



9.1 MOF 253- Pt performance electrocatalyst for Oxygen Reduction Reaction

V. Ávila Vázquez, I.L. Escalante-García, V. H. Collins Martínez, S.M. DurónTorres

¹Universidad Autónoma de Zacatecas, Área de Ciencias Químicas, Carretera Zacatecas-Guadalajara km 6, Ejido "La Escondida", Edificio 6, C.P. 98160, Zacatecas, Zac.

²S.C. Depto. de Ingeniería y Química de Materiales, Centro de Investigación en Materiales Avanzados, Miguel de Cervantes 120, Complejo Industrial Chihuahua, 31190 Chihuahua, Mexico

* Corresponding author: duronsm@prodigy.net.mx

ABSTRACT

Metal organic frameworks (MOFs) are a new class of coordination polymers that have been attractive for clean and efficient energy conversion applications as well as electrocatalysts for energy conversion in fuel cells. Briefly, the MOFs are solid materials formed by metal ions (or clusters) coordinated to multidentate organic molecules. In this investigation, we present the results for the electrochemical and physicochemical characterization of MOF 253 using Pt as metal ion for the Oxygen Reduction Reaction (ORR). The material was synthesized by solvothermal and microwave methods with the aim of optimizing the catalytic load of Pt used in the fuel cell. The results show that the Pt-MOF 253 exhibits electrochemical activity towards the ORR and a nanometric particle size. Overall, these materials can be a promising possibility as electrocatalysts for fuel cell.

Keywords: MOF-Pt, Fuel Cell, ORR

1. Introduction

Metal-organic frameworks, or MOFs (also known as coordination polymers), have emerged as an extensive class of crystalline materials with ultrahigh porosity (up to 90% free volume) and enormous internal surface areas, extending beyond 6 000 - 10 000 m²/g. These properties, together with the extraordinary degree of variability for both the organic and inorganic components of their structures, make MOFs of interest for potential applications in clean energy, most significantly as storage media for gases such as hydrogen and methane, and as high-capacity adsorbents to meet various separation needs. Additional applications in membranes, thinfilm devices, catalysis, and biomedical imaging are increasingly gaining importance [1-5]



One of the novel MOF applications is the catalysis of fuel cells. An H₂/O₂ proton exchange membrane (PEM) fuel cell is a generator of electrical power based on the electrochemical oxidation of hydrogen at the anode and the electrochemical reduction of oxygen at the cathode. In these systems, electrocatalysts are necessary to accelerate both half-cell reactions. Today, only platinum and platinum-alloy electrocatalysts are used in all PEM fuel cell prototypes. However, in the context of a strong economy, platinum will always be expensive, hence hindering the large scale commercialization of these clean and efficient electrical energy sources [6-9].

The platinum catalysts account for 33% of the overall stack costs. Due to kinetic limitations for the oxygen reduction reaction (ORR), the required platinum content at the cathode is about an order of magnitude larger than at the anode. Therefore, in terms of cost reduction, the replacement of platinum and platinum-alloy catalysts is especially welcome at the cathode [10-13].

The goals of this study are: (i) to compare the activity, performance, and stability of the new Pt-MOF and Ru-MOF in oxygen reduction reaction (ORR) catalysts, (ii) to study the effect of the metal in the reaction; (iii) to try to correlate any improvement in the catalyst stability measured in (ii) to some properties measured for the same catalysts during their physico-chemical and electrochemical characterization.

2. Materials and Methods

2.1. Synthesis of MOF-Pt and MOF- Ru

Pt and Ru based MOF-253 materials as the electrocatalyst precursor were synthesized in two steps according to the reported procedure [14-16]. For the microwave synthesis the procedure was followed with the time change: to synthesize MOF-253 (first step), 151 mg of AlCl₃·6H₂O was dissolved in DMF (10 mL), followed by the addition of 153 mg of 2,20-bipyridine-5,50-dicarboxylic acid (bpydc). The obtained mixture was then placed in a Teflon capped vial and heated at 120 °C for 6 min in microwaves. The resulting white microcrystalline powder was then filtered and washed with DMF. To obtain fully desolvated framework, this powder was subsequently washed with methanol in microwaves for 5 min, then collected by filtration and finally dried at 180 °C under dynamic vacuum for 12 h.

In order to introduce Pt atoms (second step), 500 mg of the desolvated MOF-253 was mixed with 386 mg of PtCl₂ (CH₃CN)₂ and 400 mg of Ru₃(CO)₁₂ respectively and acetonitrile (15 mL). This mixture was then heated at 85 °C in a Teflon-capped vial for 5 min.



The resulting solid was collected by filtration and immersed in acetonitrile (15 mL). The total immersion time was three days and the solvent was replaced with fresh acetonitrile after each 24 h. Finally, the product (hereafter referred to as Pt-MOF and Ru-MOF) was collected by filtration and dried at 150 °C for 12 h under vacuum.

2.2. Pyrolytic transformation of the Pt-based MOF into electrocatalysts

To prepare the PEMFC electrocatalysts, the Pt-MOF and Ru-MOF materials were heat treated at temperatura 1000°C. A quartz tube (6 mm diameter) containing 100 mg of the sample was weighed and placed inside a furnace. The tube was sealed airtight and then purged with argon for 1 h prior to the treatment. The materials were typically heated at the ramp rate of 1 °C per min for 4 h under flow of argon at a rate of 20 mL per min. The yield after the heat treatment was normally about 50 wt.

2.3 Physicochemical characterization

A JEOL JEM-2200FS high resolution transmission electron microscope was used for evaluate the size particle, and the specific area of the MOF and Pt-MOF previous pyrolyzed were established by Brunauer – Emmett – Teller (BET) analysis of the nitrogen adsorption-desorption isotherms recorded at 77 K using a Micromeritics ChemiSorb 2720. All the samples were degassed by heating at 200°C under flow of nitrogen prior to measuring the surface area [17-20].

2.4 Electrochemical characterization

2.4.1 Electrodes preparation

The electrodes were prepared from a catalytic ink comprising 6 µL of Nafion® (5 wt. %, Aldrich), 10 µL of ethanol spectroscopic grade, 6 mg of Pt-MOF 253. Later, the resulting suspensions were hold in an ultrasonic bath for 0.5 h in aim to gain additional dispersion of mixture. Subsequently, a volume of each ink was deposited on a clean polished glassy carbon disk electrode (GCE) ($A = 0.07068 \text{ cm}^2$). The coated GCEs were dried in a furnace at 80°C for 10 min. In order to comparison a Pt supported on Vulcan electrode were used. Finally, MOF-253, Ru-MOF and Pt- MOF before pyrolyzed, Ru-MOF and Pt- MOF pyrolyzed were used as working electrodes for the ORR kinetic studies. All the current values reported in this paper are normalized to the electrode geometric area.

2.4.2 Electrochemical characterization of electrodes

All the experiments were performed in a double-compartment electrochemical glass cell. An Hg/Hg₂SO₄/0.5 M H₂SO₄ (ESM = 0.7V vs. NHE) electrode was used as reference which was positioned as close to the working electrode as possible by means of a Luggin capillary. A Pt-mesh was used as counter-electrode and the aqueous electrolytic medium was 0.5 M H₂SO₄ at room temperature. The electrochemical measurements were performed using an EG&G PAR VersaSTAT 3 Potentiostat/Galvanostat. In this study, all measured values of potential are reported respect to the normal hydrogen electrode (NHE).

Cyclic voltammetry (CV) was carried out to evaluate the effect of different step of the synthesis for make the Ru-MOF and Pt-MOF, the electrodes by scanning the potential at a rate of 50 mV s⁻¹ between -2.2 V and 1.7 V for Pt-MOF and -2 V and 1.8 V. For Ru-MOF under a N₂ atmosphere electrolyte solution. Oxygen reduction experiments were performed using rotation speeds of 100, 625, and 1600 rpm in a potential range of 0.5 to -1.4 V at a scan rate of 5 mVs⁻¹ in oxygen-saturated H₂SO₄. The rotation rate was controlled by a PINE MSR_X precision rotating system.

3. Results and Discussion

The Table 1 shows the specific surface area and the particle size, the área decrease when the Pt is added may be due to the restructuration between Pt and MOF, while the size particle obtained is nanometric [20-21].

Table 1. BET specific surface area and size particle of MOF materials

Sample	S _{BET} (m ² gr ⁻¹)	Size particle(nm)
MOF	81	-
Pt-MOF previous pyrolyzed	4	-
Pt-MOF pyrolyzed	-	8 -12

The Figure 1 shows the compares the cyclic voltammograms obtained for the steps the formation of the Pt-MOF, the insert corresponds to the final steps of synthesis, when the Pt-MOF is pyrolyzed present an increase in the current obtained in comparison with the previous steps of formation (MOF and Pt-MOF previous pyrolyzed) this may indicate an restructuration of the atoms of Pt above carbon support.

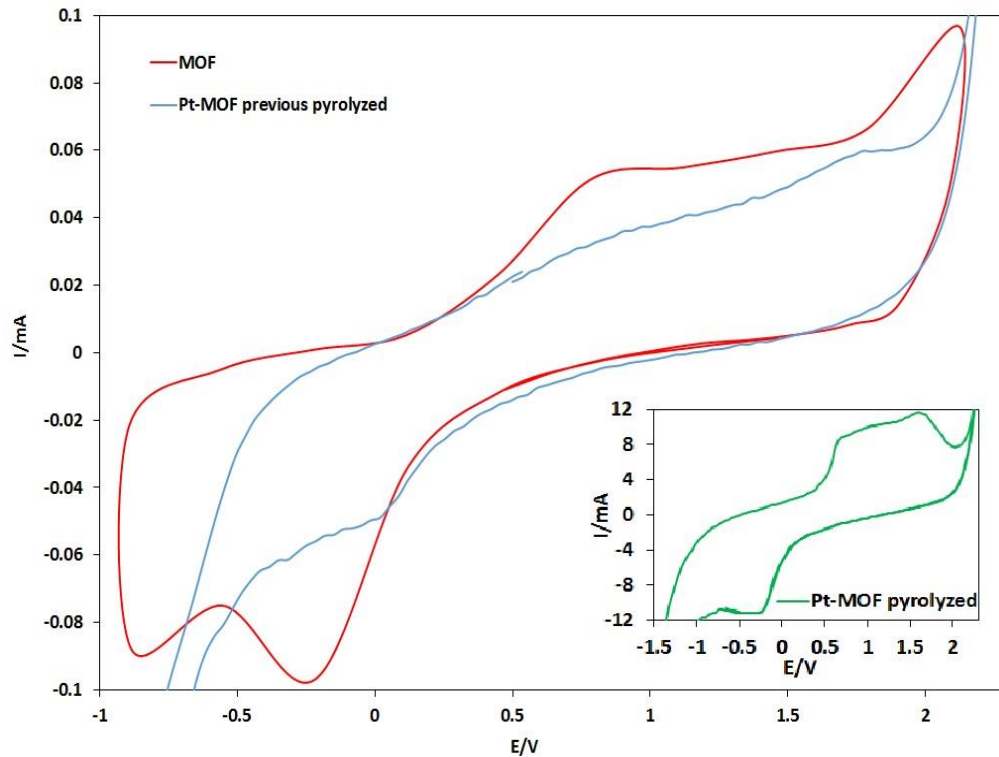


Fig 1. Cyclic voltammogram the steps synthesis of Pt-MOF in N_2 saturated 0.5 M H_2SO_4 and room temperature at 50 mV s^{-1} .

The Figure 2 shows the compares the cyclic voltammograms obtained for the steps the formation of the Ru-MOF, the current obtained is less in comparison with the Pt-MOF. The electrochemical behavior of Pt as a electrocatalyst for ORR was already known [22-23], and this was also confirmed with the results presented in this work.

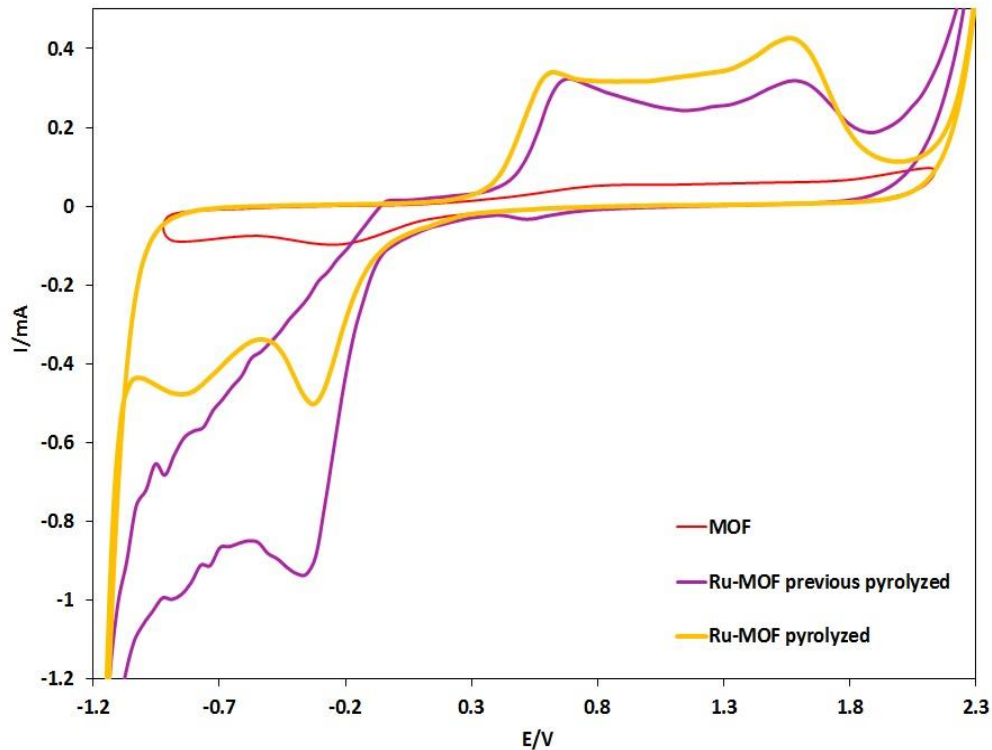


Fig 2. Cyclic voltammogram the steps synthesis of Ru-MOF in N_2 saturated $0.5\text{ M H}_2\text{SO}_4$ and room temperature at 50 mV s^{-1} .

The Figure 3 show the comparison electrochemical behavior between the materials synthesized (Pt-MOF and Ru-MOF) and the Pt-Vulcan used who reference, is possible appreciate differences in the typical profile of the behavior of the Pt support on vulcan in acidic medium. The window of potential wide suggests that the ORR is more irreversibly and therefore slow in the materials synthesized.

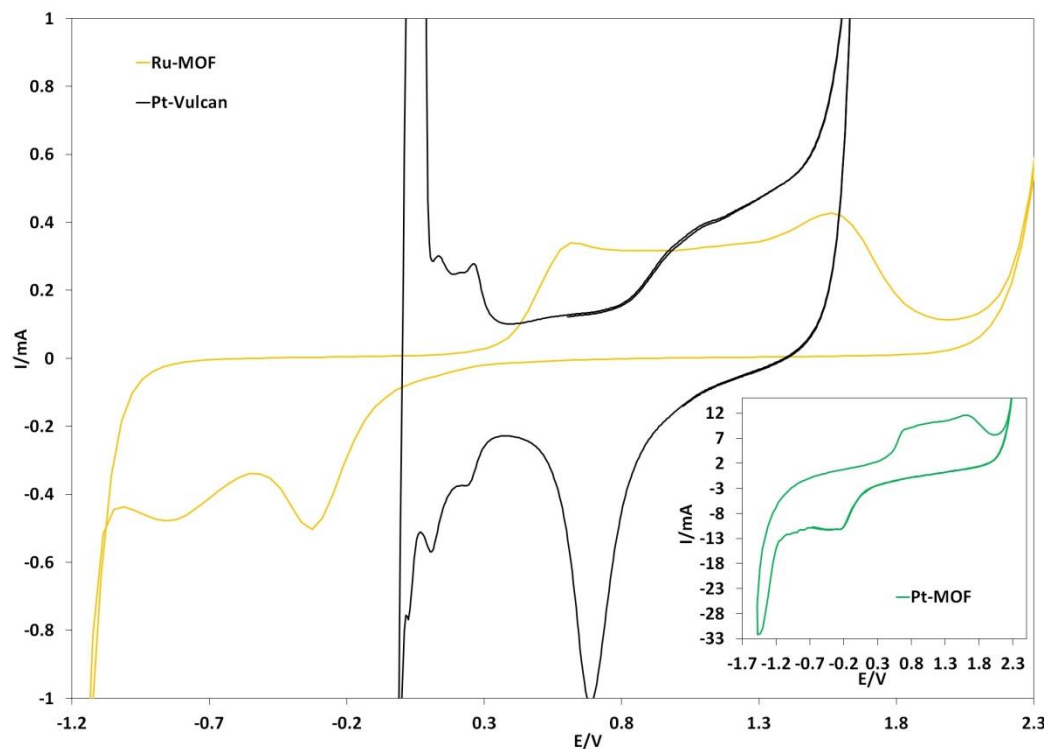
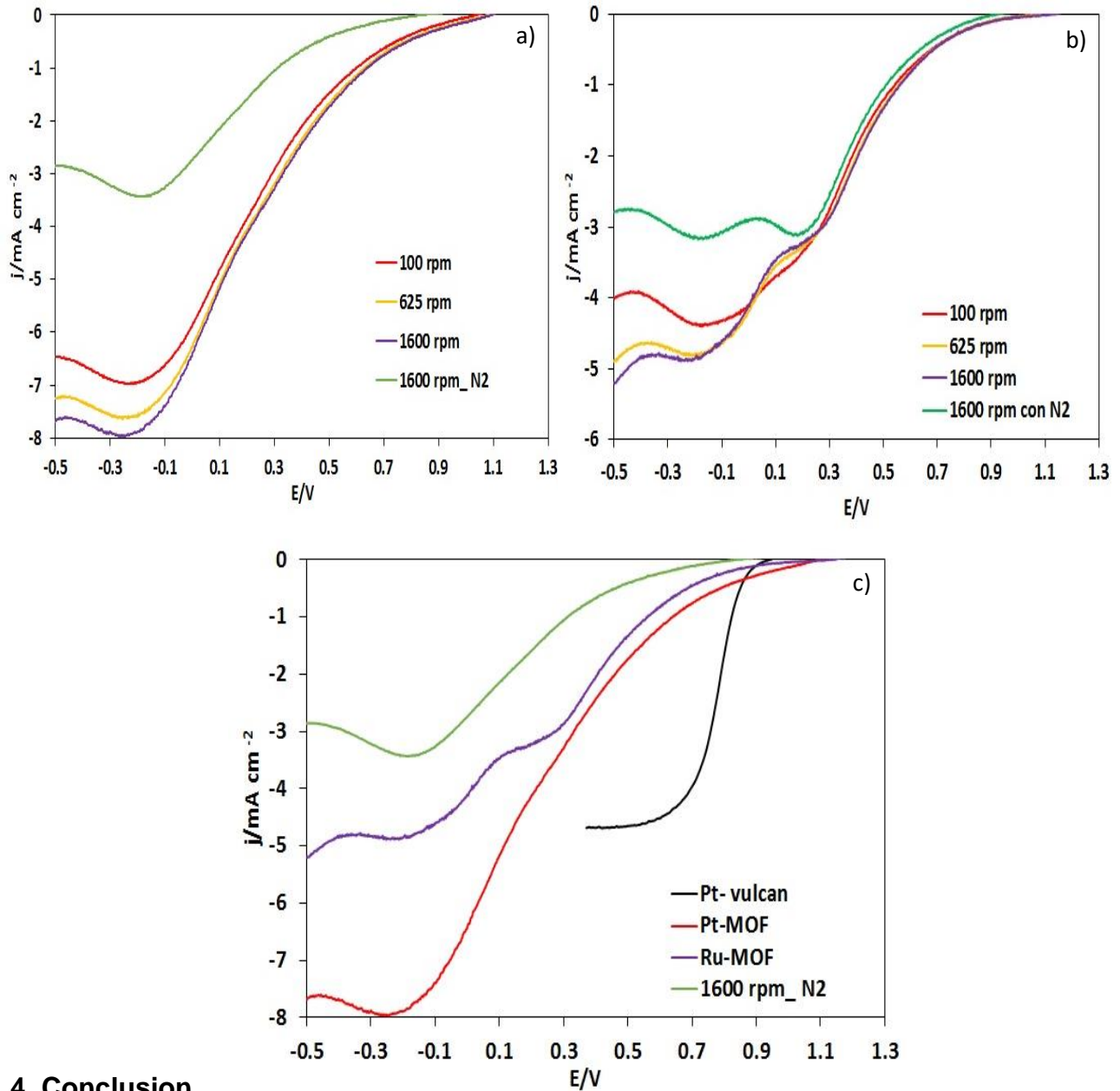


Fig 3. Cyclic voltammogram the Pt-vulcan, Pt-MOF and Ru-MOF in N_2 saturated 0.5 M H_2SO_4 and room

temperature at 50 mV s^{-1} .

Figure 4 a) shows the j - E diagrams obtained for Pt-MOF, 4 b) Ru-MOF and 4 c) comparison between Pt-vulcan and material synthesized (only 1600 rpm), for ORR using the RDE technique at a rotating speed of 100, 625 and 1600 rpm (Figure 4 a) and 4 b)). The used this technique confirmed that both materials synthesized present electrochemical activity for ORR. The difference in the limiting currents for materials compared (Pt-MOF and Ru-MOF) may be attributed a better coverage and electrochemical activity of the Pt catalyst and to the physical properties, such as the porosity and nature of the catalyst-MOF film on the glassy carbon electrode (Figure 4 a) and 4b)). Finally the RDE curves in the Figura 4 c) show the classical mixed, kinetic and diffusion control zones; although these regions are better defined when the Vulcan is used who support, confirmed that the ORR is more slow with the Pt-MOF and Ru-MOF increased the overpotential to which the ORR is carried out.



4. Conclusion

In this study, it was possible to prepared materials electrocatalytic nanometric of Pt-MOF and Ru-MOF for the ORR in one alone process of synthesys and with a catalytic load of very much minor Pt, compared with Pt traditional electrocatalysts supported on vulcan. This indicates that the materials based on Pt-MOF or Ru-MOF can be an option for use in fuel cell type PEM.

Nevertheless, is necessary to optimize the synthesis and diminish the overpotentials obtained with the use of the MOF.

Acknowledgements

The authors wish to thank the Mexican CONACyT for financial support of this work and the SMH and XVII International Congress of the Mexican Hydrogen Society.

References

- [1] Janiak Ch., Vieth J. K., *New J. Chem*, 2010:34: 2366-2388.
- [2] Zhou Hong-Cai, Long J. R., Yaghi O. M., *Chem. Rev.*, 2012:112: 673-674.
- [3] Joe Zhoua Hong-Cai, Kitagawa Susumu, *Chem. Soc. Rev.*, 2014: 43:5415-5418.
- [4] Falcaro P, Ricco R, Doherty C. M., Liang K, Hillb A. J., Stylesb M. *J. Chem. Soc. Rev.*, 2014:43:5513-5560..
- [5] Gao W-Y, Chrzanowski M., Ma S., *Chem. Soc. Rev.*, 2014:43:5841-5866.
- [6] Zhu Q-L., Xu Q., *Chem. Soc. Rev.*, 2014:43, 5468-5512.
- [7] Wang H., Yin F., Li G., Chen B., Wang Z., *Int. J. Hydrogen Energy*, 2014:39:16179-16186.
- [8] Luz I., Llabrés i Xamena F.X., Corma A., *J. Catal.*, 2010: 276, 134-140.
- [9] Aijaz A., Xu Q., *J. Phys. Chem. Lett* 2014: 5: 1400-1411.
- [10] Corma A., García H., Llabre´s X. Francesc X. , *Chem. Rev.*, 2010:110, 4606-4655.
- [11] Yang L., Lorouche N., Chenitz R., Zhang G., Lefèvre M., *Electrochim Acta*, 2015:159, 184-197.
- [12] Kramm U. I., Lefèvre M., Larouche N., Schmeisser D., Dodelet J.-P., *J. Am. Chem. Soc.*, 2014: 136, 978-985.
- [13] Morozan A., Sougrati Tahar M., Goellner V., Jones D., Stievano L., Jaouen F., , *Electrochim. Acta*, 2014:119, 192-205.
- [14] Ge L., Yang Y., Wang L., Zhou W., Dre M. R. , Chen Z., Zou J, Zhu Z., *Carbón*, 2015:82, 417-424..
- [15] Yin F., Li G., Wang H., *Catal. Commun.* 2014:54, 17-21.
- [16] Lee J., Jeong B., Ocon J. D., , *Curr. Appl. Phys.*, 2013:13, 309-321.
- [17] Jahan M., Bao Q., Loh P. K., *J. Am. Chem. Soc.*, 2012:134, 6707-6713.
- [18] Afsahi F, Vinh- Thang H, Mikhailenko S., Kaliaguine S, *J. Power Sources*, 2013:239: 415-423..
- [19] Bloch E. D., Britt D., Lee Ch. ,Doonan Ch. J., Uribe-Romo F. J., Furukawa H., Long J. R., Yaghi O. M., *J. Am. Chem. Soc.*, 2010:132: 14382-14384.
- [20] Ren Y., Chia Hui G., Gao Z., , *Nano Today*, 2013:8: 577-597.
- [21] Ma Tian Y., Dai S., Jaroniec M., Qiao Shi Z., *J. Am. Chem. Soc.*, 2014:136: 13925-13931.



- [22] Zhao S, Yin H., Du L., He L., Zhao K., Chang L., Yin G., Zhao H., Liu S., Tang Z., *ACS Nano*, 2014: 8, 12660-12668.
- [23] Xia W., Mahmood A., Zou R., Xu Q., *Energy Environ. Sci.*, 2015:8:1837-1866.