

Rhenium oxide modified $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ catalysts for selective oxidation of dimethyl ether to dimethoxy dimethyl ether

Qingde Zhang,^a Yisheng Tan,^{a*} Guangbo Liu,^{a b} Junfeng Zhang,^a Yizhuo Han^{a*}

Catalyst characterization

XRD

XRD patterns were measured on a Bruker Advanced X-Ray Solutions/D8-Advance using Cu K α radiation. The anode was operated at 40kV and 40mA. The 2Theta angles were scanned from 5° to 70°.

FT-IR spectra

FT-IR spectra were measured on a Bruker Tensor 27 instrument with MCT detector.

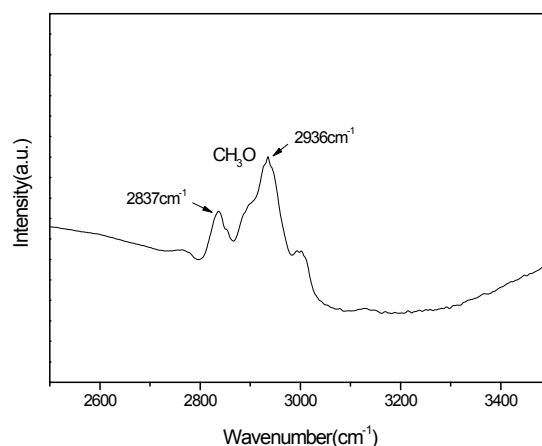


Fig. SI-1. DMM desorption over 5%Re-20%PW₁₂/TiO₂ at 513K

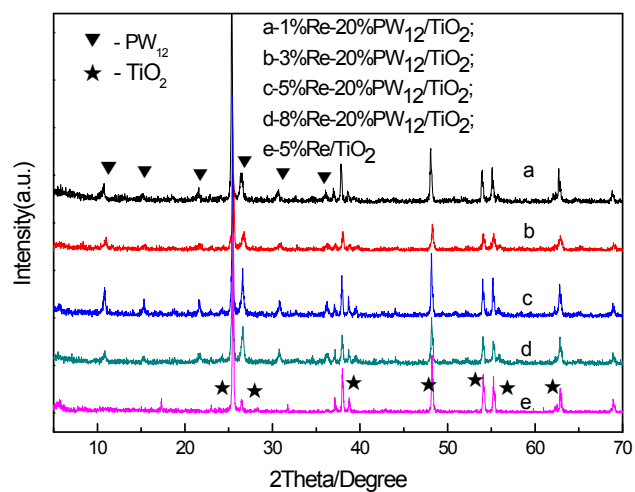


Fig. SI-2. XRD patterns of the catalysts.

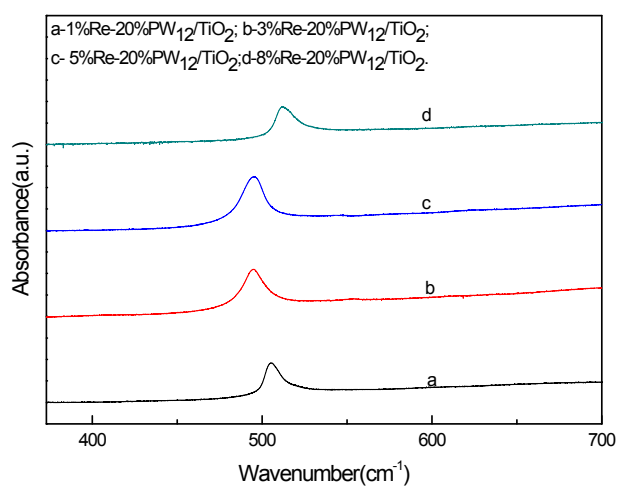


Fig. SI-3. H_2 -TPR profiles of Re- $\text{PW}_{12}/\text{TiO}_2$ with different Re loading

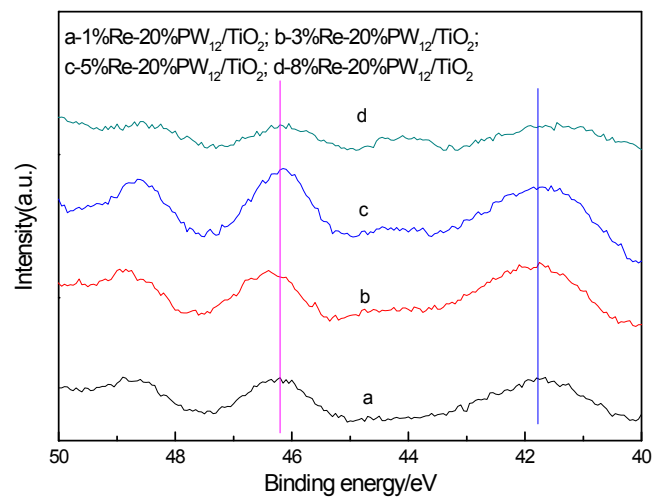


Fig. SI-4. Re 4f XPS spectra for the Re-PW₁₂/TiO₂ catalysts

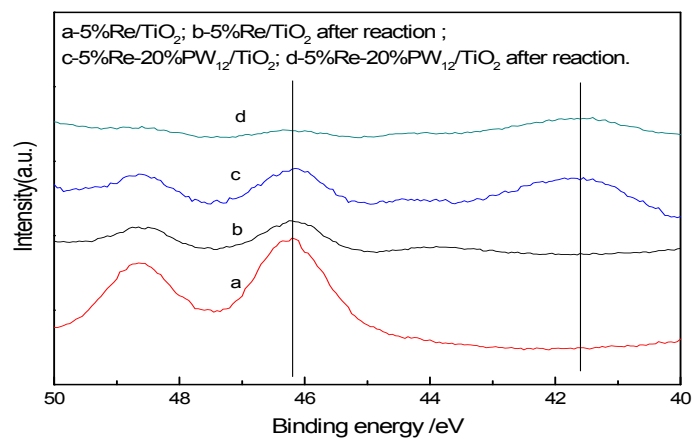


Fig. SI-5. XPS of the catalysts.

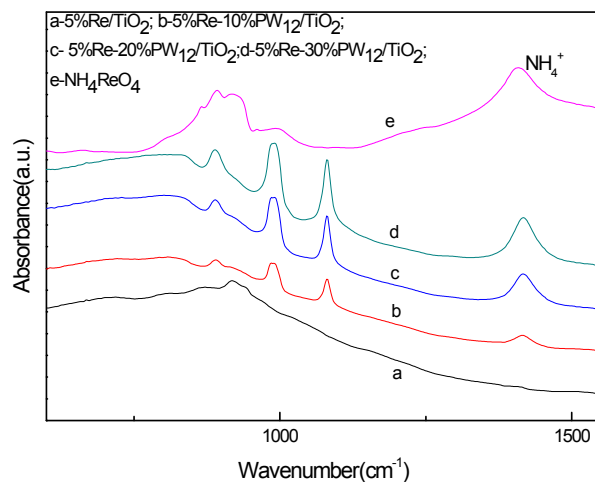


Fig. SI-6. FT-IR spectra of Re-PW₁₂/TiO₂ catalyst

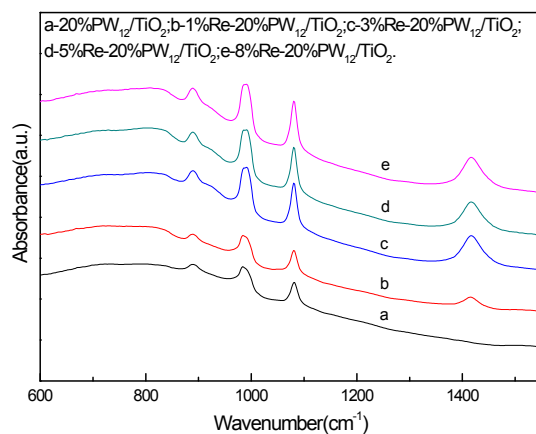


Fig. SI-7. FT-IR spectra of Re-PW₁₂/TiO₂ catalyst

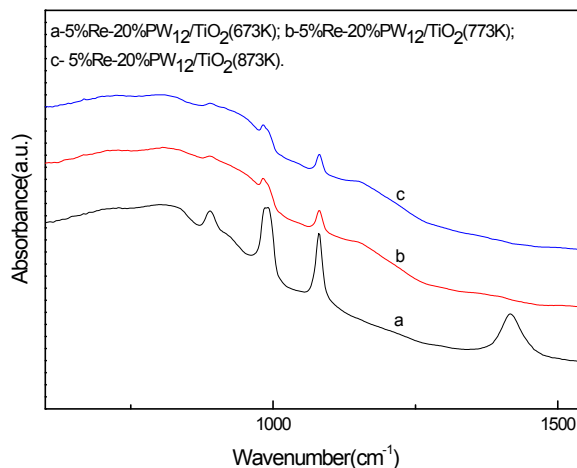


Fig. SI-8. FT-IR spectra of Re-PW₁₂/TiO₂ calcined at different temperatures

Table SI-1 Effects of different feedstocks on the formation of DMM₂ over 5%Re-20%PW₁₂/TiO₂

Reactant	DME conversion(%)	DMM conversion(%)	Selectivity(C-mol%)								
			DMM	DME	DMM ₂	CH ₃ OH	HCHO	MF	CO	CH ₄	CO ₂
DME+Ar ^a	2.3	-	0.5	-	0	22.5	68.1	0.1	0.8	3.4	4.6
DMM+Ar ^b	-	31.2	-	56.8	4.0	5.3	3.3	30.6	0	0	0
DME+DMM+Ar ^c	7.9	33.6	-	-	4.4	19.4	43.2	27.4	1.4	1.2	3.0

Reaction conditions: atmospheric pressure, 513K, cat.: 1 ml, 3600h⁻¹. ^a nAr:nDME = 1.3:1.2, ^b nAr:nDMM=1.3:1, ^c nAr:nDME:nDMM=1.3:1.2:1.

Table SI-2 Results of H₂-TPR integration

Catalyst	Reduction peak
	Area
5%Re-10%PW ₁₂ /TiO ₂	231180
5%Re-20%PW ₁₂ /TiO ₂	473705
5%Re-30%PW ₁₂ /TiO ₂	320506

Table SI-3 Results of Re⁴⁺ and Re⁷⁺ for 5%Re-20%PW₁₂/TiO₂

Catalyst	Re ⁴⁺	Re ⁷⁺	Ratio
	Area (%)	Area (%)	S _{Re4+} /S _{Re7+}
The fresh	59.4	40.6	1.5
The used	64.4	35.6	1.8