

Bimetallic Mesoporous MCM-41 Nanoparticles with Ta/(Ti, V, Co, Nb) with Catalytic and Photocatalytic Properties

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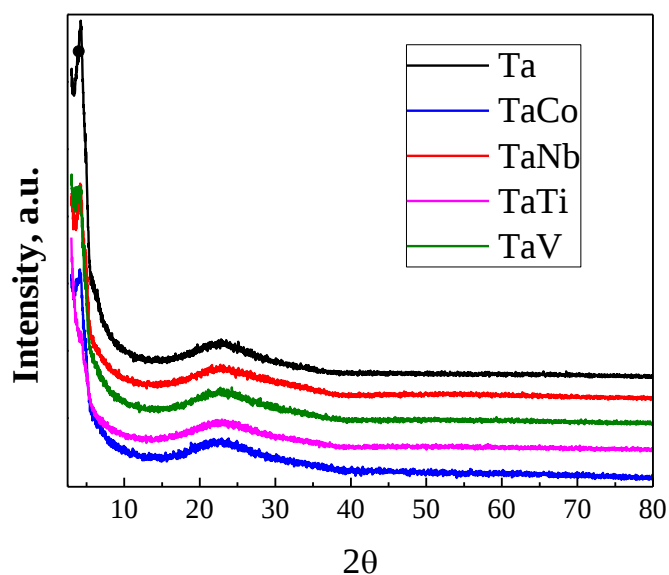


Figure S1. The high angles XRD diffractograms of TaMe/MCM-41 samples.

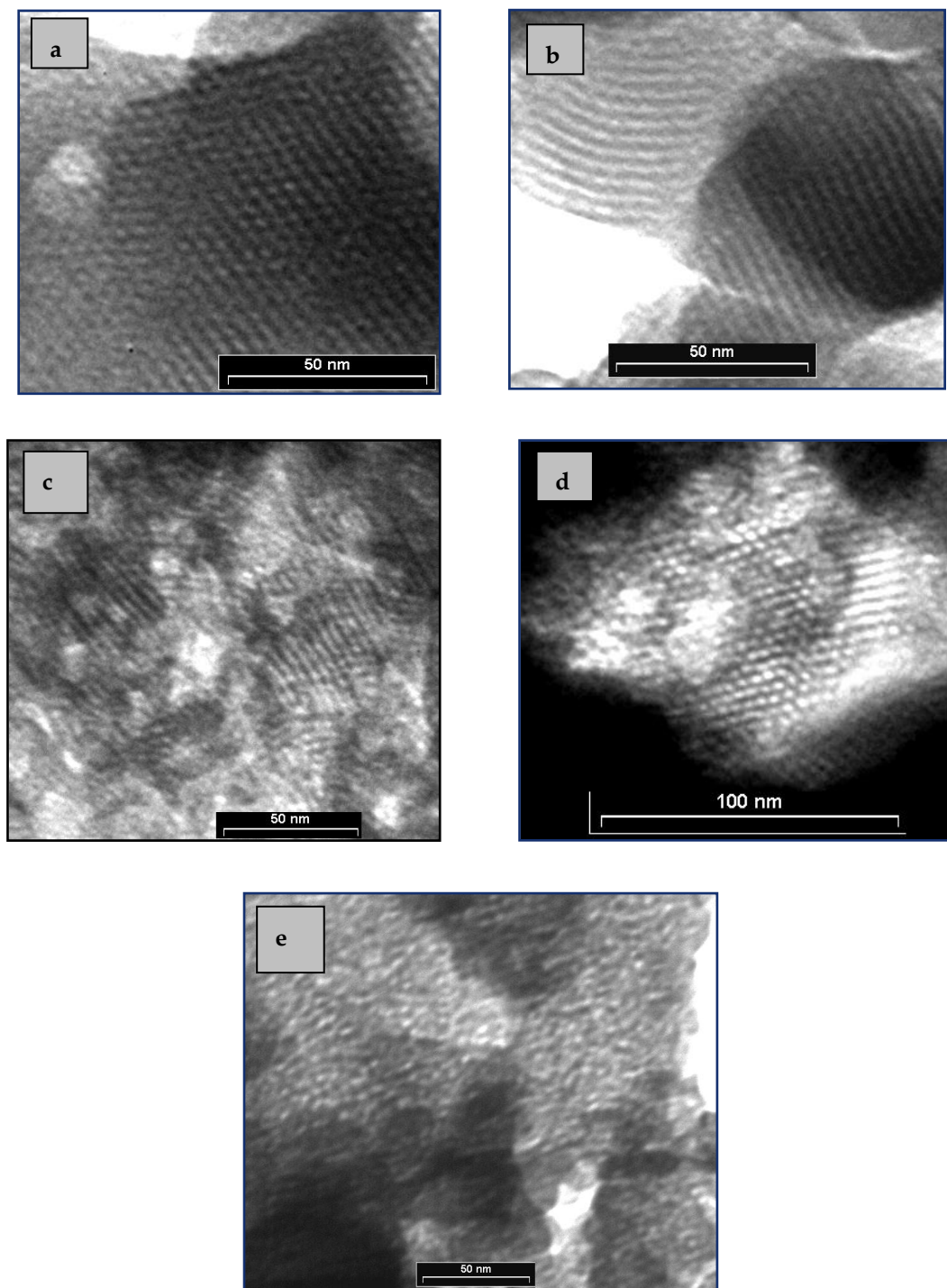


Figure S2. TEM images of Ta-MCM-41 (a); TaV-MCM-41 (b); TaTi-MCM-41 (c); TaNb-MCM-41 (d) and TaCo-MCM-41 (e) samples.

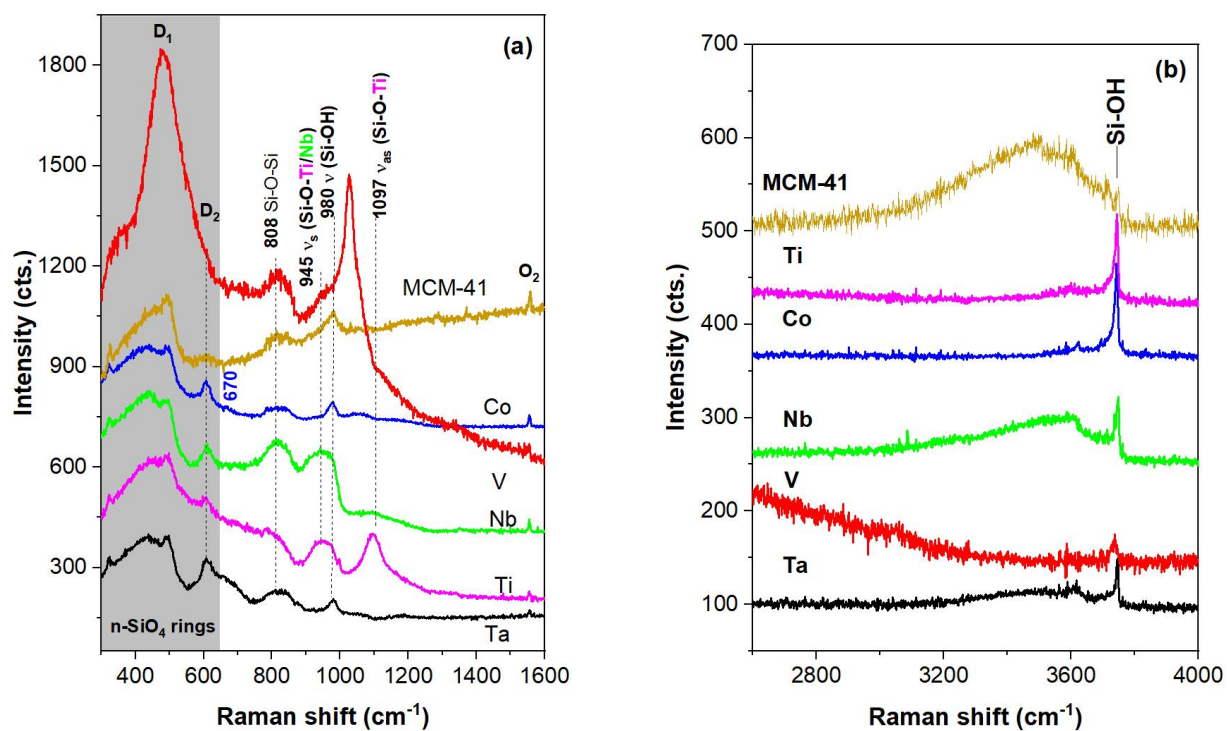


Figure S3. Raman spectra of the monometallic (Ta, V, Ti, Nb, Co)-MCM-41 and MCM-41 samples

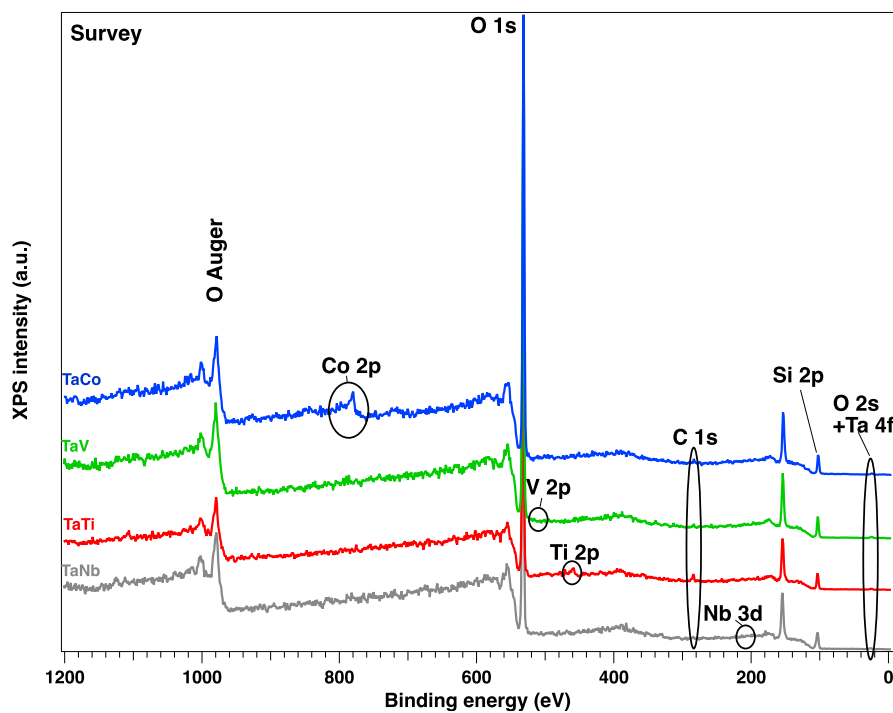


Figure S4. XPS full scan survey spectra for the bimetallic Ta/Me samples.

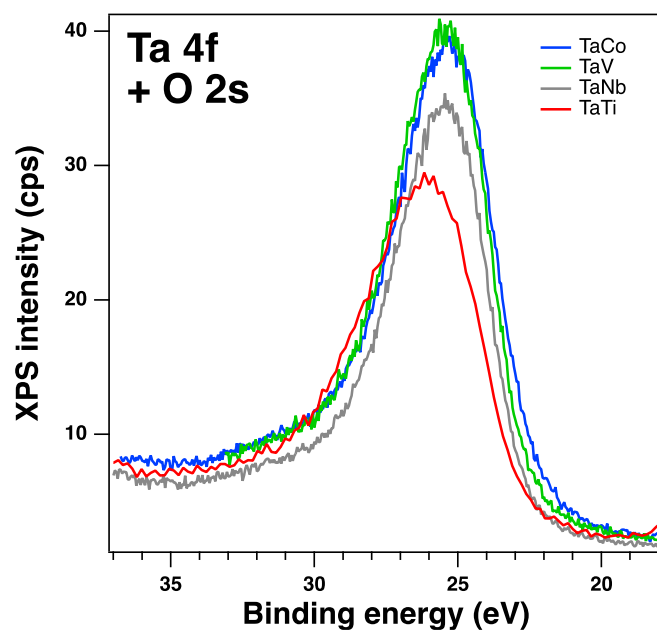


Figure S5. XPS spectra of Ta 4f for the bimetallic samples.

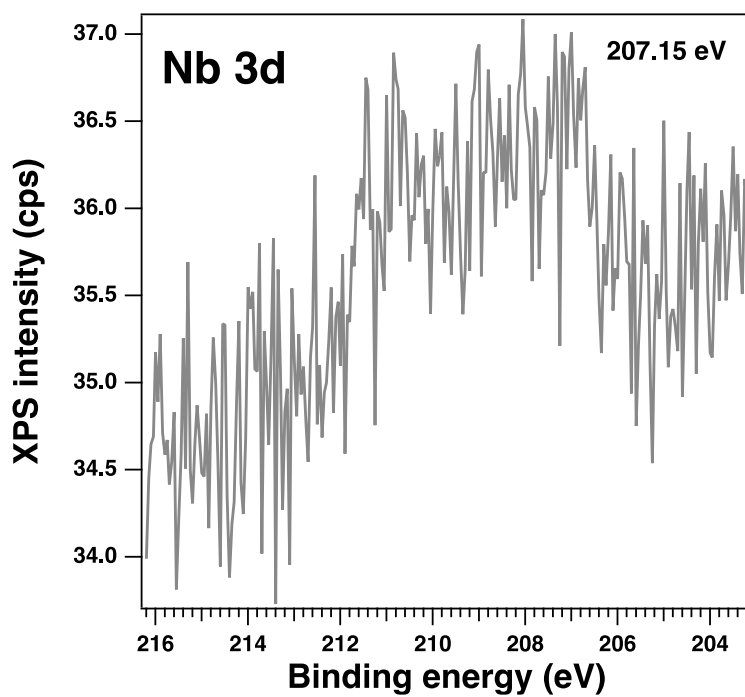


Figure S6. XPS spectra of Nb 3d for the sample TaNb-MCM-41 sample.

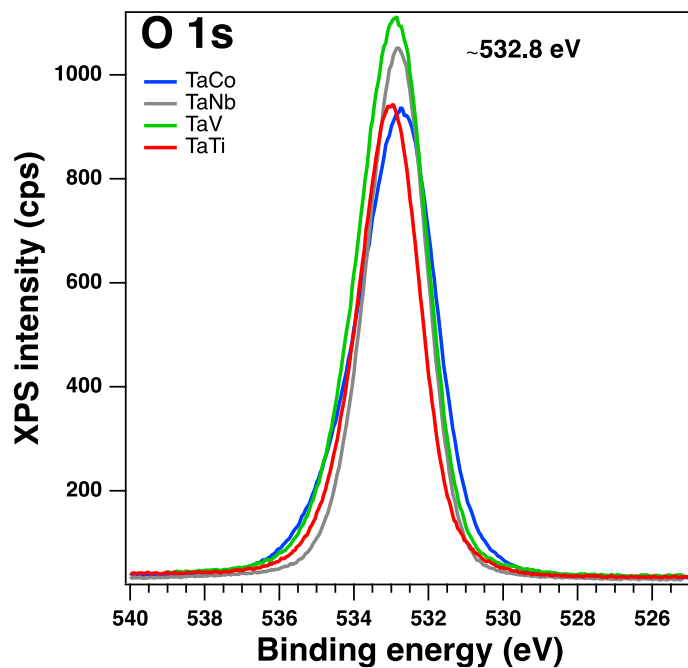


Figure S7. XPS O1s high resolution spectra for the bimetallic Ta/Me-MCM-41 samples.

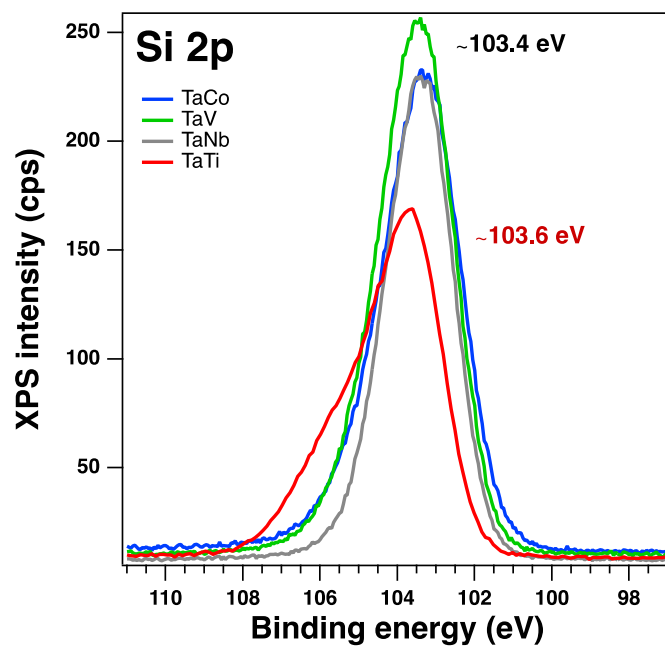


Figure S8. XPS Si2p high resolution spectra for the bimetallic Ta/Me-MCM-41 samples.

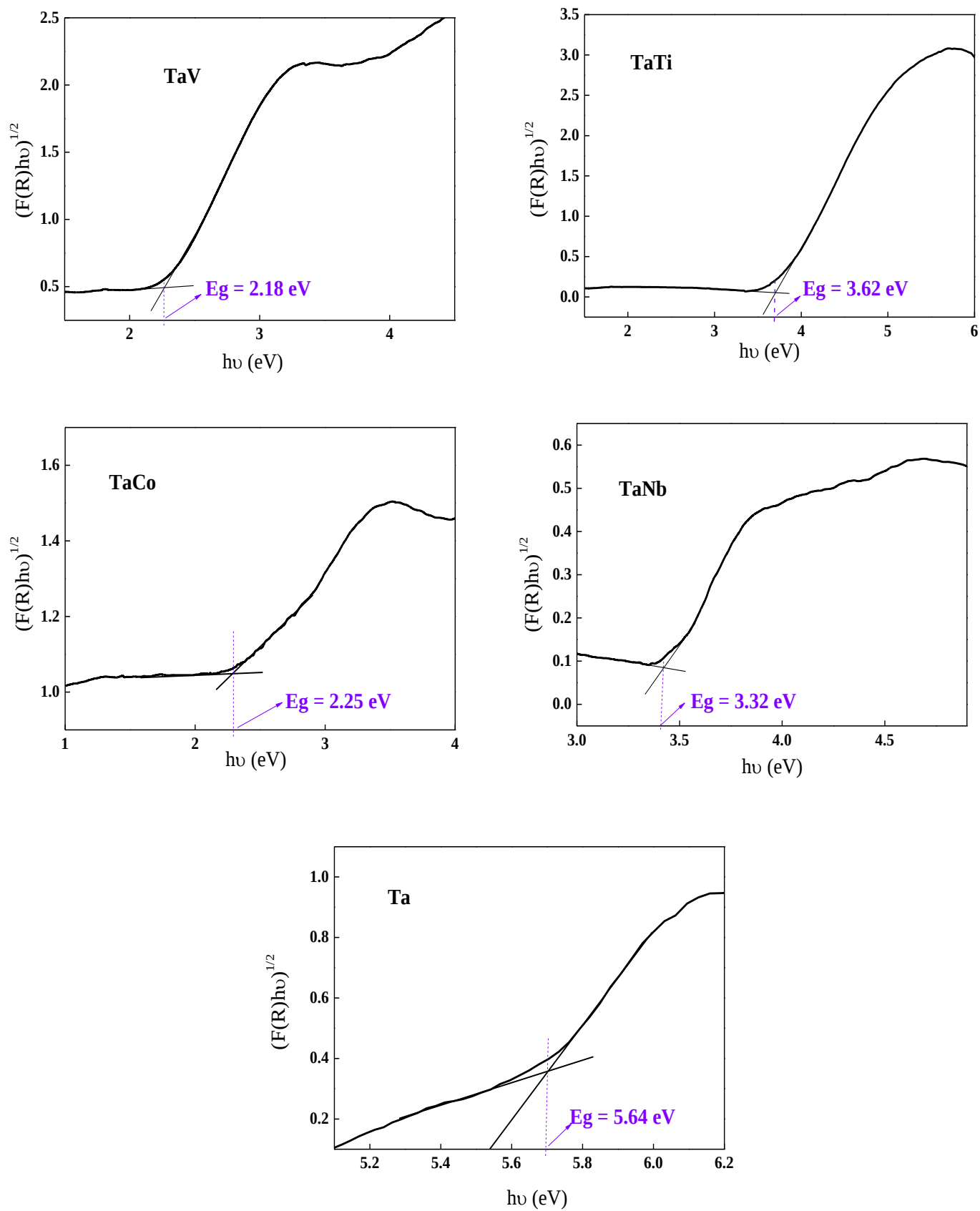


Figure S9. Estimation of the band gap energy by the simplified analysis of the Tauc plot.

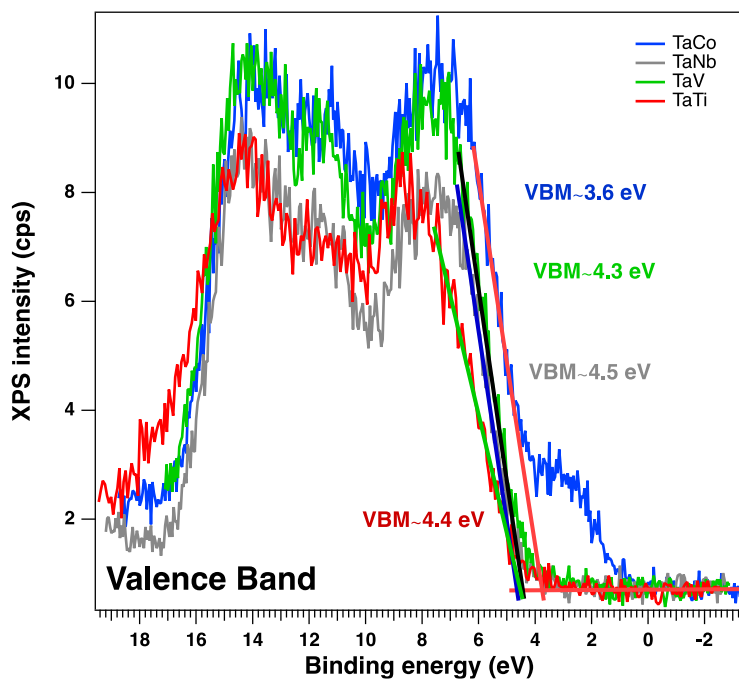


Figure S10. XPS valence band spectra of the bimetallic Ta/Me-MCM-41 samples. Linear fits and the valence band maximum energy are shown on each spectrum.

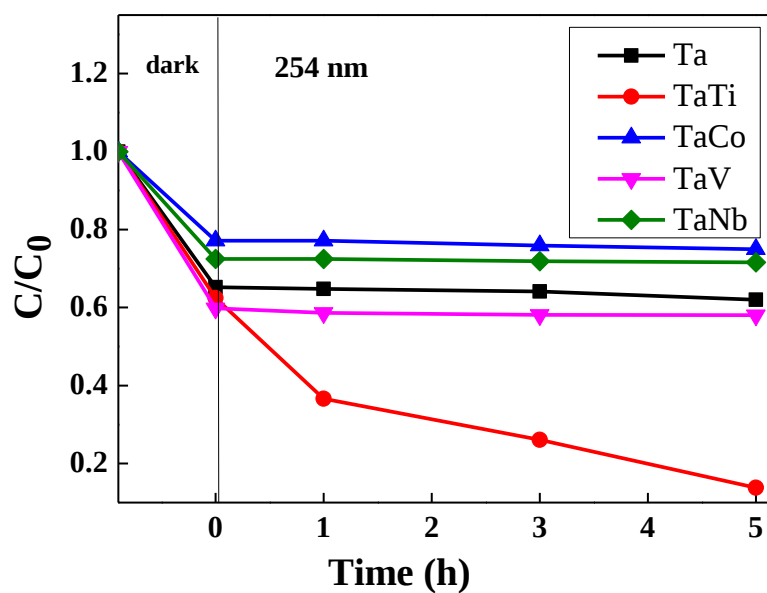


Figure S11. Photodegradation of methyl orange in aqueous solution.

Table S1. 2 θ (100) position, interplanar spacing (d) and lattice parameter (a_0) of the samples

Sample code	2 $\theta_{(100)}$ (deg)	d ₍₁₀₀₎ (nm)	a ₀ (nm)
Ta	2.31	3.82	4.42
TaCo	2.30	3.83	4.43
TaTi	2.40	3.67	4.24
TaV	2.33	3.77	4.36
TaNb	2.34	3.76	4.35

Table S2. Peak position and assignments for the monometallic (Ta/Nb/Ti/Co/V)-MCM41 catalysts.

Peak position (cm ⁻¹)					Assignments	Reference
Ta	Nb	Ti	Co	V		
					<650 cm ⁻¹ n-SiO ₄ rings	42,43
				356	δ (O-V-O) in polymeric VO _x	44, 45
360	368				5,6,7-SiO ₄ rings	42
441	443	440	436		5,6,7-SiO ₄ rings	42
497	490	495	497	481	D ₁ modes (4- SiO ₄ rings)	42
				552	Silicalite framework breathing modes	44
608	610	607	608		D ₂ modes (3- SiO ₄ rings)	42
660					TaO ₆	46
			664		CoO ₆ in Co ₃ O ₄	47
	822	800	798	821	ν_s (Si-O-Si) and surface polymerized niobia	42, 46
828			838		ν_s of the [SiO ₄] units	42
	935				surface polymerized niobia species (820-935 cm ⁻¹)	46
958		954		958	ν_s (Si-O-Si/Ti/V)	48,49
980	975		976		ν (Si-OH) and TaO _x species (965-980 cm ⁻¹)	42,46,50
				1028	Pyramidal structure of (SiO) ₃ V=O when vanadium content is less than 2wt.% (1033-1036 cm ⁻¹)	44
1050	1091		1052		Antisymmetric stretching ν (Si-O)	42
		1100			ν_{as} (Si-O-Ti) with Ti ⁴⁺	48
1185	1150			1123		
0.9923	0.9918	0.9847	0.9897		R ²	
					>3000 cm ⁻¹	50
	3233				ν (OH) moodes of H ₂ O involved in a tetrahedral structure	50
3600	3594	3595	3623		MeO-H and free H ₂ O	49,50
3700	3690		3695		HO-H dangling	50
3747	3746	3743	3745	3740	SiO-H and Free SiO-H	50

Table S3. Peak position and assignments for the Ta and bimetallic Ta(Nb, Ti, Co, V) catalysts within 260-1200 cm⁻¹ and 2600-4000 cm⁻¹ ranges.

Peak position (cm ⁻¹)					Assignments	Ref.
Ta	Ta	TaTi	TaCo	TaV	<650 cm ⁻¹ <i>n</i> -SiO ₄ rings	42,43
	Nb					
				355	δ (O-V-O)	44,45
360	348	375	362		5,6,7-SiO ₄ rings	42
441	447		435		5,6,7-SiO ₄ rings and E _g modes of the extra-framework rutile (445 cm ⁻¹)	42
497	496	497	495	486	D ₁ modes (4- SiO ₄ rings), bending modes of the framework Me/Si-O-Si speciation	42
608	608	607	612	609	D ₂ modes (3- SiO ₄ rings)	42
	615	616			ν(Nb-O-Nb) polymerized Nb species (607-650 cm ⁻¹) and A _{1g} modes in extra-framework rutile (612 cm ⁻¹)	53 and 43
660		685	670		ν(Ta-O) in TaO ₆	46
	689				Nb ₂ O ₅	53
			707		Co ₃ O ₄ (690 cm ⁻¹)	47
	801	798	796		ν _s modes of the siloxane bridges Si-O-Si	42
828			830		ν _s modes of the siloxane bridges Si-O-Si	42
958		945			ν _s (Si-O-Ti/Nb)	49, 51
980	978	985	973		ν (Si-OH), ν(Si-NBO) in Q ² units, ν(Nb=O) of isolated NbO ₄ and TaO _x species (965-980 cm ⁻¹)	42,52-55 and 18
				1030	(SiO) ₃ V=O stretching modes	26
				1060	Shorter V=O bonds	56
1050	1056		1065		Q ⁴ units in silica framework	42,52
		1097			ν _{as} (Si-O-Ti) with Ti ⁴⁺	48
1185		1164	1187			
					>3500 cm ⁻¹ (hydroxyl stretching modes)	
3617		3602	3623	3547	Me-OH and free H ₂ O	49
3746	3744	3744	3744	3738	Isolated Si-OH in MCM-41	50
0.9923	0.9943	0.9949	0.9857	0.9970	R ²	

vs,as-symmetric, asymmetric stretching, δ-bending vibrations. NBO is non-bridging oxygen. Q₂ represents SiO₄ tetrahedra with 2NBO.