Photo-Fenton Oxidation of Acetic Acid on Supported LaFeO$_3$ and Pt/LaFeO$_3$ Perovskites

Diana Sannino[1*], Vincenzo Vaiano[1], Lyubov A. Isupova[2], Paolo Ciambelli[1]

[1]University of Salerno, Department of Industrial Engineering, Via Ponte Don Melillo, 84084, Fisciano, Italy
[2]Boreskov Institute of Catalysis, SB RAS, pr. Lavrentieva, 5, 630090 Novosibirsk, Russian Federation
dsannino@unisa.it

Photo-Fenton process uses Fe^{2+} as homogeneous catalyst, hydrogen peroxide and UV light to mineralize organic pollutants by the formation of highly reactive hydroxyl radicals. Several limitations to this process are present, such as the limited operational pH range to avoid oxyhydroxide sludge formation and the catalyst recovery. Heterogeneous photo-Fenton process based on structured catalyst can avoid a subsequent separation stage, overcoming these disadvantages. In this work, the comparison of performances of LaFeO$_3$ and Pt/LaFeO$_3$ perovskites supported on different honeycomb monoliths, made of cordierite or corundum, were studied. Photo-Fenton oxidation of acetic acid ashowed that LaFeO$_3$ supported on corundum honeycomb was more active than on cordierite monolith. The addition of Pt on catalysts did not help to increase their performance in the studied reaction. Photo-Fenton oxidation tests carried out on catalysts having different content of LaFeO$_3$ evidenced the existence of an optimal loading of active phase.

1. Introduction

Most industrial processes generate wastewater containing organic compounds that exhibit low biodegradability and are accumulated in the land and water. In the last years, advanced oxidation processes have emerged as efficient technologies for the destruction of various classes of biorecalcitrant pollutants in waters. Photo-Fenton reaction offers a simple and cost-effective source of hydroxyl radicals since its reagents are inexpensive, environmentally benign and relatively easy to transport and handle (Pariente et al., 2008; Yaping et al., 2008; Pignatello, 1992). Homogeneous photo-Fenton process uses hydrogen peroxide, Fe^{2+} as homogeneous catalyst and UV light to mineralize organic pollutants by the formation of highly reactive hydroxyl radicals. Several limitations to this process are present, such as the operational pH range (2-4) to avoid ferric oxohydroxide sludge formation and the difficult of catalyst recovery (Kuznetsova et al., 2004). The heterogeneous photo-Fenton process based on structured catalyst overcames these disadvantages, also avoiding the catalyst separation step. High photo-Fenton activity was found on LaMeO$_3$ (Me= Fe, Mn, Co, Ni, Cu) perovskites supported on cordierite honeycombs in the acetic acid removal (Sannino et al., 2008; Sannino et al., 2009; Sannino et al. 2010a). LaFeO$_3$ resulted the best catalysts for this

process in terms of reaction rate. Photo-Fenton activity was closely related to the amount of active phase supported on monolitic support. The rate of total organic content (TOC) removal decreased during the time because of the occurring side H_2O_2 decomposition to O_2 that subtracts the oxidant to the photo-Fenton reaction. By dosing H_2O_2 during the photo-Fenton reaction, enhanced TOC removal with minimization of required amount of H_2O_2 for the oxidation of organic compounds was found (Sannino et al., 2010b). In this work, the performances of $LaFeO_3$ and $Pt/LaFeO_3$ perovskites supported on corundum honeycomb monoliths has been studied in the photo-Fenton oxidation of acetic acid and compared to those of $LaFeO_3$ and $Pt/LaFeO_3$ perovskites supported on cordierite honeycomb monoliths

2. Experimental

2.1 Catalysts preparation and characterization
The structured supports were prepared following the procedure reported elsewhere (Isupova et al., 2005; Isupova et al., 2002). $LaFeO_3$ was supported on corundum and cordierite honeycombs by impregnation of thin wall (0.25 and 0.4 mm for corundum and cordirite respectively) monolithic support (triangular channels size = 1.5 mm for corundum and 2.5 mm for cordierite). Solutions of nitrates salts with added citric acid and ethylene glycol were used. After drying at 100-200 °C, a film of polymerized metal-ether complexes strongly adhering to the monolithic support walls was formed. After annealing at temperatures exceeding 500 °C, the organic residue is burned, and grainy porous perovskite supported layer emerges. Samples obtained were calcined in air at 900 °C for 4h. Some monoliths were subsequently impregnated with H_2PtCl_6, solutions, then dried and calcined in air at 500 °C for 4 h. $Fe_2(C_2O_4)_3$ (provided by Carlo Erba) was chosen as the reference homogeneous photo Fenton catalyst. The X-ray diffraction patterns were obtained with a URD-6 diffractometer using CuKα- radiation. Particle sizes were estimated from the broadening of 400 diffraction peak (cubic index). The samples pore structure was characterized by high pressure mercury porosimetry (HPM) using an Auto-Pore 9200 machine, and the specific surface area (S.S.A) was determined by a routine BET procedure using the Ar desorption data.

2.2 Photo-Fenton reactions
Photo-Fenton oxidation tests were carried out on 160 mL volume solution in a properly designed sealed stainless-steel batch photoreactor. Acetic acid aqueous solutions containing TOC of 500 mg/L (0.021 mol/L, pH 3.9) and H_2O_2 (0.083 mol/L) were used. As UV source, mercury vapors lamp at nominal power of 8W and emitting at 254 nm was used. Monolithic catalysts were placed in the reactor. When the lamp was switched on, the reaction started. Very small samples of treated solution (500 μl) were taken for analysis every hour, to avoid changing in the contact time during the test. Continuous mixing of model wastewaters was realized by nitrogen fine bubbling under monolith holder (Q=250 mL/min (STP)) and external recirculation of wastewater (flow rate=7 L/min). Before re-entering into the reactor the solution was cooled by a cold trap to keep the temperature constant at 25°C. At the reactor outlet the gases pass through a cold trap (0°C) in order to assure water condensation, prior to the gas analyzer (Quantra

Fourier transform ion cyclotron resonance mass spectrometer, Siemens) for measurements of CO and CO_2 concentrations. The catalytic properties of monolithic samples were tested in the photo-Fenton reaction under atmospheric pressure at 25 °C using samples mass comprised between 14 ÷ 16 g. TOC has been determined by the high temperature catalytic combustion on Pt/Al_2O_3 catalyst in air flow (250 mL/min (STP)) at 680°C of vaporized solution samples. Combustion products were monitored by NDIR continuous analyzers (Hartmann & Braun Uras 10E), measuring CO and CO_2 gaseous concentrations at the combustion reactor outlet. Both CO and CO_2 concentration continuous data were integrated to calculate TOC. The H_2O_2 concentration in the liquid samples was determined by $H_2O_2/TiOSO_4$ complex ($\lambda = 405$ nm) UV-Vis analyses.

3. Results

3.1 Catalysts characterization
All the prepared samples are listed in Table 1.

Table 1: List of prepared catalysts

Catalyst	$LaFeO_3$ loading wt%	Pt loading wt%	Honeycomb support	Geometrical surface */volume** ratio mm^2/mm^3
$2LaFeO_3$-A	2.23	0	corundum	2511
$4LaFeO_3$-A	4.5	0	corundum	2513
$11LaFeO_3$-A	10.64	0	corundum	2846
$17LaFeO_3$-A	17.39	0	corundum	2577
$0.1Pt/11LaFeO_3$-A	11.39	0.1	corundum	2536
$11LaFeO_3$-C	10.50	0	cordierite	2513

*by the sum between the external area of cylindrical monolith and the area of all internal triangular channels; ** volume of the single piece of monolith

Monolithic corundum-support showed a specific surface area of about $4m^2/g$, integral pore volume of 0.35 cm^3/g and mean pore radius of about 0.12μm (Isupova et al., 2002). According to X-ray analysis the particle size of supported perovskites was in the range 10–30 nm with orthorhombic structure as previously found (Isupova et al., 2002). For all corundum supported catalysts, the specific surface area was about $4–6m^2/g$. Porosimetry tests showed that, in the range of pore sizes exceeding 30 nm, the pore size distribution was similar for both support and supported systems, the volume of narrow (<10 nm) pores was decreased for 0.05 cm^3/g due to perovskites supporting. The characterization of $11LaFeO_3$-C is reported by Sannino et al. (2010b). This last catalyst showed the better performances among those supported on cordierite (Sannino et al., 2010b).

3.2 Photo-Fenton oxidation tests

The analysis of the gas evolved during run time from the sealed photoreactor allowed to evidence the presence of only CO_2 indicating that complete mineralization of acetic acid was obtained in photo-Fenton oxidation. TOC removal and H_2O_2 conversion for heterogeneous photo-Fenton on $11LaFeO_3$-A and $11LaFeO_3$-C in comparison with
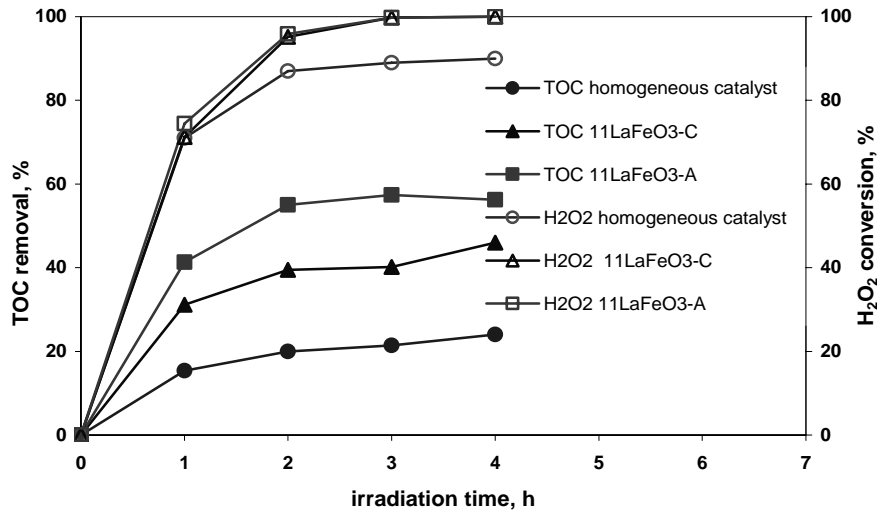

Figure 1: TOC removal and H_2O_2 conversion as a function of irradiation time for homogeneous, $11LaFeO_3$-A and $11LaFeO_3$-C catalysts.
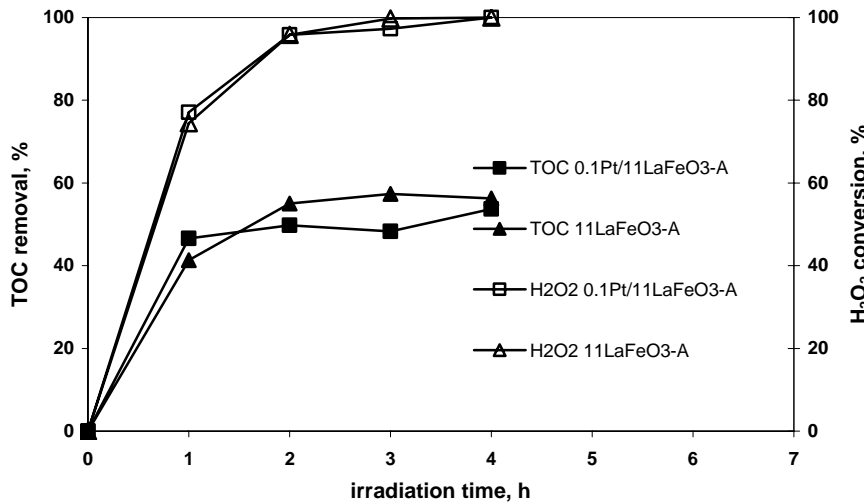

Figure 2: TOC removal and H_2O_2 conversion as a function of irradiation time for different Pt loading on $11LaFeO_3$-A catalyst.

homogeneous reaction are reported in Figure 1. The activity of homogeneous catalyst Fe^{2+} was lower than both $LaFeO_3$ supported perovskites. TOC removal was higher on $11LaFeO_3$-A than on $11LaFeO_3$-C, altough both limited by the oxidant consumption because of the occurring H_2O_2 decomposition side reaction. No metal leaching after the tests indicated that no homogeneous contribution to TOC removal could be present.

Considering the higher perovskite particle dispersity in corundum samples, due to its higher specific surface area and porosity with respect to cordierite monolithic support (Isupova et al., 2005), the higher activity of $11LaFeO_3$-A could be explained. The effect of Pt loading on $11LaFeO_3$-A catalyst is shown in Figure 2. After 1 hour of irradiation time, TOC removal reached 41 and 47 % respectively, on $11LaFeO_3$-A and $0.1Pt/11LaFeO_3$-A catalysts, while its value after 4 hours was similar for $11LaFeO_3$-A (56%) and $0.1Pt/11LaFeO_3$-A (54%). The modification by Pt didn't show relevant effect on the activity of $LaFeO_3$ based sample, suggesting a low acetic acid activation on supported Pt clusters. The effect of the perovskites active phase loading was investigated with $LaFeO_3$ based catalysts supported on corundum and the obtained results are reported in Figure 3. TOC removal after 1 hour of irradiation increased from 23 to about 41% with increase of perovskite load from 2.23 to 10.64 wt % and decreased to about 30% for $LaFeO_3$ loading of 17.39 wt % evidencing the existence of an optimal content of active phase. The final value of TOC removal was in the range 53-58% for $2LaFeO_3$-A, $11LaFeO_3$-A and $17LaFeO_3$-A catalysts while on $4LaFeO_3$-A reached 65 %, better using the available oxidant.
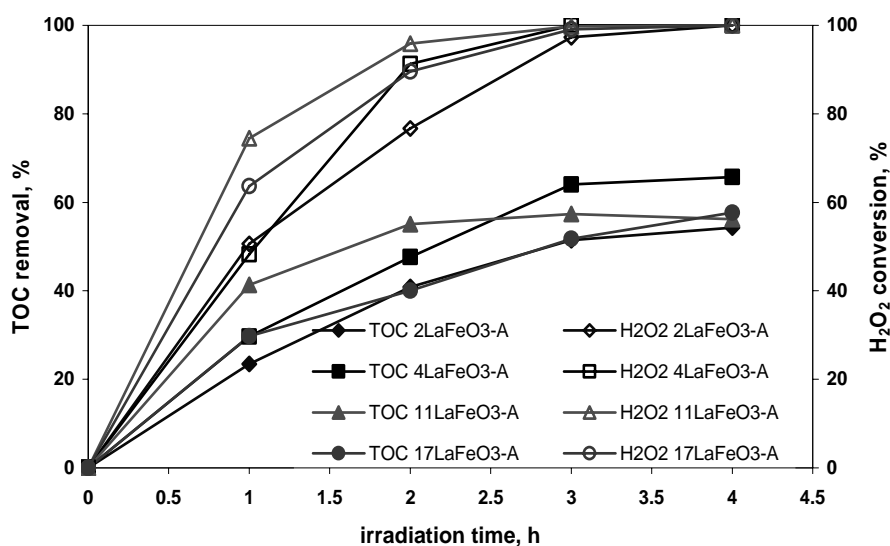

Figure 3: TOC removal and H_2O_2 conversion as a function of irradiation time for different $LaFeO_3$ loading on corundum monolith.

4. Conclusions

Heterogeneous photo-Fenton process allows to obtain higher TOC removal efficiency with respect to the homogeneous process. $LaFeO_3$ supported on corundum honeycomb was more active than on cordierite monolith. The addition of Pt on catalysts did not help to significantly increase their performance in the studied reaction. Photo-Fenton oxidation tests carried out on catalysts having different content of $LaFeO_3$, evidenced the existence of an optimal loading of the perovskites active phase.

References

Isupova L. A., Alikina G. M., Tsybulya S. V., Salanov A. N., Boldyreva N. N., Rusina, E. S., Ovsyannikova I. A., Rogov V. A., Bunina R. V. and Sadykov V. A., 2002, Honeycomb-supported perovskite catalysts for high-temperature processes, Catalysis Today, 75, 305-315.

Isupova L. A., Sutormina E.F., Kulikovskaya N.A., Plyasova L.M., Rudina N.A.,. Ovsyannikova I.A, Zolotarskii I.A. and Sadykov V.A., 2005, Honeycomb supported perovskite catalysts for ammonia oxidation processes, Catalysis Today, 105, 429-435.

Kuznetsova E.V., Savinov E.N., Vostrikova L.A. and Parmon V.N., 2004, Heterogeneous catalysis in the Fenton-type system FeZSM-5/H_2O_2, Applied Catalysis B: Environmental, 51, 165-170.

Pariente M. I., Martınez F., Melero J. A., Botas J. A., Velegraki T, Xekoukoulotakis P. N. and Mantzavinos D., 2008, Heterogeneous photo-Fenton oxidation of benzoic acid in water: Effect of operating conditions, reaction by-products and coupling with biological treatment, Applied Catalysis B: Environmental, 85, 24-32.

Pignatello J.J., 1992, Dark and photoassisted iron (3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environmental Science and Technology, 26 (5), 944–951.

Sannino D., Ciambelli P., Ricciardi M. and Isupova L. A., 2008, Wastewater treatment by high efficiency heterogeneous photo-fenton process, PCT application, WO2008IT00343 20080523.

Sannino D., Ciambelli P., Ricciardi M. and Isupova L. A., 2009, Catalyst and heterogeneous photocatalytic Fenton process for sewage treatment, Russian patent RU2347611.

Sannino, D., Isupova, L. A., Ciambelli, P. and Vaiano V, 2010a, Heterogeneous photo-fenton oxidation on nanosized Pt/perovskites as efficient process for organic pollution removal in wastewaters, Technical Proc of the CTSI Clean Technology and Sustainable Industries Conference and Expo, Anaheim, CA, USA, 372-375.

Sannino, D., Vaiano V, Isupova, L. A.and Ciambelli, P., 2010b, Structured catalysts for photo-Fenton oxidation of acetic acid, Catalysis Today, DOI: 10.1016/j.cattod.2010.11.025.

Yaping A. and Jiangyong H., 2008, Photo-Fenton degradation of 17β-estradiol in presence of α-FeOOHR and H_2O_2, Applied Catalysis B: Environmental, 78 (3–4), 250–258.