The glidarc plasma: an innovative method for the synthesis of heterogeneous catalysts

F. Hanon, E.M. Gaigneaux

Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium

Abstract: The goal of our research is to understand how the synthesis of catalysts by glidarc plasma (GP) does work, and how the methodology could be improved, with the ultimate objective to develop new catalysts thanks to this new economically and ecologically interesting route. We investigate the factors that have an impact on the ability of a precursor to react by GP, how the post-discharge is working and how this step can be used in a better way to develop interesting catalysts while making the method quicker.

Keywords: glidarc plasma, post-discharge, catalysts, (hydr)oxides, precipitation, radicals

1.Introduction

In the aim of preparing greener and cheaper catalysts, glidarc plasma (GP) appears as a promising technique (Fig.1). The glidarc reactor is a system operating at atmospheric pressure and quasi-ambient temperature. The radicals (OH°, NO°) generated by the discharge can induce the precipitation of the corresponding metals or (hydr)oxides of the precursor solutions exposed to the plasma. The fact that no precipitating agent is needed to induce the formation of the catalyst makes this method fast, easy and ecological.



Fig.1: Scheme of the glidarc plasma reactor

This method has already proved efficient for the synthesis of e.g. TiO_2 , SnO_2 , MnO_2 , FeO_x (photo)catalysts with interesting properties (Fig.2) [1-2]. For some of them (MnO_x and FeO_x), it was additionally observed that implementing a post-discharge (PD) step in their synthesis brings them valuable new properties as phase transformation, higher specific surface area and better catalytic activity (Fig.2) [3-4].



Fig.2: Scheme of the catalysts synthesis by glidarc plasma with and without the post-discharge step

In the literature, it is suggested that the reason why metallic precursors form precipitates during the discharge is mainly due to the principal species it generates (OH° and NO°). A similar explanation is proposed for the PD, saying that the solids transformation is due to the species generated during this step (H₂O₂, HNO₃ and HNO₂). However, these hypotheses were never proven, and some unexpected behaviours are observed. Actually, these explanations do not consider other factors that may also have an impact on the catalysts synthesis. Typically, the strong redox potential of the radicals should induce the reaction of any metal salt capable of forming a precipitate by redox reaction... but this is not the case, meaning that other factors need to be considered. Therefore, the aim of our research was to scrutinize the impact of different parameters on the ability of a metal precursor to form a precipitate when exposed to a GP and on the modification that a plasma-synthesized solid undergoes during the PD step. All this was done in order to understand more rigorously how the synthesis of catalysts by GP does work, and how the methodology could be improved, with the ultimate objective to develop new catalysts thanks to this innovative economically and ecologically interesting route.

2. Methodology

To synthesize catalysts by GP, metal precursors solution is exposed to the discharge until a precipitate appears (between 5min and 2h). If a PD maturation is done, the suspension obtained after the discharge is placed at 25° C for up to 72h or at 100°C for up to 3h. The solid is then recovered by centrifugation, dried overnight at 110°C and calcined at 400°C for 2h under air (Fig.1, Fig.2).

3. Results

We first tried to understand why some precursors do or do not form a precipitate when exposed to the GP. We discovered that the acidification of the medium due to HNO₃ and HNO₂ created during the discharge is one of the reasons why some metals or (hydr)oxides cannot be formed. Typically, all metal salts observed to precipitate under GP are indeed able to give a metal or (hydr)oxide in acidic medium contrary to the majority of the metallic precursors that do not precipitate under GP (Al, Bi, Co, Ni, ...). Knowing this, we tried to induce the precipitation of other precursors by controlling the pH of the solution during the exposure to a range where metal or (hydr)oxide can be obtained. This has been done by adding a buffer capable of withstanding the plasma discharge to the precursor solution (previously found by Moussa et al. [5]) or by using a precursor directly able to play the role of buffer (such as acetate salt). However, even under these conditions, a precipitate is not always obtained. This means that the acidification of the medium is not the only factor that explains the reactivity of a precursor through the GP.

We also understood that the oxidation state of the precursor and its ability to react spontaneously with water also dictate its capability to react by GP. Precisely, it seems that the plasma species can only carry out a redox reaction of a metal salt if it already tends to react by itself with air or water (by hydrolysis or redox reaction). Typically, among the precursors that react by GP, some tend to be spontaneously but slowly oxidized or reduced to (hydr)oxides in water (KMnO₄, TiCl₃, Fe(SO₄)₂, (NH₄)₂Fe(SO₄)₂) and others form an intermediate by hydrolysis before reacting with the plasma species (HAuCl₄, SnCl₂, SnSO₄).

Furthermore, we tried to understand how the plasma species interact with the precursor by observing how the reactive species (OH° , HNO_3 , HNO_2 , ...) are formed in the solution. The formation of OH° was monitored by exposing a coumarin solution to the plasma discharge. The reaction between OH° and coumarin creates a fluorescent product, the 7-hydroxycoumarin, which can be quantified by fluorescence spectrophotometry. Acidic species such as

HNO₃ and HNO₂ are easily quantified by measuring the pH of the medium during the exposure. By comparing the amount of OH^o and H⁺ species formed in a non-stirred aqueous solution, we observed that the majority of the reactive species are formed at the gas-liquid (G-L) interface and that they slowly diffuse down into the liquid phase during the exposure (Fig.3). Knowing this, we proved that the reaction between the plasma species and the precursor occurs mainly at the G-L interface. Indeed, when a metal salt (FeSO₄ or KMnO₄) is exposed to the discharge without stirring the solution during the exposure, the precipitate forms at the G-L interface before dispersing into the solution.



Fig.3: pH and amount of 7-hydroxycoumarin formed (due to the reaction between OH° and coumarin) in distilled water exposed to the GP without stirring at the interface G-L and in bulk

Finally, by using different types of gas sent between the electrodes (N₂, Ar, O₂), we confirmed that the types of species created have an impact on the ability of a precursor to react by GP. First, with Ar, the precipitation of precursors capable of reacting by humid air GP is indeed not observed, demonstrating the importance of certain species on the reaction. Furthermore, even when only N₂ or O₂ is used, some precursors (KMnO₄) can still precipitate. This means that there is not only one type of species (OH^{\circ} or NO^{\circ}) that reacts with the precursor to induce its precipitation. Even in the presence of N₂ or O₂ only, oxidizing and reducing species that induce the redox reaction of the precursor are created.

Regarding the PD step, we first investigate whether the PD species mentioned in the literature (H_2O_2 , HNO_2 and HNO_3) are indeed formed during this step. By UV-visible spectroscopy, we observed that HNO_2 is formed during the discharge but tends to be converted during the PD to HNO_3



Fig.4: pH and concentration of NO_2^- and NO_3^- in distilled water exposed to the GP during 45min then to a PD of 1, 2 and 3h at 100°C and of 24, 48 and 72h at 25°C

Although we proved that some species are formed during the PD step, we still did not know whether they have an impact the transformation of GP-synthesized solid. By submitting GP-synthesized FeO_x to a PD with and without the presence of PD species, we discovered that these species actually have no effect on how the precipitates transform since the same solids are obtained in both types of treatment. (Fig.5, Table.1) This PD is in fact mostly a thermal and temporal effect that allows the particles to grow.



Fig.5: Scheme of the FeO_x synthesis by GP + PD (3h-100°C) with and without the presence of PD species

Table 1: XPS, EDX, XRD, specific surface area and T50 for the benzene conversion of GP-synthesized $FeO_x + PD$ (3h-100°C) with and without the presence of PD species

			1						1		
Samples	Fe (% at)		O (%at)		S (%at)		N (% at)	Cristalline phases formed (from XRD) (%)		Specific surface area (m ² /g)	T50 for benzene total oxidation
	XPS	EDX	XPS	EDX	XPS	EDX	XPS	Fe ₂ O ₃	Fe2(SO4)3		(°C)
(NH ₄) ₂ Fe(SO ₄) ₂	27.7	30	65.6	67	5.3	2	1.3	63	37	112	333
+ PD (3h-100°C)											
(NH ₄) ₂ Fe(SO ₄) ₂	28.1	31	65.3	66	5.2	3	1.1	73	27	105	328
+ PD (3h-100°C)											
fresh water											

With this information, we optimized the GP synthesis by combining the PD thermal effect directly during the discharge by removing the cooling system during the exposure (Fig.1). This allowed to develop characteristics similar to those obtained along the PD, as larger surface area, smaller amount of "contaminating" phases (metals sulphates and hydroxychlorates) and thus better catalytic activity, while drastically decreasing the catalyst synthesis time (Fig.6). For example, in the total oxidation of benzene, SnO₂ synthesized from SnCl₂ by GP is catalytically more active when a PD step is performed but is even more active when synthesized under heat during the discharge. Furthermore, the SnO₂ synthesized by GP is much more active than when formed through another method (precipitation through base addition) (Fig.7).



Fig.6: Surface composition, specific surface area and T50 for the benzene total oxidation on solids obtained with Sn precursors exposed to the GP

(Fig.4). However, H_2O_2 never formed neither during the discharge nor during the PD.



Fig.7: Conversion of benzene to CO₂ as a function of the temperature of reaction of SnO₂ synthesized from SnCl₂ by GP and by precipitation through base addition

However, while adding a thermal effect directly during the discharge to achieve a PD-like effect works very well with Sn salts, this is not the case for all types of precursors. Indeed, with Fe salts, not using the cooling system during the synthesis promotes the development of "contaminating" phases and agglomeration of the particles, resulting in a solid less catalytically active. In this case, it appears that the temporal effect of the PD is necessary in the synthesis of FeO_x to transform it into more catalytically active solid (Fig.8).



Fig.6: Surface composition, specific surface area and T50 for the benzene total oxidation on solids obtained with Fe precursors exposed to the GP

Thus, adding a PD step in the GP synthesis of catalysts still allows the development of better catalysts and improves the yield of the synthesis by recovering more catalyst at the end. However, depending on the precursor used and the type of precipitate it develops, it may be preferable to perform a PD at room temperature, at a higher temperature, or to directly heat the system during the plasma exposure.

4. Conclusion

Our newly acquired better understanding of the impact of each factor during the discharge and the PD for the GP catalysts synthesis allowed us to adapt more easily the synthesis conditions to develop new catalysts with new properties. Furthermore, we are now able to propose different types of systems (without PD, with PD at room temperature or at 100°C, without PD but without cooling system) depending of what is preferred between fast synthesis, better yield, less energy brought to the system or better catalytic activity. This reinforces the interest of the GP by developing valuable solids while using interesting synthesis conditions compared to some classical methods such as greener and faster steps.

5. Acknowledgements

The authors thank the F.R.S.-F.N.R.S for the FRIA thesis grant awarded to F. Hanon, F. Devred for technical and logistical support, F.W. Boyom Tatchemo and S. Hermans for helping in the interpretation of some results, and B. Elias for the access to the fluorescence spectrophotometer setup.

6. References

[1] A. Tiya-Djowe; et al., J. Mater. Sci., 55, 4792–4807 (2020).

[2] A. Tiya-Djowe, et al., Catal. Today, 334, 104–112 (2019).

[3] A. Tiya-Djowe, et al., Appl. Catal. B Environ., 176– 177, 99–106 (2015).

[4] F. W. Boyom-Tatchemo, et al., Nanorods. Appl. Catal. Gen., 616, 118-109 (2021).

[5] D. Moussa et al., Eur. Phys. J. Appl. Phys., 29, 308-312 (2005)