Supplementary Information (SI) for Journal of Materials Chemistry C.

Optimization of Photocatalytic Activity in Transition Metal-Modified Mesoporous Silicas: Fine-Tuning Properties to Elucidate Radical Reaction Pathways by EPR

Fabrizio E. Viale[1], Elin L. Winkler[2], Enio Lima Jr.[2], Gerardo F. Goya[3], Tamara B. Benzaquén[1], Verónica R. Elías[1], Griselda A. Eimer[1], Gabriel O. Ferrero[1].*

[1] CITeQ-UTN-CONICET, Universidad Tecnológica Nacional, Fac. Regional Córdoba, Maestro López esq. Cruz Roja, Ciudad Universitaria, CP: 5016 Córdoba Capital, Argentina.

[2] INN-CNEA-CONICET, Centro Atómico Bariloche, Av. Bustillo Km 9,5, CP: 8400, San Carlos de Bariloche, Argentina.

[3] INMA, Universidad de Zaragoza, C/ Mariano Esquillor Gómez s/n, CP: 50018, Zaragoza, España.

*Corresponding autor

E-mail address: gferrero@frc.utn.edu.ar

S1 - Paramagnetic species detected

Table S1. Paramagnetic species detected by fitting the EPR spectra from Ti/Mn(x)/M R8 materials suspensions in aqueous DMPO/DMSO solutions after 10 min of 390 nm UV/Vis irradiation.

Paramagnetic species	Peak shape	Source for the species
Mn^{2+}	Intense outer peaks	Doping agents in the MgO crystal used for calibration and as one of the Mn species in the Ti/Mn/M material.
•OH	Four resonance peaks	Splitting of the resonance line due to hyperfine interaction of the unpaired electron spin with the nuclear spin of both nitrogen and hydrogen atoms.
•OOH (akin to $•O_2^-$)	Six low-intensity resonance peaks	Partial convolution of 12 resonance lines due to hyperfine interaction of the unpaired electron spin with the nuclear spin of one nitrogen and two hydrogen atoms, forming an adduct of short life and low affinity.
$•CH_3$	Six broad resonance peaks	DMSO rupture under UV/Vis irradiation (as DMPO/$•CH_3$ lines are already present in the blank sample) and/or a secondary reaction of DMSO with either •OH or •OOH.
•C(OH)R	Six resonance peaks	Secondary reaction of DMSO with •OH
•N	Three broad resonance peaks	Interaction of the electron spin of oxidized (with either •OH or •OOH) DMPO with the nuclear spin of a nitrogen atom.

S2 – Hyperfine parameters for species in aqueous DMPO/DMSO solutions

Table S2. EPR parameters obtained from fitting the spectra of suspensions of Ti/Mn(x)/M R8 samples in aqueous DMPO/DMSO solutions after 10 min of 390 nm UV/Vis irradiation.

	Mn^{2+} (MgO)	•OH	•OOH	$•CH_3$	•C(OH)R	•N
g[a]	2.0040 (3)[g]	2.0030 (3)[g]	2.0038 (3)[g]	2.0029 (3)[g]	2.0022 (3)[g]	2.0033 (3)[g]
w (Oe)[b]	3.63 (4)[g]	1.16 (2)[g]	0.92 (1)[g]	2.36 (4)[g]	1.50 (2)[g]	1.79 (2)[g]
LS[c]	0.06 (2)[g]	1.00 (2)[g]	1.00 (2)[g]	0.50 (2)[g]	1.00 (2)[g]	0.85 (2)[g]
H_{SF}^{Mn} *(Oe)*[d]	87.0 (1)[g]					
H_{SF}^{N} *(Oe)*[e]		15.4 (2)[g]	12.6 (1)[g]	15.8 (2)[g]	15.8 (2)[g]	14.5 (1)[g]
H_{SF}^{H} *(Oe)*[f]		14.2 (2)[g]	10.5 (2)[g] 2.6 (3)[g]	23.3 (2)[g]	29.1 (1)[g]	

[a] g: gyromagnetic ratio; [b] w: line width; [c] LS: line shape coefficient (values between 0 and 1, with 0 for Gaussian distribution and 1 for Lorentzian); [d] H_{SF}^{Mn}: hyperfine interaction for unpaired electrons of Mn^{2+}; [e] H_{SF}^{N}: hyperfine interaction between an unpaired electron spin and nuclear spin from a N atom; [f] H_{SF}^{H}: hyperfine interaction between an unpaired electron spin and nuclear spin from a H atom; [g] All the numbers in parentheses refer to standard errors relating to the last digit.

S3 – Hyperfine parameters for species in aqueous DMPO/DMSO/isopropanol solutions

Table S3. EPR parameters obtained from fitting the spectra of different suspensions of Ti/Mn(x)/M R8 samples in aqueous DMPO/DMSO/8% vol. isopropanol solutions after 10 min of 390 nm UV/Vis irradiation.

	Mn^{2+} (MgO)	•OH	•OOH	$•CH_3$	•C(OH)R	•N
g[a]	2.0040 (3)[g]	2.0031 (3)[g]	2.0037 (3)[g]	2.0031 (3)[g]	2.0026 (3)[g]	2.0032 (3)[g]
w (Oe)[b]	3.93 (4)[g]	1.49 (2)[g]	0.65 (1)[g]	2.21 (3)[g]	1.04 (2)[g]	1.79 (2)[g]
LS[c]	0.00 (2)[g]	1.00 (2)[g]	1.00 (2)[g]	0.55 (2)[g]	1.00 (2)[g]	0.85 (2)[g]
H_{SF}^{Mn} *(Oe)*[d]	87.1 (1)[g]					
H_{SF}^{N} *(Oe)*[e]		15.2 (2)[g]	13.6 (2)[g]	15.7 (2)[g]	15.6 (2)[g]	14.8 (1)[g]
H_{SF}^{H} *(Oe)*[f]		14.4 (2)[g]	10.5 (2)[g] 2.8 (3)[g]	23.1 (2)[g]	27.9 (1)[g]	

[a] g: gyromagnetic ratio; [b] w: line width; [c] LS: line shape coefficient (values between 0 and 1, with 0 for Gaussian distribution and 1 for Lorentzian); [d] H_{SF}^{Mn}: hyperfine interaction for unpaired electrons of Mn^{2+}; [e] H_{SF}^{N}: hyperfine interaction between an unpaired electron spin and nuclear spin from a N atom; [f] H_{SF}^{H}: hyperfine interaction between an unpaired electron spin and nuclear spin from a H atom; [g] All the numbers in parentheses refer to standard errors relating to the last digit.