

Achieving Ultra-Low-Sulfur Model Diesel through Defective Keggin-Type Heteropolyoxometalate Catalysts

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1. The Rietveld Method for Structure Refinement

X-ray diffraction analyses were performed on a X-ray diffractometer (Rigaku Model Miniflex 600), with a source of Cu 40 kV and $\lambda = 1.54 \text{ \AA}$ in a 2θ angle ranging from 10° to 50° , with a step size of 0.01° and a speed of $4^\circ/\text{min}$. The crystalline structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SBA-15}$ nanoparticles was refined with the Rietveld method using the JAVA based software namely Materials Analysis Using Diffraction (MAUD). The oxygen deficiency in the crystalline structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SBA-15}$ was obtained from their oxygen occupancy refinements. The weighted profile R factors (R_{wp}) are estimates of the analysis as a whole are also reported for the refinements of each sample. For the structural refinement, the atomic fractional coordinates and theoretical occupancy number are reported in **Table S1** and **Table S2**.

Table S1. Atomic fractional coordinates in the orthorhombic structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

Space Group: Pcca
SG Number: 54
Cryst Sys: orthorhombic

Atom	#	OX	Site	x	y	z	Occupation
P	1	5	4 d	0.25	0	0.4457	1
W	1	6	8 f	0.3217	0.2467	0.4503	1
W	2	6	8 f	0.0953	0.1126	0.4413	1
W	3	6	8 f	0.3617	0.0729	0.5802	1
W	4	6	8 f	0.1352	-0.0606	0.3122	1
W	5	6	8 f	0.2128	0.1816	0.5794	1
W	6	6	8 f	0.2041	0.1764	0.3123	1
O	1	-2	8 f	0.2749	0.0863	0.4926	1
O	2	-2	8 f	0.1955	0.0392	0.3988	1
O	3	-2	8 f	0.2824	0.1124(7)	0.2879	1
O	4	-2	8 f	0.1784	0.0526	0.6029	1
O	5	-2	8 f	0.3503	-0.1821	0.5061	1
O	6	-2	8 f	0.2478	-0.2422	0.3856	1
O	7	-2	8 f	0.0967	0.0013	0.5058	1
O	8	-2	8 f	0.3646	0.1606	0.3848	1
O	9	-2	8 f	0.2923	0.1442	0.6214	1
O	10	-2	8 f	0.1595	0.0655	0.2699	1
O	11	-2	8 f	0.2598	0.2769	0.5237	1
O	12	-2	8 f	0.127	0.1992	0.3682	1
O	13	-2	8 f	0.3757	0.1955	0.5232	1
O	14	-2	8 f	0.0753	0.0148	0.3686	1
O	15	-2	8 f	0.3536	0.3633	0.4354	1

O	16	-2	8 f	0.0216	0.1686	0.4567	1
O	17	-2	8 f	0.4208	0.0856	0.6408	1
O	18	-2	8 f	0.0859	-0.1119	0.2507	1
O	19	-2	8 f	0.1791	0.258	0.641	1
O	20	-2	8 f	0.1968	0.2729	0.2521	1
O	21	-2	8 f	0.4772	0.1521	0.1213	1
O	22	-2	8 f	0.496	0.3258	0.0936	1
O	23	-2	8 f	0.1603	0.4131	0.4379	1
O	24	-2	4 e	0.25	0.5	0.3434	1
O	25	-2	8 f	0.3358	0.4003	0.253	1
O	26	-2	8 f	0.4539	0.4057	0.3034	1
O	27	-2	8 f	0.0468	0.3681	0.3384	1
O	28	-2	4 c	0	0.1782	0.25	1
O	29	-2	8 f	0.0513	0.3609	0.0809	1
O	30	-2	8 f	0.1681	0.4194	0.1511	1
O	31	-2	4 e	0.25	0.5	0.0579	1
O	32	-2	8 f	0.4218	0.4631(9)	0.0396	1
H	1	1	8 f	0.455	0.1363	0.1626	1
H	2	1	8 f	0.4987	0.1014	0.1106	1
H	3	1	8 f	0.4858	0.2662	0.097	1
H	4	1	8 f	0.5139	0.3428	0.132	1
H	5	1	8 f	0.4656	0.3564	0.0904	1
H	6	1	8 f	0.1712	0.3435	0.4353	1
H	7	1	8 f	0.1176	0.4195	0.4486	1
H	8	1	8 f	0.1682	0.443	0.3965	1
H	9	1	8 f	0.1831	0.4424	0.4707	1
H	10	1	8 f	0.2729	0.4527	0.3136	1
H	11	1	8 f	0.2197	0.4629	0.3737	1
H	12	1	8 f	0.3263	0.3465	0.2257	1
H	13	1	8 f	0.3051	0.4064	0.2886	1
H	14	1	8 f	0.3748	0.3916	0.2726	1
H	15	1	8 f	0.3358	0.4595	0.2255	1
H	16	1	8 f	0.4545	0.4651	0.3167	1
H	17	1	8 f	0.4142	0.3938	0.2857	1
H	18	1	8 f	0.482	0.4005	0.2671	1
H	19	1	8 f	0.0814	0.3704	0.3576	1
H	20	1	8 f	0.0446	0.3126	0.3183	1
H	21	1	8 f	0.0211	0.3681	0.3678	1
H	22	1	8 f	0.0229	0.1366	0.2189	1
H	23	1	8 f	0.0275	0.2187	0.2746	1
H	24	1	8 f	0.0561	0.3051	0.0632	1
H	25	1	8 f	0.0222	0.3567	0.1071	1
H	26	1	8 f	0.0832	0.3725	0.1046	1
H	27	1	8 f	0.179	0.3678	0.1771	1
H	28	1	8 f	0.197	0.4306	0.121	1
H	29	1	8 f	0.1324	0.406	0.1296	1
H	30	1	8 f	0.1634	0.4713	0.1769	1
H	31	1	8 f	0.2626	0.4552	0.0305	1
H	32	1	8 f	0.2292	0.4522	0.0699	1
H	33	1	8 f	0.4386	0.5069	0.0305	1

H	34	1	8 f	0.4486	0.4136	0.0468	1
H	35	1	8 f	0.3965	0.4473	0.0065	1
H	36	1	8 f	0.4016	0.4734	0.0748	1

Table S2. Atomic fractional coordinates in the cubic structure of H₃PW₁₂O₄₀.

Space Group P n -3 m Z							
SG Number 224							
Cryst Sys cubic							
Atom	#	OX	SITE	x	y	z	Occupation
P	1	5	2a	0.75	0.75	0.75	1
W	1	6	24 k	0.7579	0.9636	0.9636	1
O	1	-2	8 e	0.8226	0.8226	0.8226	1
O	2	-2	24 k	0.6463	0.8537	0.0133	1
O	3	-2	24 k	0.8687	0.8687	0.0462	1
O	4	-2	24 k	0.7412	0.0629	0.0629	1
O	5	-2	6 d	0.75	0.25	0.25	1

2. Surface Acidity Measurements and Extinction Coefficient

In situ Fourier-transform infrared (FTIR) spectra of pyridine adsorption on the catalysts were recorded on a 170-SX FTIR spectrometer. Before pyridine adsorption, sample wafer was heated at 300 °C for 60 min under vacuum to eliminate the adsorbed water or impurities on the surface. Then solid wafer was exposed to pyridine, by breaking inside the spectrometer cell, a capillary containing 50 µl of liquid pyridine. After 15 min of adsorption, the excess of pyridine in IR cell was eliminated under vacuum (10⁻⁵ torr) at same temperature. The IR spectra were recorded at 50, 100, 200, 300 and 400 °C, respectively.

We used the band at 1445 cm⁻¹ for L acid sites calculation. The area of this band was calculated using computer software. The number of acid sites or concentration was calculated by considering mass of the sample, surface area and thickness of the solid wafer, amount of pyridine adsorbed on the sample wafer. The quantitative calculation of the number of Lewis acid sites and Brønsted acid sites was made with respect to the integrated area of the IR band at 1450 cm⁻¹ and 1540 cm⁻¹, respectively. The extinction coefficients E_B = 1.0086 mmol/cm² for Brønsted acid sites and E_L = 0.9374 mmol/cm² for Lewis acid sites were used for the data calculation. Before the measurement, we need to measure the extinction coefficient of the sample. The extinction coefficient is a measure of how strongly a chemical species attenuates light at given wavelength. The integrated molar extinction coefficient (IMEC) of IR band characteristic of pyridine adsorbed on Brønsted and Lewis acid sites is defined by the Equations (S1) and (S2).

$$IMEC = \int \varepsilon d\sigma \quad (S1)$$

$$A = \varepsilon c D \quad (S2)$$

Where

σ = wavenumber (cm⁻¹)

A = absorbance, $\log_{10} \left(\frac{I_0}{I} \right)$

ε = molar extinction coefficient $\left(\frac{dm^3}{mol \text{ cm}} \right)$;

c = concentration $\left(\frac{mol}{dm^3} \right)$;

D = path length (cm) (herein it is the thickness of the sample wafer)

$$C_{(B)} = \frac{\pi r^2}{IMEC_B} \frac{A_{IB}}{w}; C_{(L)} = \frac{\pi r^2}{IMEC_L} \frac{A_{IL}}{w}$$

$$E_{(B)} = \frac{\pi r^2}{IMEC_B}; E_{(L)} = \frac{\pi r^2}{IMEC_L}$$

$$C_{(B)} = E_B \frac{A_{IB}}{w}; C_{(L)} = E_B \frac{A_{IL}}{w}$$

$C_{(B)}$ = Concentration of pyridine adsorbed on B acid sites (mmol/g)

$C_{(L)}$ = Concentration of pyridine adsorbed on L acid sites (mmol/g)

r = radius of sample disk (cm)

w = weight of sample wafer (g)

A_{IB} = Integrated absorbances of the band approximately at 1540 cm^{-1} (cm^{-1})

A_{IL} = Integrated absorbances of the band approximately at 1450 cm^{-1} (cm^{-1})

$$E_{(B)} = \frac{\pi r^2}{IMEC_B}; E_{(L)} = \frac{\pi r^2}{IMEC_L}$$

$IMEC_B$: Integrated molar extinction coefficient of pyridine on B acid sites.

$IMEC_L$: Integrated molar extinction coefficient of pyridine on L acid sites.