

**Supporting information**

**Polyoxometalate catalysts with co-substitution of VO<sup>2+</sup> and transition  
metals and their catalytic performance in isobutane oxidation**

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## Supplementary Figures and Tables

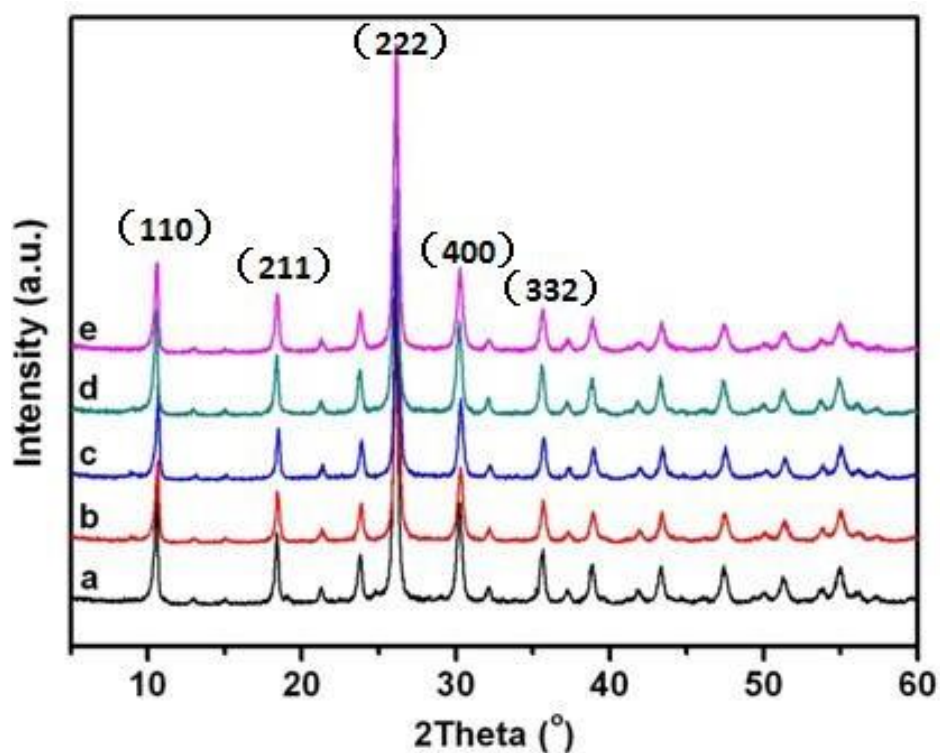
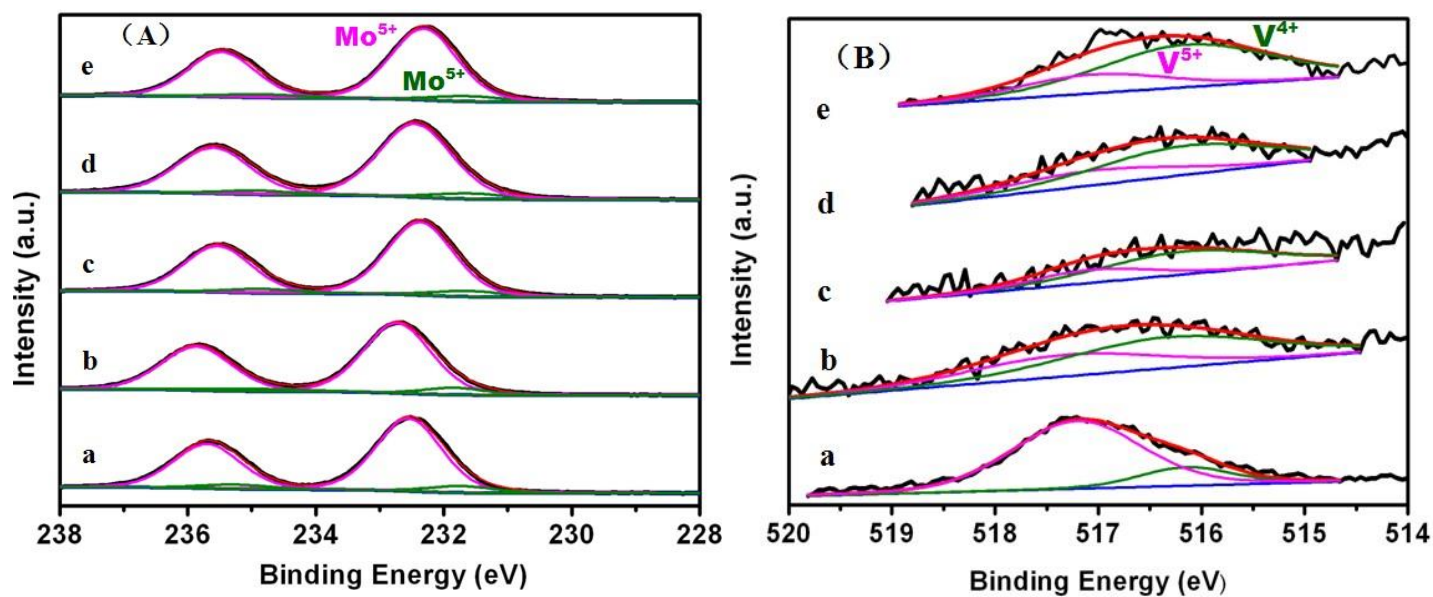


Figure.S1 XRD patterns of V-containing Cs-salt of HPCs with the incorporation of different transition metals. a:  $\text{Cs}_{2.0}\text{V}_{0.3}\text{Cu}_{0.2}\text{PMo}_{12}\text{O}_{40}$ ; b:  $\text{Cs}_{2.0}\text{V}_{0.2}\text{Fe}_{0.2}\text{PMo}_{12}\text{O}_{40}$ ; c:  $\text{Cs}_{2.0}\text{V}_{0.2}\text{Ce}_{0.2}\text{PMo}_{12}\text{O}_{40}$ ; d:  $\text{Cs}_{2.0}\text{V}_{0.3}\text{Ni}_{0.2}\text{PMo}_{12}\text{O}_{40}$ ; e:  $\text{Cs}_{2.0}\text{Cu}_{0.2}\text{PMo}_{11}\text{VO}_{40}$



**Figure S2 XPS spectra of Mo 3d (A) and V 2p (B) for V-containing Cs-salt of HPCs with the incorporation of different transition metals. a:  $\text{Cs}_{2.0}\text{Cu}_{0.2}\text{PMo}_{11}\text{VO}_{40}$ ; b:  $\text{Cs}_{2.0}\text{V}_{0.3}\text{Cu}_{0.2}\text{PMo}_{12}\text{O}_{40}$ ; c:  $\text{Cs}_{2.0}\text{V}_{0.2}\text{Fe}_{0.2}\text{PMo}_{12}\text{O}_{40}$ ; d:  $\text{Cs}_{2.0}\text{V}_{0.2}\text{Ce}_{0.2}\text{PMo}_{12}\text{O}_{40}$ ; e:  $\text{Cs}_{2.0}\text{V}_{0.3}\text{Ni}_{0.2}\text{PMo}_{12}\text{O}_{40}$**

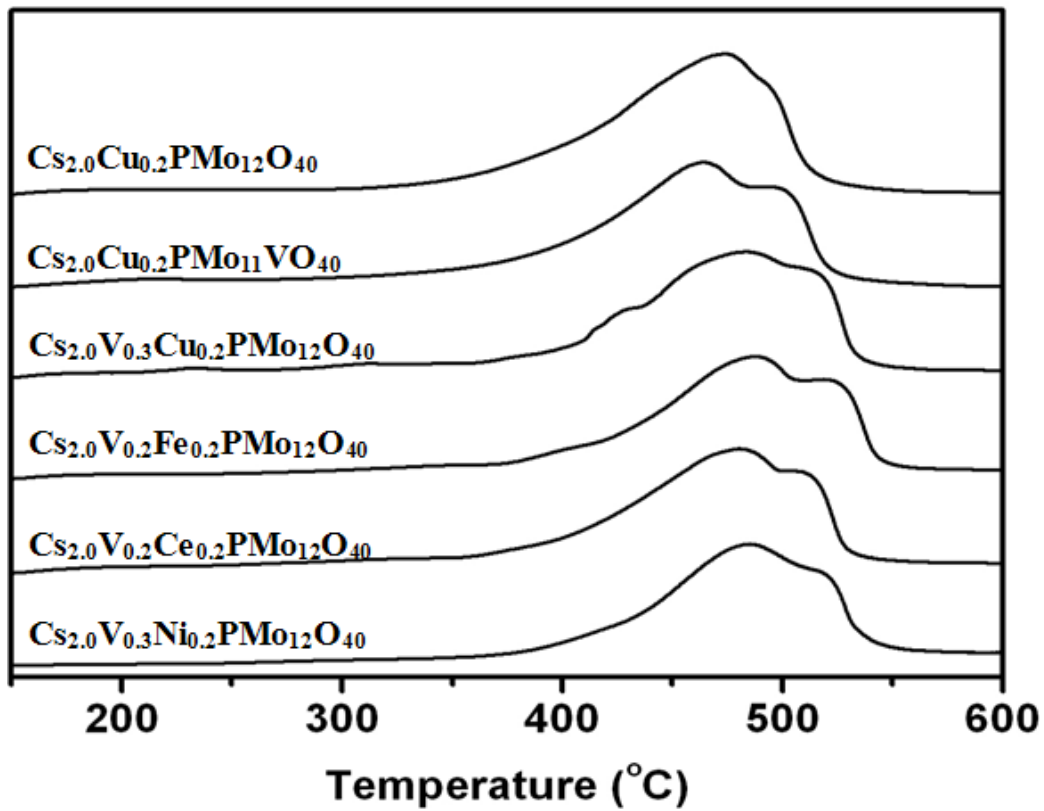


Figure.S3 NH<sub>3</sub>-TPD patterns of Cs salt of V-containing HPC with the incorporation of different transition metals.

**Table S1 Chemical analysis of the catalysts after calcination at 300°C**

Catalysts	Atomic ratio			
	Cs/P	M/P (M=Cu, Fe, Ni, or Ce)	V/P	Mo/P
Cs <sub>2.0</sub> V <sub>0.3</sub> Cu <sub>0.2</sub> PMo <sub>12</sub> O <sub>40</sub>	2.02	0.21	0.30	11.6
Cs <sub>2.0</sub> Cu <sub>0.2</sub> PMo <sub>11</sub> VO <sub>4</sub>	2.00	0.24	1.10	11.0
Cs <sub>2.0</sub> V <sub>0.3</sub> Ni <sub>0.2</sub> PMo <sub>12</sub> O <sub>4</sub>	1.94	0.22	0.29	11.6
Cs <sub>2.0</sub> V <sub>0.2</sub> Fe <sub>0.2</sub> PMo <sub>12</sub> O <sub>4</sub>	1.99	0.24	0.22	12.1
Cs <sub>2.0</sub> V <sub>0.2</sub> Ce <sub>0.2</sub> PMo <sub>12</sub> O <sub>4</sub>	1.90	0.23	0.24	12.8

**Table S2 Adsorption amount of NH<sub>3</sub> on the surface of Cs salt of V-containing HPC with the incorporation of different transition metals.**

Catalysts	Adsorption amount of NH <sub>3</sub> (mmol/g)			Total acidity (mmol/g)
	150~350 °C	350~450 °C	450~600 °C	
Cs <sub>2.0</sub> Cu <sub>0.2</sub> PMo <sub>12</sub> O <sub>40</sub>	0.1094	0.5714	0.7437	1.4245
Cs <sub>2.0</sub> V <sub>0.3</sub> PMo <sub>12</sub> O <sub>40</sub> *	0.0294	0.5732	0.5610	1.1636
Cs <sub>2.0</sub> V <sub>0.3</sub> Cu <sub>0.2</sub> PMo <sub>12</sub> O <sub>40</sub>	0.1191	0.6248	0.9018	1.6457
Cs <sub>2.0</sub> Cu <sub>0.2</sub> PMo <sub>11</sub> VO <sub>4</sub>	0.1676	0.5255	0.7240	1.4171
Cs <sub>2.0</sub> V <sub>0.3</sub> Ni <sub>0.2</sub> PMo <sub>12</sub> O <sub>4</sub>	0.0565	0.3888	0.9349	1.3802
Cs <sub>2.0</sub> V <sub>0.2</sub> Fe <sub>0.2</sub> PMo <sub>12</sub> O <sub>4</sub>	0.1133	0.3417	0.9512	1.4052
Cs <sub>2.0</sub> V <sub>0.2</sub> Ce <sub>0.2</sub> PMo <sub>12</sub> O <sub>4</sub>	0.1548	0.4059	0.8314	1.3921

\* : From our previous study in Appl. Catal. A. Gen., 2018, 556:104-112