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RESEARCH NOTE

Effect of the Nature of Carbon Catalysts on Glyphosate Synthesis

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Aqueous solutions of PMIDA (N-phosphonomethyliminodiacetic acid) were oxidized, using air, to obtain glyphosate (N-(phosphonomethyl)glycine) an active herbicide. The oxidative decarboxylation reaction was catalyzed selectively by active carbons obtained from different precursors and modified by specific thermal treatments. The activities were highly dependent upon the functional groups present on the carbon surface. Nitrogen-containing functional groups greatly enhanced the oxidation rates; these groups were either issued from the carbon precursors or introduced by thermal treatment under NH_3 of active carbons. The highest rates of PMIDA oxidation were obtained using nonactivated carbons treated with NH_3 at 900°C. Activities were also enhanced by thermal treatments at 900°C under N_2 which eliminated the acidic sites from the carbon surface, and possibly created active basic sites.

N-(phosphonomethyl)glycine (N-PMG) or glyphosate has been the subject of growing interest since its discovery in the 1970s. This molecule, sold under the name of Roundup®, is a herbicide with a broad spectrum of activity. It is very effective even on plant roots and has little harmful effects on the environment because of its biodegradability and absence of toxicicity for animal life (1). Due to its commercial success, many synthesis routes were described in the literature (2). The most important approach for the industrial production of N-PMG involves Mannich's condensation of iminodiacetic acid with paraformaldehyde and phosphorous acid yielding N-phosphonomethyliminodiacetic acid (PMIDA); this intermediate is then converted to glyphosate by an oxidative decarboxylation reaction (Scheme 1) which is catalyzed either under homogeneous conditions (e.g., with H_2O_2/H_2SO_4 or O_2/Co(II) systems) or in the presence of activated carbons or Pt–C catalysts with O_2 or air as the oxidizing agent. Whereas mechanistic aspects on homogeneous oxidation catalyzed by organometallic complexes were described (3–5), the influence of carbon catalysts on the oxidative decarboxylation reaction was, to our knowledge, never investigated. Active carbons are mainly employed as supports for metals and oxide catalysts, but they are by themselves active catalysts for chlorination, hydrodechlorination, and oxidation reactions (6). They are also used in the industrial production of chemical intermediates such as phosgene or sulfuryl chloride and for the catalytic removal of SO_2 or NO_x from flue gases. Oxidized carbons were also shown to be effective catalysts for acid–base reactions (7). As far as glyphosate synthesis is concerned, there are a few patents claiming the use of active carbons as catalysts for the oxidative decarboxylation of PMIDA. Different commercial active carbons were evaluated in this reaction and it was established that the reaction was faster at $pH < 4$ or $pH > 6$ (8). It was also claimed that the removal of surface oxides from activated carbon catalysts by thermal treatment may produce a two-fold increase of activity (9). The present work was intended to determine the influence of the chemical and physical properties of different carbons on the rate of PMIDA oxidative decarboxylation. Carbon catalysts, prepared from different natural or synthetic organic materials and submitted to various activating treatments, were evaluated. Then, some of them were modified by different post-treatments in order to improve their activity.

The oxidative decarboxylation of PMIDA was studied with various carbons including active carbons, carbon blacks, and graphite. The characteristics and the origin of these catalysts are given in Table 1. Extrudates were ground into powder and sieved to keep the particules under 80 μm. These carbons were submitted to various physical and chemical treatments described hereafter. Oxidations were carried out at room temperature for 24 h either with NaOCl solution (15% active chlorine) or with HNO_3 (68 wt%). To remove carboxylic groups, carbons were heated in a quartz boat under a flow of nitrogen at 2°C min^{-1} from 25 to 450, 700, or 900°C and this temperature was maintained for 15 h. The treated carbon was cooled to room temperature under nitrogen flow and used rapidly. Introduction of nitrogen was

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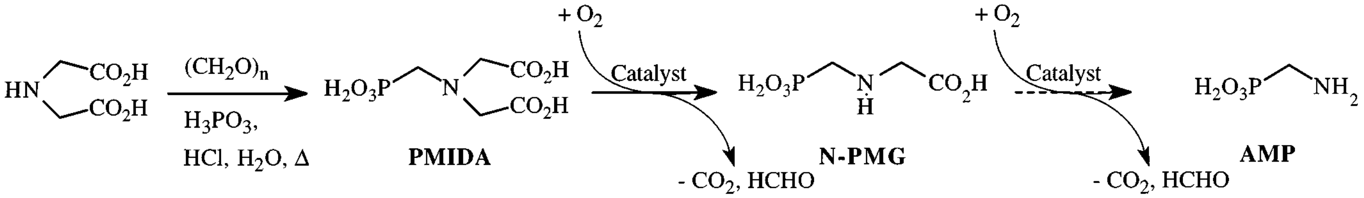

SCHEME 1. Synthesis of N-PMG (glyphosate) by oxidation of PMIDA.

realized by heating carbons at 5°C min^{-1} from 25 to 900°C under flowing nitrogen and maintained at this temperature for 5 h in a gas flow of ammonia (20 L h^{-1}; >99.96% purity). The carbon was cooled to 25°C under nitrogen and used rapidly. BET areas and pore volumes were obtained from nitrogen adsorption isotherms measured with a conventionnal sorptometer. Samples were outgassed by heating up to 200°C for 6 h under reduced pressure.

The catalytic oxidation of PMIDA was carried out in a 500-mL thermostated glass reactor equipped with mechanical stirring, condenser, thermometer, pH electrode (Mettler Toledo HA405-SC-S8/225), and inlet/outlet gas tubings equipped with a gas flowmeter. Then 12 g of PMIDA, 300 mL permuted water (0.17 mol L^{-1}), and 3 g of carbon were introduced in the reactor. The suspension was stirred continuously at 800 rpm under flowing nitrogen, heated to 95°C and maintained at this temperature for 90 min to ensure a complete dissolution of PMIDA; then, the nitrogen flow was stopped and air was flowed at 20 L h^{-1} which corresponded to time zero of the reaction. Samples of the reaction mixture were taken periodically and analyzed by HPLC (UV and RID detections) on a Hamilton PRP-X400 column with 5 m*M* K_2HPO_4 (pH 2.15) as eluent. The specific and areal activities of carbon catalysts, expressed in mmol h^{-1} g^{-1} and mmol h^{-1} m^{-2} 10^{-3}, respectively, were calculated from the slope of the linear curve giving the glyphosate yield as a function of time.

It was first verified that PMIDA was stable at the reaction temperature (95°C) in the presence of air and in the absence of active carbon. In contrast, in the absence of air but in the presence of active carbon, PMIDA underwent a low conversion (1%) to glyphosate. This oxidation could be attributed to small amounts of residual molecular oxygen or to oxygen from the oxygenated functional groups initially present on carbons. The oxidation was performed with different masses of carbon from 1 to 5 g; the initial rate of reaction increased linearily with catalyst mass, which indicated that the reaction kinetic was not limited by external mass transfer. In order to run the reaction until complete conversion of PMIDA within a 1 day time period, all the subsequent catalytic tests were conducted with 3 g of catalyst. The oxidation of PMIDA started as soon as air was flown in the reactor. The pH of the reaction medium increased steadily from its initial value of 1.5 and glyphosate was detected in solution by HPLC. The oxidative decarboxylation of PMIDA followed a similar kinetics on all the carbon catalysts investigated. This behavior is exemplified by the curve giving the product distribution as a function time (Fig. 1) obtained with the 4S catalyst described in Table 1. Until almost the complete conversion of PMIDA, the only reaction products formed were glyphosate and the decarboxylation co-products, CO_2 and HCHO. This means that a 100% selectivity to the desired product was achieved. The glyphosate yield was proportional to the reaction time

TABLE 1

Characteristics of Carbons and Activities in PMIDA Oxidation

Catalysts	Origin	S_{BET} (m^2 g^{-1})	Microporous volume (cm^3 g^{-1})	Specific activity r_S (mmol h^{-1} g^{-1})	Areal activity r_A (mmol h^{-1} m^{-2} 10^{-3})
4S	Active carbon from wood[a]	1164	0.88	2.8	2.4
CBP	*id*	146	0.05	0.3	2.1
AC40	*id*	1300		1.5	1.1
HSAG 300	graphite[b]	364	0.05	0.1	0.3
Vulcan XC72R	carbon black[c]	295	0.06	0.5	1.8
SX1G	Active carbon from peat[d]	1055	0.73	4.0	3.8
SNK	Active carbon from N-containing polymer[e]	1112	0.46	4.0	3.6

[a] From CECA.
[b] From Lonza.
[c] From Cabot.
[d] From Norit.
[e] From V. Strelko's laboratory (ISPE, Kiev, Ukraine).

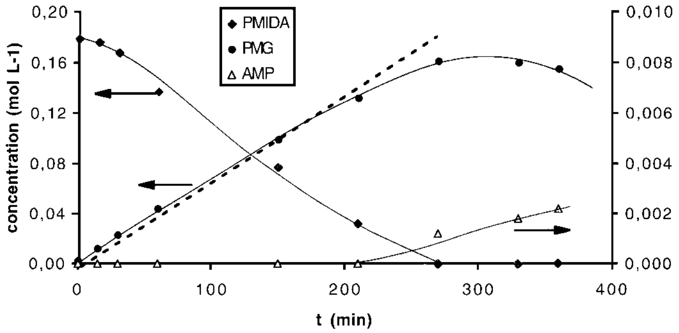

FIG. 1. Products distribution versus time for the oxidation with air at 95°C of 300 mL of aqueous solution of PMIDA (0.18 mol L^{-1}) over 3 g of active carbon 4S treated at 900°C under nitrogen.

which means that the conversion of PMIDA followed a zero order rate law. Then, at total PMIDA conversion, the yield of glyphosate started to decrease because it was converted into aminomethyl phosphonic acid (AMP) by a second oxidative decarboxylation (Scheme 1). These data indicate that PMIDA molecules are strongly adsorbed on the carbon surface. The glyphosate concentration, measured by analysis of solutions at total PMIDA conversion, was in the range 0.155–0.16 mol L^{-1}, i.e., smaller than the initial amount of PMIDA (0.17 mol L^{-1}). This was attributed to the retention in the catalyst pores of up to 10% of the glyphosate formed. It was verified with blank adsorption experiments carried out under nitrogen on 3 g of carbon suspended in 0.17 mol L^{-1} solution of glyphosate at 95°C, that the amount of glyphosate adsorbed on the carbon corresponded well to the deficit in glyphosate yield. The influence of the initial pH of the reaction medium on the reaction rate was investigated. Reactions carried out with 0.17 mol L^{-1} of PMIDA dissolved in 300 mL of 0.1 *M* solution of H_3PO_4 (pH 1) were 14% slower than those conducted in water (initial pH 1.5). In contrast, addition of even small amounts of KOH resulted in a large drop of activity, e.g., at pH 2.1 the catalyst experienced a four-fold rate decrease, and it was inactive at basic pH. The negative effect of alkali addition could be attributed to the formation of phosphonomethylimido diacetate ions which remained in the water solution rather than being adsorbed on the catalyst.

The specific and areal rates of activated carbons, carbon blacks, and graphite used without any pretreatment were compared in Table 1. Carbons with small surface areas (HSAG 300 graphite, Vulcan XC72R carbon black, and CBP activated carbon) had low specific activities. However, the comparison of areal rates indicates that there is no correlation between the activity and the surface area of catalysts which means that the catalytic activity in PMIDA oxidation depended on factors other than the surface area of the catalyst.

Since low active catalysts (graphite and carbon blacks) contained negligible amounts of mineral impurities with respect to active carbons, one may assume that these species, particularly transitions metal cations such as Fe^{2+} or Fe^{3+}, were the active sites for the oxidative decarboxylation of PMIDA. This hypothesis can be ruled out since we have verified that the addition of metallic salts such as $FeCl_2$ to catalyst AC40 produced the opposite effect, namely a rate decrease. Furthermore, SNK carbon issued from the carbonization of a synthetic polymer and thus containing no metal impurities was one of the most active catalysts (Tables 1 and 3). Therefore, one can conclude that mineral impurities including transitions metals ions were not involved in the mechanism of PMIDA oxidation.

Active carbons contain variable amounts of oxygenated functional groups such as carboxylic and phenolic groups (10). It may be assumed that these groups play a role in the adsorption of PMIDA as well as in the mechanism of oxidation. Catalyst 4S was submitted to different oxidizing treatments with NaOCl or with HNO_3 to increase the number of oxygen-containing groups (Table 2). The amount of acidic functional groups titrated with sodium hydroxide increased from 0.2 mmol g^{-1} for the untreated carbon to 1.3 and 2.9 mmol g^{-1} for the samples treated with HNO_3 and NaOCl, respectively. The specific activities of the latters were lower (1.5 and 1.1 mmol h^{-1} g^{-1} for HNO_3 and NaOCl, respectively) than that of the untreated carbon (2.8 mmol h^{-1} g^{-1}); the larger the amount of functional groups was, the lower the activity. The negative effect on the reaction rate of acidic functional groups was corroborated by experiments designed to eliminate these groups from active carbon 4S by thermal treatment under nitrogen at 450, 700, and 900°C. A TPD analysis indicated that oxygenated groups were eliminated at temperatures higher than 700°C. This was in accordance with the NaOH titration indicating that no acidic functions remained on the carbon treated at 900°C (Table 2). The specific rate measured on the active carbon treated at 900°C was 40% higher than those of samples still containing oxygenated functional groups. Such thermal treatment was known to create basic groups (pyrone-type basic groups) (11) which could be responsible for the catalytic activity.

The structure of active carbons is based on disoriented small graphite planes (12) which behave as large

TABLE 2

Influence of Acidic Groups on the Activity of Carbon 4S

Catalyst treatments	S_{BET} (m^2 g^{-1})	Acidic groups (mmol g^{-1})	Specific activity r_S (mmol h^{-1} g^{-1})	Areal activity r_A (mmol h^{-1} m^{-2} 10^{-3})
none	1164	0.2	2.8	2.4
NaOCl/RT	1243	1.3	1.5	1.2
HNO_3/RT		2.9	1.1	
N_2/900°C	940	≈ 0	4.0	4.2

polyaromatic molecules (graphene). It was shown by Voll and Böhm (13) that nitrogen atoms can substitute carbon atoms in the graphene structure under the form of −NH− or −N= functional groups (pyridine-like nitrogen) (14). It was inferred that the insertion of nitrogen atoms increases the electron density of the graphene structure which may favor electron transfer reactions, particularly oxidation reactions. Thus, nitrogen-containing active carbons were efficient catalysts for the oxidation of SO_2 to H_2SO_4 (15, 16). In the present investigation, the total nitrogen content of carbon catalysts were determined by elemental analysis. The data given in Table 3 show that the fresh (untreated) active carbons with the highest nitrogen content exhibited the largest specific and areal rates for the oxidative decarboxylation of PMIDA. Thus, active carbon SNK (2.1 wt% N_2), prepared by carbonization of nitrogen-containing polymers, and carbon Norit SX1G (0.34 wt% N_2), produced from peat, were more active than active carbon 4S derived from wood (0.03 wt% N_2). To corroborate these findings, nitrogen was incorporated in active carbon 4S by heating the sample at elevated temperatures in the presence of ammonia vapors, which, according to Stöhr *et al.* (14) should result in nitrogen incorporation in the structure. The treatment with NH_3 vapors at 900°C caused a partial gasification of the carbon accompanied with a 20 to 30% weight loss and a 30% increase of the surface area (Table 3). As expected, both the specific rate and the areal rate were greatly enhanced which indicates that additional active sites were created on the carbon surface. Starting from CBP, a low surface area raw carbon which was not activated by physical or chemical treatment, the same treatment under ammonia, produced a dramatic increase of the specific activity, and due to the low surface area of this carbon, the areal rate attained a record value of 11 mmol h^{-1} g^{-1}.

Considering the oxidation mechanism proposed in homogeneous conditions involving radical intermediates (4, 5) or N-oxide formation (18), we may assume that electronic transfers are also involved in the mechanism of oxidation by activated carbons, leading to the formation of activated oxygen (radical or peroxide) which can react with PMIDA. A similar interpretation, that is to say the insertion of nitrogen in the carbon structure enhancing the formation of active oxygen, was given previously for the oxidation of SO_2 (14, 17). However, the data given in Table 3 show that the activities were not proportional to the nitrogen content which means that the structure of the nitrogen functional groups could play a more important role than the sole nitrogen content. However the nature of these nitrogen groups was not yet established. It is noteworthy from the data given in Tables 2 and 3 that the treatment of active carbon 4S at 900°C under nitrogen also produced a marked increase of activity, although this treatment did not result in any significant incorporation of nitrogen (Table 3). As discussed in the previous section, this treatment produced a complete elimination of the acidic groups initially present on the carbon. Garten and Weiss (19) have proposed that this type of treatment should lead to the formation of various basic sites such as γ-pyrone. The activity enhancement for the oxidative decarboxylation of PMIDA experienced by active carbon 4S treated at 900°C under nitrogen may also be correlated with the presence of basic sites.

This study brings for the first time experimental results which throw some light on the synthesis of glyphosate by oxidative decarboxylation of PMIDA on active carbon catalysts. Although the mechanism of this reaction is not understood yet, some crucial factors controlling the activity have been identified. The activities of carbon catalysts were greatly enhanced by the presence of basic sites involving nitrogen atoms incorporated in the carbon structure. These heteroatoms were present either because the parent organic materials contained nitrogen or because nitrogen was incorporated in the active carbon by high temperature ammonia treatments. However, other types of basic sites formed by thermal treatment of the activated carbons at high temperature under nitrogen were also acting as active sites although they did not involve nitrogen heteroatoms. Future works will have to establish the precise nature of the basic sites on the active carbons, whether nitrogen-containing or not, which enhance the rate of PMIDA oxidative decarboxylation; this is a prerequisite step before one could account for the mechanism of this important industrial reaction.

TABLE 3

Influence of the Nitrogen Content on the Activities of Different Carbons

Catalysts	N total (%)	S_{BET} (m^2 g^{-1})	Microporous volume (cm^3 g^{-1})	Specific activity r_S (mmol h^{-1} g^{-1})	Areal activity r_A (mmol h^{-1} m^{-2} 10^{-3})
4S	0.03	1164	0.88	2.8	2.4
4S/N_2/900°C	0.05	940	0.7	4.0	4.2
4S/NH_3/900°C	4.2	1501	1.14	5.1	3.4
CBP		146	0.05	0.3	2.1
CBP/NH_3/900°C		462	0.20	5.1	11.0
Norit SX1G	0.34	1055	0.73	4.0	3.8
SNK	2.1	1112	0.46	4.0	3.6

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