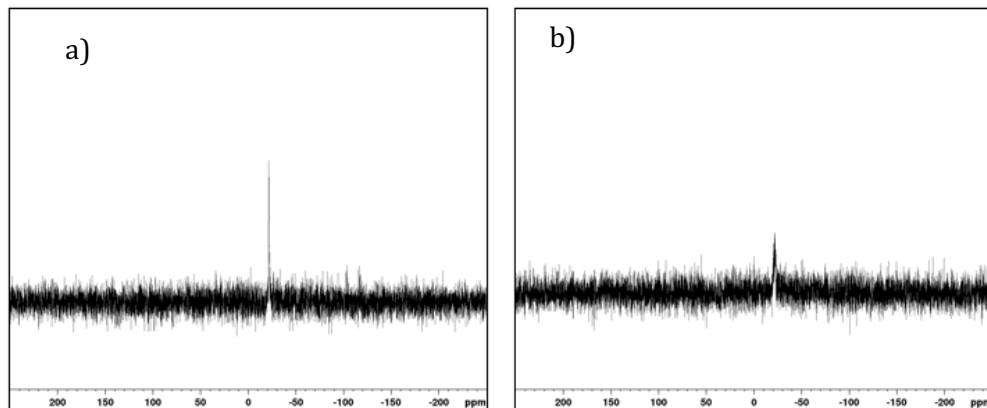
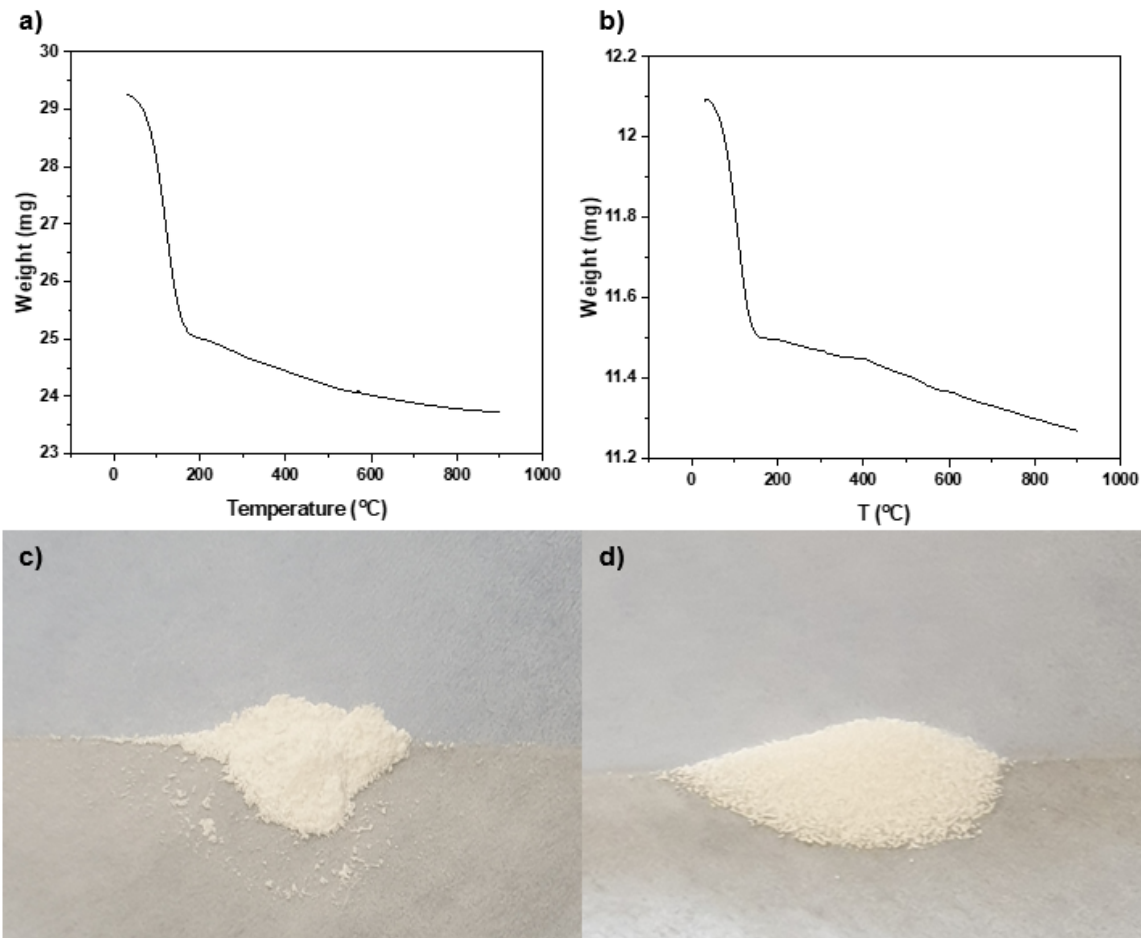


Figure S11. HAADF-STEM images and EDX maps of fresh (a) and spent (b) Ni-POM-WD/SBA-15



**Figure S12.**  $^{31}\text{P}$  MAS NMR of fresh (a) and spent (b) Ni-POM-WD/SBA-15



**Figure S13.** Thermogravimetric Profile of a) Fresh and b) Spent Ni-POM-WD/SBA-15 1 wt% and Image of c) Fresh and d) Spent Ni-POM-WD/SBA-15 1 wt%

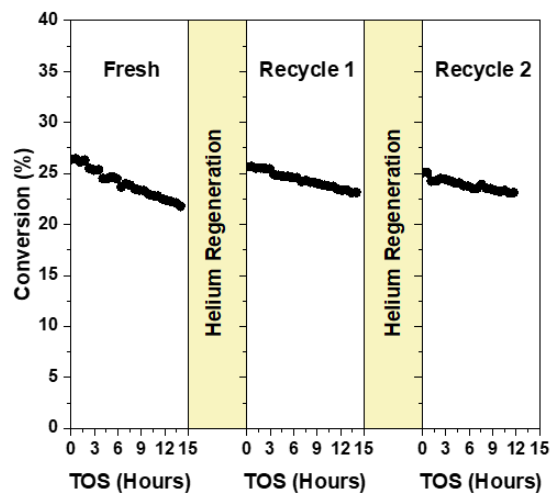


Figure S14. Ethylene Conversion vs. TOS of the Regenerated Ethylene Oligomerization

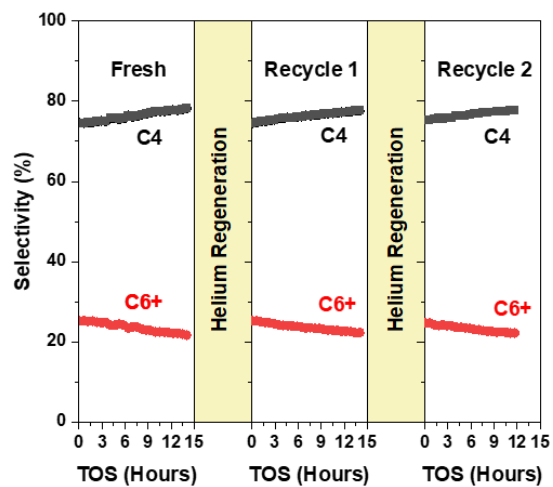


Figure S15. Product Selectivity vs. TOS of the Regenerated Ethylene Oligomerization

### 3. Single Crystal X-ray Crystallography Details

#### 3.1 Experimental Details

An arbitrary sphere of data was collected on a pale green block-like crystal, having approximate dimensions of  $0.195 \times 0.140 \times 0.115$  mm, on a Bruker APEX-II diffractometer using a combination of  $\omega$ - and  $\phi$ -scans of  $0.5^\circ$  [1]. Data were corrected for absorption and polarization effects and analyzed for space group determination [2]. The structure was solved by dual-space methods and expanded routinely [3]. The model was refined by full-matrix least-squares analysis of  $F^2$  against all reflections [4]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ( $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl,  $1.2U_{\text{eq}}(\text{C})$  for all others).

#### 3.2 Discussion

The nickel doped, tungstate Dawson ion crystallizes as pale green block-like crystals from an aqueous solution. There are three molecules of the Dawson anion, 24 associated potassium cations and 24 waters of crystallization in the unit cell of the rhombohedral space group R-3.

The anion consists of a tungsten-based Dawson structure, modified by the inclusion of nickel for a tungsten atom. Due to the high symmetry of the structure, and location within the unit cell of the anion about the  $-3$  center, the nickel atom is disordered with the capping tungsten atoms. Furthermore, this triangular cap is rotationally disordered, resulting in two identical locations where the nickel could be positioned, within the asymmetric unit. The premise that the nickel is located in this capping region, and not within the body of the anion, is due to the reduced electron density (beyond that which would be associated with disorder) observed at the capping tungsten site. As a result of this, the tungstate oxygen atoms are also disordered.

The cations and waters of crystallization were modeled as partial occupancy atoms. These molecules are disordered about the anion, within the lattice. There is no fixed position that can be directly associated with one species or another. The model provided is a “best model” fit to the data. Due to the heavy disorder, water hydrogen atoms cannot be located. Their contribution to the chemical formula has been calculated and included, but they are not present within the model.

#### 3.3 Crystal Summary

Table 1. Crystal data and structure refinement for nd1936.

Identification code	nd1936
Empirical formula	$\text{H}_{18}\text{K}_8\text{NiO}_{70}\text{P}_2\text{W}_{17}$
Formula weight	4697.04
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal

Space group	R-3	
Unit cell dimensions	$a = 19.997(2) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 19.997(2) \text{ \AA}$	$\beta = 90^\circ$
	$c = 14.480(4) \text{ \AA}$	$\gamma = 120^\circ$
Volume	5014.3(16) $\text{\AA}^3$	
Z	3	
Density (calculated)	4.666 $\text{g.cm}^{-3}$	
Absorption coefficient ( $\mu$ )	30.051 $\text{mm}^{-1}$	
F(000)	6138	
Crystal color, habit	pale green, block	
Crystal size	0.195 × 0.140 × 0.115 $\text{mm}^3$	
$\theta$ range for data collection	1.833 to 28.341°	
Index ranges	-26 ≤ h ≤ 26, -26 ≤ k ≤ 26, -19 ≤ l ≤ 19	
Reflections collected	32335	
Independent reflections	2784 [ $R_{\text{int}} = 0.0482$ ]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.1288 and 0.0388	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	2784 / 0 / 175	
Goodness-of-fit on $F^2$	1.110	
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0341$ , $wR_2 = 0.0888$	
R indices (all data)	$R_1 = 0.0441$ , $wR_2 = 0.0987$	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.559 and -2.024 $\text{e}^- \cdot \text{\AA}^{-3}$	

### 3.4 References

- [1] *APEX-3*. Bruker AXS. Madison, Wisconsin, USA. **2016**.
- [2] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, & D. Stalke. *J. Appl. Crystallogr.* **2015** 48, 3.
- [3] G. M. Sheldrick. *Acta Crystallogr.*, **2015**, A71, 3.
- [4] G. M. Sheldrick. *Acta Crystallogr.*, **2015**, C71, 3.