**Table SI1**. Catalytic activities of **AsWRuZn-2** with different amounts for the oxidation of n-hexadecane under green conditions.[a]

| Catalyst | Catalyst amount $mg^{-1}$ | Conv [%] | TOF [h-1] | Product selectivity [%] and distribution | |
|---|---|---|---|---|---|
| | | | | Ketones (7-One:6-One:5-One:4-One:3-One:2-One) | Alcohols (7-Ol:6-Ol:5-Ol:4-Ol:3-Ol:2-Ol) |
| AsWRuZn-2 | 2.5 | 38.38 | 2796 | 51.4 （13.5:6.4:8:6.8:7.3:9.4） | 22.3 （7.6:3:4.8:2.9:3.2:0.8） |
| | 5 | 46.98 | 1711 | 52.7 （13.6:6.8:8.7:7:7.6:9） | 20.7 （6.9:2.2:5.3:2.4:2.9:1） |
| | 10 | 51.49 | 938 | 55.4 （13.8:7.5:9.4:7.3:8.1:9.3） | 19.1 (5.6:2.4:4.9:2:3:1.2) |
| | 15 | 44.87 | 545 | 53.9 （13.3:7.5:8.8:7.4:7.9:9） | 20.6 （6.5:2:5.1:3:2.9:1.1） |

[a]Reaction conditions: n-hexadecane: 5 mL, airflow rate: 30 mL·$min^{-1}$, temperature: 150ºC, reaction time: 6 h.

**Table SI2.** Catalytic activities of **AsWRuZn-2** with different reaction time for the oxidation of n-hexadecane under green conditions.[a]

| Catalyst | Reaction time [h] | Conv [%] | TOF [$h^{-1}$] | Product selectivity [%] and distribution | |
|---|---|---|---|---|---|
| | | | | Ketones (7-One:6-One:5-One:4-One:3-One:2-One) | Alcohols (7-Ol:6-Ol:5-Ol:4-Ol:3-Ol:2-Ol) |
| AsWRuZn-2 | 0.5 | 2.23 | 487 | 55.6 (12.7:6.7:6.9:7.4:13.3:8.6) | 38.2 (15.5:4.4:6:4.2:6.9:1.2) |
| | 1.5 | 8.99 | 655 | 48.9 (12.6:6.5:7:6.2:8.4:8.2) | 32.1 (12.5:3.9:5.7:4.5:4.9:0.6) |
| | 3 | 24.78 | 903 | 51.5 （13:7:8.1:6.7:7.8:8.9） | 23.6 （8.2:3.1:4.9:2.9:3.6:0.9） |
| | 4 | 35.47 | 969 | 50.3 （13.7:6.2:8.1:6.5:7.5:8.3） | 20.4 （6.7:2.3:4.4:2.6:3.4:1） |
| | 5 | 47.29 | 1064 | 54.1 （13.4:7.4:8.3:7.8:8.7:8.5） | 16.6 （5.3:1.8:4.1:1.8:2.5:1.1） |
| | 6 | 51.49 | 938 | 55.4 （13.8:7.5:9.4:7.3:8.1:9.3） | 19.1 (5.6:2.4:4.9:2:3:1.2) |
| | 7 | 55.84 | 871 | 50.4 (12.1:7.3:8.9:6.7:7:8.4) | 16.8 (4.5:2.2:4.8:1.7:2.5:1.1) |
| | 8 | 59.35 | 810 | 58.6 (14.3:8.5:9.6:7.7:8.3:10.2) | 17.3 (5.2:2.1:4.6:1.8:2.5:1.1) |
| | 12 | 73.93 | 673 | 53.7 (13.5:7.1:9.6:7.1:7.8:8.6) | 17.1 (4.9:.2:4.8:1.7:2.2:1.3) |

[a]Reaction conditions: n-hexadecane: 5 mL, airflow rate: 30 mL·$min^{-1}$, temperature: 150ºC, catalyst: 10mg.

**Table SI3.** Reported catalytic activity of polyoxometalates as catalysts for n-hexadecane oxidation with air.[a]

| Catalyst | Conv [%][c] | TOF [$h^{-1}$][d] | Product selectivity [%] | |
|---|---|---|---|---|
| | | | Ketones | Alcohols |
| **Blank**[1,2] | **3.9** | **-** | **55** | **24** |
| **Cu20**[1] | **7.3** | **279** | **35** | **37** |
| **KNa-1**[2] | **38.3** | **636** | **52** | **22** |
| **CsNa-2**[2] | **33.7** | **570** | **50** | **29** |
| **CsNa-3**[2] | **34.0** | **605** | **51** | **25** |
| **Na-4**[2] | **31.8** | **570** | **50** | **23** |
| **$Fe_4Se_2W_{18}$**[3] | **3.0** | **17** | **51.2** | |

[a] Identical reaction conditions: n-hexadecane: 5 mL, airflow rate: 30 $mL \cdot min^{-1}$, temperature: 150ºC, catalyst amount: 10mg, reaction time: 6h

**References:**

[1] Chen, L. F.; Hu, J. C.; Mal, S. S.; Kortz, U.; Jaensch, H.; Mathys, G.; Richards, R. M. *Chem. Eur. J.* **2009**, *15*, 7490.

[2] Bi, L. H.; Al-Kadamany, G.; Chubarova, E. V.; Dickman, M. H. L.; Chen, F.; Gopala, D. S.; Richards, R.; Keita, M. B.; Nadjo, L.; Jaensch, H.; Mathys, G.; Kortz, U. *Inorg. Chem.* **2009**, *48*, 10068.

[3] Chen, L. F.; Zhu, K. K.; Bi, L. H.; Suchopar, A.; Reicke, M.; Mathys, G.; Jaensch, H.; Kortz, U.; Richards, R. M. *Inorg. Chem.* **2007**, *46*, 8457.

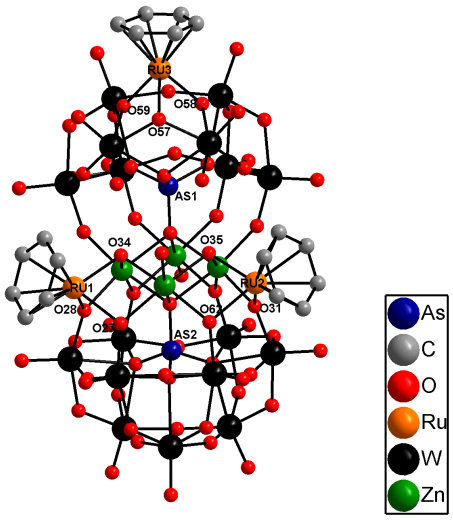


**Figure SI1**. The atom-labeling scheme of the ball-and-stick representation of polyanion $[\{B\text{-}\alpha\text{-}AsW_9O_{34}\}\{B\text{-}\beta\text{-}AsW_8O_{31}\}\{Zn_4(OH)_2(H_2O)_2\}\{(RuC_6H_6)_3\}]^{6-}$ (AsWRuZn-**2**).

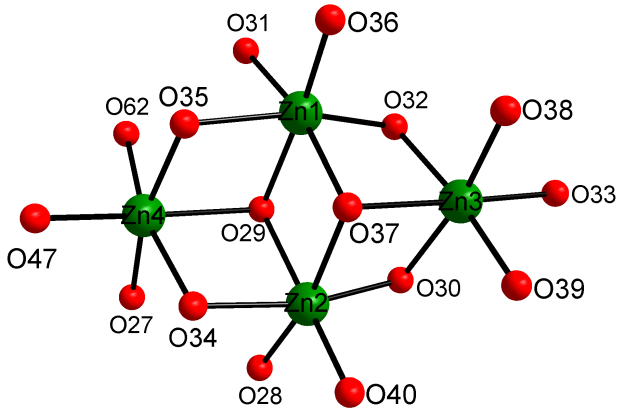


**Figure SI2.** The atom-labeling scheme of the central tetrameric unit $Zn_4O_{16}$ in **AsWRuZn-2**. The balls represent zinc (olive) and oxygen (red).

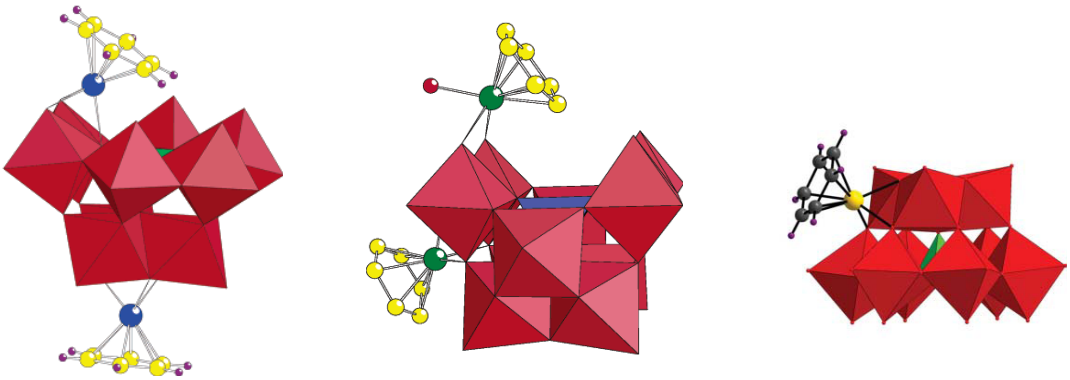

**Figure SI3.** Polyhedral/ball and stick representations of the polyanions (left) $[(RuC_6H_6)_2XW_9O_{34}]^{6-}$ (X = Si, Ge) (**13**), (middle) $[\{Ru(C_6H_6)(H_2O)\}\{Ru(C_6H_6)\}(\gamma\text{-}XW_{10}O_{36})]^{4-}$ (X = Si, Ge) (**14**) and $[(RuC_6H_6)XW_9O_{34}]^{7-}$ (X = P, As) (**15**) (right).

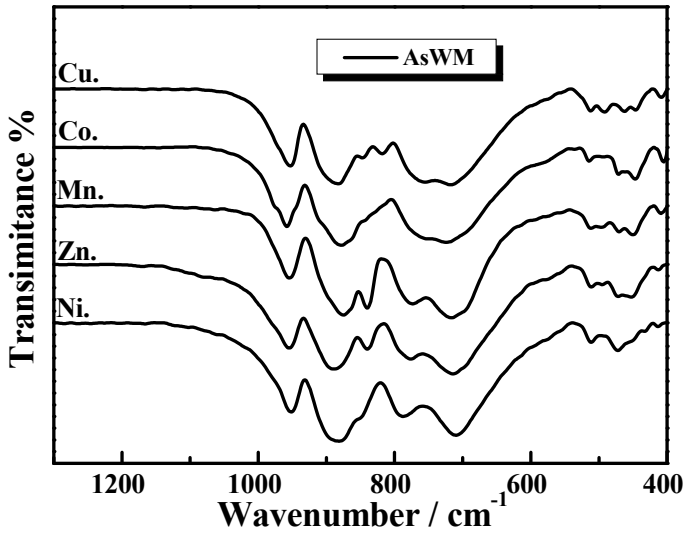


**Figure SI4.** IR spectra of **AsWM-6-10**.

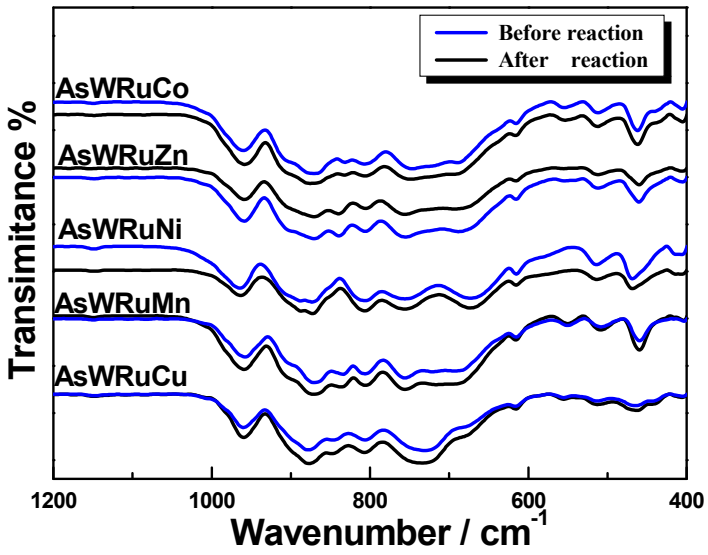


**Figure SI5.** IR spectra of **AsWRuM-1-5** before (blue) and after (black) catalytic reactions.

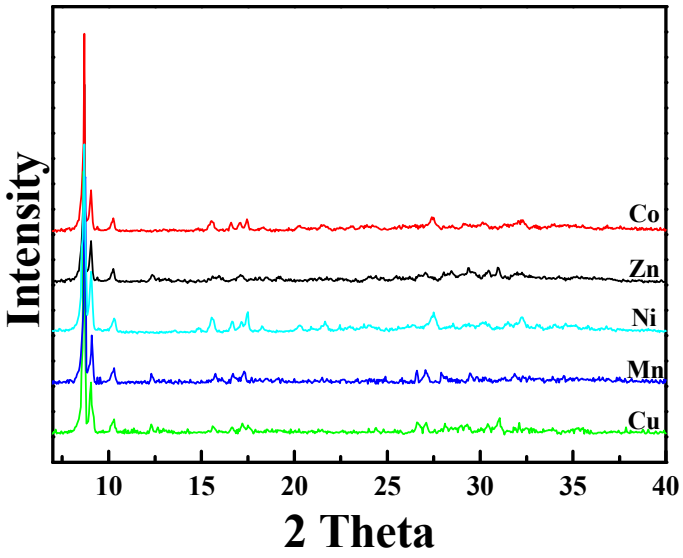


**Figure SI6.** The powder XRD diffraction patterns of compounds **AsWRuM-1-5** after the following treatment process.

The treatment procedure of the samples for powder XRD measurements is described below:

1) The crystals of five compounds were picked out under microscopy to ensure their purities;

2) These crystals were dried in vacuum dryer for one week to obtain powder samples;

3) The powder samples were further crushed to fine powders for XRD measurements.