

Iron Oxide Nanoparticles for Photocatalysis under Visible Light

**Nabil Tabaja^{1,2,3}, Sandra Casale¹, Dalil Brouri¹, Anne Davidson^{1*},
Joumana Toufaily^{2,3}, Tayssir Hamieh²,
S. Sladkevich⁴ and Richard Cole⁴**

¹*Sorbonne Universités, Institut des Matériaux de Paris Centre, Laboratoire de Réactivité de Surface, UMR-CNRS 7197, 4 Place Jussieu, 75252 Paris cedex 05, France.*

²*Université Libanaise, Faculté des Sciences, Laboratoire des Matériaux, Catalyse, Environnement et Méthodes Analytiques (MCEMA), Hadath, Liban*

³*Université Libanaise, Ecole Doctorale en Sciences et Technologies, Hadath, Liban.*

⁴*Sorbonne Universités, Institut Parisien de Chimie Moléculaire, UMR 8232 – case 45 ; 4 Place Jussieu, 75252 Paris cedex 05, France*

E-mail: anne.davidson@upmc.fr, nabil.tabaja@hotmail.com

To complement already available results about the activity of Fe/SBA-15 catalysts for methanol photocatalytic oxidation under visible light ^[1] we use here complementary techniques, TOC and CP-MAS to obtain information about the selectivity of the reaction, i.e., to quantify formaldehyde, but also demonstrate that no CO₂ is formed and that formic acid and methyl formate are formed. We use Fe-oxides or ferrites (Co/Fe, Ni/Fe) nanosized particles of three types:

- 1) replicated nanoparticles, crystallized with a spinel unit-cell inside the pores of several kinds of highly ordered porous SBA-15 silica (see SAED in Fig. 1B),
- 2) replicated nanoparticles extracted from silica by a conventional NaOH treatment, as illustrated in Fig.1,
- 3) nanoparticles with a hematite-unit-cell, grown outside silica grains and formed during calcination because of a thermally induced diffusion of Fe³⁺ cations.^[2]

Degussa TiO₂ P25 is introduced as a well-recognized reference. Formaldehyde formation is analyzed first by a colorimetric method and using a first order kinetic rule. With the pure visible irradiation that we have used, this product formation is much more rapid (Table 1, 5 times more) with semi-conducting replicated Fe-oxide nanoparticles (Fe wt 12%) than with pure Degussa P25. Large extracted nanoparticles are two times more rapid than parent particles inserted inside silica. An important lixiviation of Fe³⁺ ions can be limited (divided by two) by increasing the proportion of hematite nanoparticles which requires the use of a silica, containing both parallel and connected mesopores. A Fenton type oxidation occurs because of the photocorrosion of iron oxides is limited if more stable, ferrite-type chemical compositions, are introduced (table 1). The more lixiviated samples (the ones which contain more Fe³⁺ in solution) are not the most active ones. Formic acid is the main product detected by GC-MS with extracted nanosized particles. TOC measurements performed at different times of catalytic reaction always give values very near to the ones obtained with blank methanol. The oxidation of formic acid into CO₂ is then hampered. Methyl formate is favoured with hematite nanoparticles. Our results are expected to help in the development of new catalysts formulation for water depollution and energy.

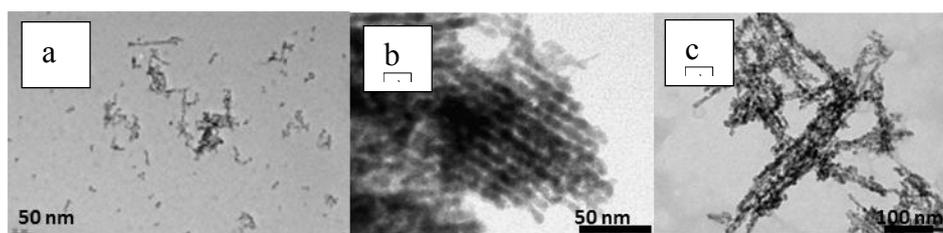


Figure 1. a) Orange liquor, suspension of small nanoparticles (stabilized with NEt_3 amine), b) Recovered bundles of attached nanoparticles in fresh catalyst 2M_Fe(12)_CYC_NO3 (2013), c) Attached nanoparticles in 0.3M+MAT_Fe(12)_CYC_NO3 catalyst after 1400 min of methanol oxidation test

Sample	Formaldehyde 300 min	Formaldehyde 1300 min	% Fe in solution	k (kinetic order 1) min^{-1}
TiO ₂ P25	2.07	2.76	-	0.007
Extracted from 2M_Fe(12)_CYC_NO3**	0.48	4.49		0.050
*2M_Fe(12)_CYC_NO3	0.64	3.16	5	0.026
*0.3M_Fe(12)_CYC_NO3	0.45	1.23	10	0.015
*0.3M+MAT_Fe(12)_CYC_NO 3	0.69	3.17	6	0.010
*0.3M+MAT_Fe(12)_CYC_Cl	4.35	0		0.014
*0.3M+MAT_Fe(6)Co(6)_CYC Cl	1.45	0.84	1	0.005
*0.3M+MAT_Fe(6)Ni(6)_CYC Cl	1.20	13.99	1	0.004

Experimental conditions: 75 mg catalyst. 100 ml aqueous solution. 0.16 mmol of methanol. 2-3 drops of H₂SO₄ (1M) to adjust pH at 2.6. 8.5 ml H₂O₂ to increase the rate of reaction. temperature 18°C to minimize photo-induced corrosion; recorded up to 1400 min of test.
**silica prepared with 2M HCl, 0.3M HCl or with 24h of maturation in water aimed at minimizing Cl-contamination.*
***75 mg of catalyst. 25 ml of NaOH 2M. 80°C/2h washing three times with water then recovery by centrifugation 5000 rpm and 10 min.*

Acknowledgement: MCEMA is greatly acknowledged for financing the PhD of Nabil Tabaja. Dr Isabelle Pellerin and Sophie Rochut, UPMC, are acknowledged for their help in GC-MS and we thank also Agilent Technologies (Les Ulis, France) for providing the GC-MS equipment necessary to complete this project.

References:

- [1] N. Tabaja, S. Casale, D. Brouri, A. Davidson, J. Toufaily, T. Hamieh, *Comptes Rendus Chimie*, **2015**, 18(3), 358.
- [2] C. Cornu, J.L. Bonardet, S. Casale, A. Davidson, G. Andre, F. Porcher, I. Gric, V. Tomasic, D. Vujevic, and N. Koprivanac, "Identification and location of iron species in Fe/SBA-15 catalysts interest for catalytic Fenton reactions", *J. Phys. Chem. C*, **2012**, 116, 3437.