Phosphorus-containing mesoporous carbon acid catalyst for methanol dehydration to dimethyl ether

María José Valero-Romero, Elisa María Calvo-Muñoz, Ramiro Ruiz-Rosas, José. Rodríguez-Mirasol, Tomás Cordero*

Universidad de Málaga, Andalucía Tech, Departamento de Ingeniería Química, Campus de Teatinos s/n, 29071 Málaga, España

ABSTRACT

Catalytic dehydration of methanol on an acid carbon catalyst prepared by chemical activation of olive stone with H_3PO_4 is reported. This preparation methodology produces carbons with a well-developed porous texture and highly thermally stable phosphorus surface complexes in form of $C–O–PO_3$ and $C–PO_3$. These P groups confer the carbon with a high oxidation resistance, surface acid and redox sites. In the absence of oxygen, the catalyst experimented a gradual deactivation due to coke deposition on the strong acid sites (P-OH) and reduction of the moderate-strength acid P-surface groups (from C–O–P to C–P type ones). The novelty of this research concerns the high catalytic stability in air atmosphere of this type of carbon with a steady state methanol conversion of 20% at 300ºC and selectivity towards dimethyl ether of 95%. The presence of oxygen in the reaction gas avoids coke deposition by continuously (re)oxidation of reduced P-surface groups, without gasification of the carbon catalyst.

KEYWORDS: Activated carbon, methanol dehydration, dimethyl ether, phosphorus, surface acidity.

1. INTRODUCTION

The development of efficient routes to transform biomass into useful chemicals and (bio) fuels is nowadays of primary importance due to depletion of petroleum and environmental concerns. Among the possible options for the valorization of biomass, the production of (bio) methanol has attracted considerable attention due to its versatility to be used as a source of a high amount of very valuable chemicals through different catalytic routes, such as methanol to gasoline (MTG process) [1, 2] or methanol to olefins (MTO process) [3-5]. Moreover, today methanol is the primary candidate, as a hydrogen carrier, for onsite or onboard production of hydrogen due to its high hydrogen to carbon ratio, low boiling point and availability [6].

The methanol dehydration reaction (MTD process) has also attracted worldwide attention to produce dimethyl ether (DME), an important environmentally benign, non-toxic and biodegradable product, whose global demand has significantly grown during the last decades, parallel to the increasingly stringent environmental regulations [7]. It is used in aerosol propellant formulations replacing banned chlorofluorocarbons (CFC) and as a building block for different chemicals, olefins and gasolines, recognized for having one of the greatest potentials as an alternative clean fuel [8]. The remarkable advantages of using DME as a fuel are its high cetane rating, similar efficiency to diesel-based fuels and the strong reduction of NO_x, sulfur dioxide, hydrocarbons and carbon monoxide emissions [9]. DME can be produced directly from syngas over bifunctional catalysts or by methanol dehydration over solid acid catalysts, such as pure or modified γ-aluminas (γ-Al_2O_3) and zeolites [10-12]. Most of these solid acid catalysts yield non-desirable hydrocarbons or are negatively affected by the presence of water. Besides, methanol dehydration produces catalysts fast deactivation owing to deposition of coke formed on the strong acid sites [13, 14]. Hence, the development of alternative catalysts that effectively succeed in overcoming the above-mentioned drawbacks would bring a great benefit. It has been claimed that the strength of the acid sites must be reduced to avoid coke deposition and to increase the selectivity to DME [8, 15, 16]. Regarding this issue, alkali metal-promoted zeolites are reported to have been used in the last years, showing an enhanced stability, wider operating temperature ranges and exhibiting a methanol conversion and dimethyl ether selectivity of more than 50 and 99 % respectively [10, 11, 17]. Other authors have also reported that an oxidative atmosphere for a dehydration reaction might enhance both the catalytic activity and stability of the catalysts by inhibiting or reducing carbon deposition and thus increasing longevity of the catalyst [18]. In addition to this, Lauagel *et al.*[17] reported that the presence of air may hinder the MTH reaction over H-[F]ZSM-4 zeolite (with low concentration of BA sites, 0.34 $\mathrm{mmol \cdot g^{-1}}$) in the dehydration of methanol, and maintain high selectivity towards DME up to 400 ºC.

Nevertheless, less effort has been focused on the study of methanol dehydration over activated carbons, despite their great potential and wide range of applications in catalysis[19]. This kind of materials have been receiving great attention in the last decades due to their great advantages, such as their very high thermal and chemical stability, high specific surface area and the possibility of having stable basic and acid surface sites as oxygen surface groups[20-22]. In addition to this, they can also be obtained from many different raw materials, including different types of lignocellulosic waste, which might give rise to not only an environmental but also an economical profit. To the best of our knowledge, there are only a few reports on the decomposition of methanol on activated carbons. Zawadzki *et al.* demonstrated that a non-oxidized carbon surface itself was not reactive in the dehydration reaction of methanol to dimethyl ether [23] and the carbon catalyst was only active after carbon oxidation by oxygen gas. Concerning this question, Moreno-Castilla *et al.* [24] studied methanol decomposition over acid activated carbons prepared by chemical treatment with different oxidizing agents. They reported that the activated carbon oxidized with $(NH_4)_2S_2O_8$ presented the strongest acid groups and showed the highest activity in the methanol dehydration reaction due to the presence of carboxylic surface groups. However, the temperature required for this reaction to take place resulted in a rapid decrease in its catalytic activity for methanol dehydration, which was associated to a gradual decomposition of the carboxylic groups present on the catalyst surface. Similar results were observed by Jasińska *et al.* using activated carbon samples oxidized with nitric acid, sulphuric acid and air [25].

Our research group has previously reported the preparation and characterization of activated carbons by chemical activation of different types of lignocellulosic waste with phosphoric acid [26, 27]. Carbons obtained by this conventional method, under certain preparation conditions, in a single step and without needing any additional chemical oxidation treatment, presented a relatively large amount of P-surface complexes. These P-surface groups showed a very high thermal stability and conferred a high oxidation resistance and surface acidity to the carbon, improving the potential of these materials for applications in catalysis [21, 28-33]. In fact, these carbon acid catalysts have proved their catalytic activity in the decomposition of 2-butanol, 2-propanol and ethanol, yielding essentially dehydration products [20, 28, 30] and this is the first time that they are studied for the decomposition of methanol. Most recently, experimental evidences were provided to explain that the presence of C–O–P type surface groups on this type of porous carbons are responsible of an interesting redox functionality of high chemical and thermal stability, as well as of the high oxidation resistance, surface acidity and high oxygen content [34]. In line with these results, the present work presents novel experimental results on the catalytic dehydration of methanol on a biomass-derived acid carbon catalyst obtained by chemical activation of olive stone waste with H_3PO_4, with special emphasis on the effect that molecular oxygen presents on the stability of the catalyst under this reaction. Therefore, the role and effect of P-surface groups of the carbon catalyst and oxygen and water vapor in the gas phase on the catalytic decomposition of methanol and on the stability of the carbon catalyst were investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Catalyst preparation

The carbon catalyst used in this work, denoted as ACP2800, was prepared through chemical activation of olive stone waste (provided by Sca Coop. And. Olivarera y Frutera San Isidro, Periana (Málaga)) with phosphoric acid, according to the experimental procedure reported in previous works [28, 34]. In brief, the carbonaceous precursor was impregnated with H_3PO_4 (85 wt. %) using an impregnation ratio of 2/1 (weight of H_3PO_4 per weight of olive stone) and dried at 60 ºC for 24 h. Subsequently, the impregnated sample was carbonized at 800 ºC for 2 h using a heating rate of 10 º/C min and a flow rate of N_2 of 150 cm^3 STP /min. The carbonized sample was then washed with distilled water until neutral pH of the eluate, dried at 100 ºC and sieved between 0.1-0.3 mm.

2.2. Catalyst characterization

Ultimate analysis (C, H, N, S amount) of the activated carbon was performed with a Leco CHNS-932 instrument. The amount of oxygen was calculated by difference.

N_2 adsorption/desorption isotherm and CO_2 adsorption isotherm at -196 and 0 ºC, respectively, were performed in an ASAP 2020 model equipment of Michromeritics. Prior to the experiments, the samples were degassed overnight at 150 ºC. From the N_2 adsorption isotherm, the apparent surface area (S_{BET}) was calculated applying the BET equation [35]. Application of the Dubinin-Radushkevich method [36] to the N_2 and CO_2 adsorption isotherm provided the micropore volume (V_{DR}^{N2}, V_{DR}^{CO2}) and the micropore surface area (A_{DR}^{CO2}). Finally, the mesopore volume (V_{mes}) was obtained as the difference between the adsorbed volume at a relative pressure of 0.95 and the micropore volume (V_{DR}^{N2}).

The surface chemistry of the fresh and used carbons was analyzed by X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD) and adsorption and temperature-programmed desorption of ammonia (NH_3-TPD), whereas the fresh carbon was also analyzed by methanol temperature-programmed surface reaction (CH_3OH-TPSR). The XPS analyses were obtained using a 5700C model Physical Electronics apparatus, with MgKα radiation (1253.6 eV). The binding energy of carbon (C_{1s}) was set at 284.5 eV and used as reference.

TPD and CH_3OH-TPSR experiments were performed in a quartz tubular reactor (i.d. 4 mm) connected to a mass spectrometer (Pfeiffer Omnistar GSD-301) and to non-dispersive infrared (NDIR) gas analyzers (Siemens ULTRAMAT 22). CO and CO_2 desorption rates were measured while heating 100 mg of sample in helium (purity 99.999%, Air Liquide) flow (200 cm^3 STP/min) from room temperature up to 900 ºC at a heating rate of 10 ºC/min. The CO and CO_2 desorption rates were measured with the non-dispersive infrared gas analyzers. The NH_3-TPD and CH_3OH-TPSR were carried out using 100 mg of catalyst that was saturated at 100 ºC with either NH_3 (20 % vol in Helium, 15 min) or methanol (4% in He, 90 min) flow (100 cm^3 STP/min), respectively. After saturation, the physisorbed probe NH_3 or CH_3OH molecules were removed from the surface of the sample by feeding pure He flow to the reactor for one hour at the same adsorption temperature. The TPD or TPSR runs were completed by heating the sample up to 500 ºC, using a heating rate of 10 ºC/min for NH_3-TPD and 5 ºC/min for CH_3OH-TPSR. Outlet concentrations were monitored by the mass spectroscopy. The registered m/z relations along with their assignations were: 2 (H_2), 4 (He), 17 (NH_3), 18 (H_2O), 26 (C_2H_4), 28 (CO), 30 (CH_2O), 31 (MeOH), 41 (C_3H_6), 44 (CO_2) and 45 (DME). The possible contribution of fragmented species on certain m/z lines was corrected by spectral subtraction considering the relative fragmentation coefficient of single compounds.

2.3. Methanol catalytic conversion

The gas phase methanol dehydration reaction was performed at atmospheric pressure using a fixed-bed quartz tubular reactor (i.d. 4 mm). For all experiments, 200 mg of catalyst

(0.1-0.3 mm) was used. Methanol was supplied to the system by using a syringe pump (Cole-Parmer® 74900-00-05 model). The reaction was carried out in air atmosphere in the temperature range 250–350 ºC and in helium atmosphere at 350 ºC. All the lines were kept at 130 ºC. The standard conditions were a methanol partial pressure of 0.02 atm and space time of 0.10 g·s/µmol (GHSV = 43 m^3_{STP} $kg^{-3}_{catalyst}$ h^{-1}). For the experiments under steam, the water vapor partial pressures were varied between 0.01 and 0.06 atm. The concentration of methanol and products in the outlet gas stream were analyzed by on line gas chromatography (490 micro-GC equipped with PPQ, 5A molsieve and Wax columns, Agilent).

3. RESULTS AND DISCUSSION

3.1. Characterization of the fresh carbon acid catalyst

The physical-chemical characteristics of the activated carbon catalyst are summarized in Table 1. The carbon catalyst showed a high specific surface area of 1380 m^2/g. The larger value of BET surface area measured with the data of the N_2 adsorption isotherm in relation to the one calculated from the CO_2 adsorption isotherm indicated a predominantly wide microporous structure for this activated carbon [37]. Besides, the high values of the mesopore volume and the external surface area confirmed that the carbon catalyst presented a significant contribution of mesoporosity. The presence of both a large surface area that provides a high amount of potentially active sites and a well-developed mesopore structure, which enhances the mass transfer rate, make this activated carbon very suitable for catalytic applications. In relation with the surface chemistry of the sample, the elements found on the activated carbon surface were mainly carbon (C, 87.1 wt. %) and oxygen (O, 9.2 wt. %), with a lower content of phosphorus (P, 3.5 wt. %) that remained quite stable on the carbon surface despite the washing process. The high surface oxygen amount observed on the activated carbon, despite having been carbonized in an inert atmosphere at high temperatures, is associated mostly to the presence of C–O–P type surface groups formed through the oxidation of C–P bonds once the carbon surface has been exposed to ambient air [34]. Combining XPS, inductively coupled plasma optical emission spectrometry (ICP-OES) and TPD characterization results, obtained from this type of activated carbon, it can be stated that these P compounds formed during the activation step seem to be homogeneously located and strongly bonded to the carbon surface [26, 34]. The maxima of the XPS P_{2P} peak is around 132.5-133.5 eV, which has been reported elsewhere as characteristic of the existence of P surface groups on carbon materials [20, 38]. From the deconvoluted XPS P_{2p} spectra of the carbon catalyst (Figure S1), the main peaks appear at 134.0 and 133.4 eV, associated to the presence of mainly C–O–P type surface groups, 33% (as in $C–O–PO_3$, $(CO)_2–PO_2$ and/or $(CO)_3–PO$), and C-P type surface groups, 50 % (as in $C–PO_3$ and/or $C_2–PO_2$), respectively [34, 39]. The contribution of more reduced P surface compounds such as $C_3–PO$ (17 %, at 132.3 eV) cannot be discarded [34]. The studies of phosphoric acid activated carbons by FTIR and solid-state NMR techniques also pointed out that the remaining P over the surface of the carbon is most likely in form of C–O–P and C–P groups[20, 40, 41].

Table 1. Porous textural and chemical properties of the fresh carbon catalyst (ACP2800).

N_2 isotherm					**XPS (Wt. %)**			**Surface acidity NH_3-TPD**
$S_{BET}^{N_2}$ (m²/g)	$V_{DR}^{N_2}$ (cm³/g)	V_{meso} (cm³/g)	$S_{DR}^{CO_2}$ (m²/g)	$V_{DR}^{CO_2}$ (cm³/g)	C_{1s}	O_{1s}	P_{2p}	µmol/g
1380	0.514	0.654	660	0.265	87.1	9.2	3.5	152

The total surface acidity for the activated carbon was determined by the amount of NH_3 desorbed in the NH_3-TPD per gram of sample (Figure 7). A value of 152 µmol/g was obtained for the fresh catalyst. The P–OH groups of these phosphate groups (as in $(CO)_2–PO_2$, $C–PO_2–$

O–C and/or C_2–PO_2), conferred to the carbon surface Brönsted acid sites, which were of primary importance in the acid character of these type of activated carbon catalysts for 2-butanol [30] and iso-propanol [20] dehydration reactions. The total acidity obtained for ACP2800 is significantly lower than that obtained also from NH_3-TPD, by conventional catalysts for the decomposition of methanol, such as HZSM-5 (Si/Al = 25)[17, 42] and Al_2O_3[43] with values about 1000 and between 227-608 µmol/g, respectively.

The chemical nature of the surface sites of the carbon catalyst has been also investigated by a methanol temperature-programmed surface reaction (CH_3OH-TPSR). This is a well-established technique to determine the chemical nature of the surface sites based on the gaseous desorption products, evolution of formaldehyde (CH_2O), dimethyl ether (CH_3OCH_3, DME) and carbon oxides indicates the presence of redox sites, acidic sites and basic sites, respectively [44-46]. This technique is also capable of providing information on surface intermediates [45, 47], as well as, monitoring the different steps of a heterogeneous catalytic process [48].

Figure 1 displays the intensity on m/z lines corresponding to the main detected compounds in the outlet gas during the TPD of ACP2800 after adsorption-desorption of methanol at 100 ºC. The main products were H_2O, CO_2, CO and H_2 (Figure 1a). A blank TPD, where the activated carbon was heated in absence of methanol, showed evolution of some of these compounds but in negligible amounts, so their presence in CH_3OH-TPSR can be ascribed to methanol decomposition. The formation of formaldehyde (Figure 1a) was also observed, indicating the presence of redox sites over the carbon surface. Finally, methanol condensation products, i.e., DME and light olefins, were also detected (Figure 1b) confirming the presence of acid sites.

Methanol seems to be mainly adsorbed in form of molecular methanol at temperatures lower than 250 ºC (Figure 1a). The methanol desorption profile shows two peaks, one at 125 ºC and a broad asymmetric peak at about 163 ºC, similar to that observed during CH_3OH-TPSR over H-ZSM-5 [48], TiO_2 [45] and molybdenum-heteropolyanions [44] catalysts. The higher methanol desorption peak has been attributed to the methanol adsorbed directly on the Brönsted sites of these catalysts, whereas the low temperature desorption peak has been associated to methanol molecules adsorbed/interacting with the methanol adsorbed directly on the Brönsted sites. Thus, formation of this protonated cluster would predict an Eley-Rideal mechanism for methanol dehydration on this type of activated carbons, which is the predominant reaction pathway in the literature for the formation of DME [48-51]. However, the presence of different adsorption acid sites for methanol decomposition cannot be discarded. In this sense, acid sites of lower strength, like that of C-O-P type, have been found on the surface of ACP2800 catalyst [32], in addition to the Brönsted acid sites of P-OH type. These less strong acid sites, of C-O-P type, may lead to the formation of DME by a different methanol reaction pathway.

The products of the dehydration of methanol, DME, m/z 45, and H_2O, m/z 18 were first observed at temperatures as low as 125 ºC and they were followed by ethylene (m/e 26) and propylene (41 m/e) desorption, which formation would require interaction between methanol and adsorbed DME molecules. The formation of these compounds at low temperature reveals that strong acid sites are present on the activated carbon. Furthermore, DME shows a broad desorption peak between 200 and 400 ºC. This temperature region coincides with the appearance of a second water peak and the onset desorption temperature of the hydrocarbons. The concentration of these compounds decayed during the ongoing TPSR, as methanol adsorbed molecules turned more isolated. This result also suggests the presence of moderate acid sites on the surface of ACP2800. Another interesting feature is that DME peak in the CH_3OH-TPSR experiment appeared at a temperature higher than that for the water peak, indicative that DME initially remains adsorbed on the acid active sites. On the other hand, remaining adsorbed methanol started to decompose in form of CO_2 at temperatures around 250 ºC and as carbon monoxide at higher temperatures, although in very small quantities.

A similar TPRS profile for methanol adsorbed on H-ZSM-5 catalyst was reported by M. Jayamurzthy *et al.* [48]. However, they also detected propane, butane and pentane with trace amount of methane and ethane at 350 ºC, indicative of the stronger acid character of H-ZSM-5 zeolite catalyst with respect to ACP2800. In fact, one of the main disadvantages for the selective formation of DME from methanol over this type of zeolites is the large amount of olefins formed [17]. Since the goal for this work is the selective formation of DME, the moderate-strength acidity of the prepared catalyst, as suggested by MeOH-TPRS results, can be seen as a positive feature.

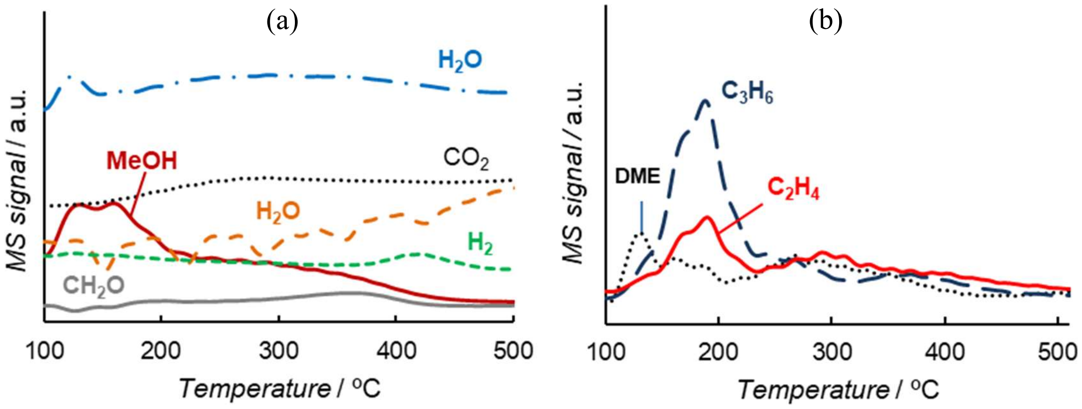

Figure 1. MS results from the CH_3OH-TPSR experiment over the ACP2800 activated carbon.

3.2. Methanol catalytic dehydration

The absence of mass and heat transfer limitations for the decomposition of methanol on the activated carbon catalyst in the fixed-bed tubular reactor used was confirmed to be negligible in the experimental conditions studied in this work by theoretical evaluation.[52, 53]

Figure 2 represents the methanol conversion, X_{MeOH}, as a function of time on stream (TOS) at reaction temperatures of 275, 300, 325 and 350 ºC in the presence of oxygen and at 350 ºC in the absence of oxygen ($P_{MeOH} = 0.02$, $W/F_{MeOH} = 0.01$ g·s/μmol). The presence of P complexes on the activated carbons surface prepared by chemical activation of lignocellulosic materials with phosphoric acid increases the oxidation resistance of the resulting carbons, as reported previously by our research group [34, 54]. Thus, this allows working at a reaction temperature as high as 350 ºC, under air atmosphere, without a noticeable gasification of the carbon catalyst. In fact, methanol dehydration in air over ACP2800 at 350 ºC for 2 h produced a carbon burn-off lower than 4 wt. %, which resulted in an increase of the carbon total pore volume of only 6 % with respect to the fresh sample (Table S1).

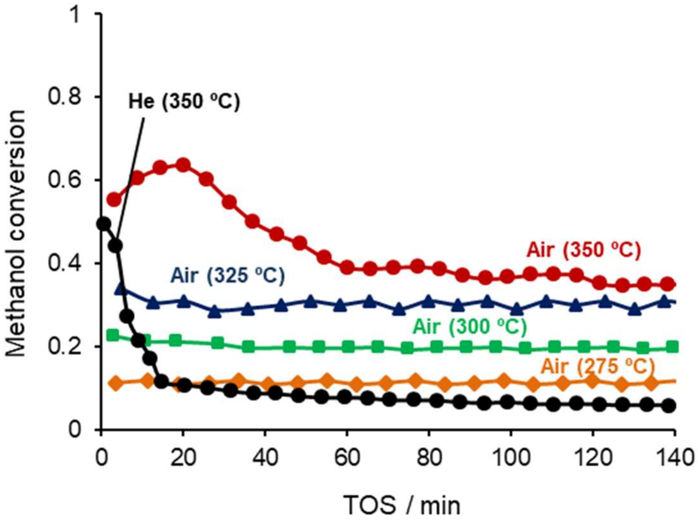

Figure 2. Methanol conversion as a function of TOS at different reaction temperatures in the presence (275, 300, 325 and 350 ºC) and absence (350 ºC) of air (P_{MeOH}=0.02 atm, W/F_{MeOH}=0.1 g·s/µmol).

As shown in Figure 2, in the absence of oxygen, methanol conversion decreased more than 80 % within the first 15 minutes of TOS, indicating that the catalyst undergoes relatively fast deactivation during the dehydration of methanol to DME. When air is used as part of the reaction gas mixture, however, a steady state was reached at temperatures from 275 to 325 ºC, in which methanol conversion remained constant. At 350 ºC, steady state conditions are also achieved, although a decrease of about 20 % from the initial methanol conversion is observed after 60 min of reaction, indicating a partial deactivation of the catalyst.

Table 2 summarizes the steady state conversion and selectivity values of the carbon-based products obtained at different reaction temperatures. When helium (He) was used as part of the reaction gas mixture at 350 ºC, the reaction product was mainly DME (selectivity of ~96%), although traces of CH_4, C_3H_6, C_2H_4 and even of dimetoxymethane (DMM) and methyl formate (MF) were detected in the product stream. Given that no molecular oxygen is present in the reaction gas, the presence of DMM and MF suggests that the carbon catalyst itself contains the oxygen source for partially oxidizing methanol. In this sense, we observed in a previous work that P surface groups of C-O-P type presented redox character [34]. Similarly, the use of air atmosphere yields DME as the main methanol dehydration product within the temperature range studied. As it is shown in Table 2, selectivity values to DME higher than 90 % were obtained at temperatures below 350 ºC. Furthermore, typical products of partial oxidation of methanol (CO_2, CO, DMM and MF) are more significant in the presence of air than those obtained in He atmosphere, although in very low quantity, and the amount of these products slightly increase with reaction temperature. In fact, the selectivity to DME slightly decreased only under air atmosphere at 350 ºC, when it is compared to that of the experiment carried out in the absence of oxygen, at iso-conversion conditions (43-42 %). The amount of CO and CO_2 produced during a blank experiment in the absence of methanol and under air atmosphere, being negligible below 325 ºC, was subtracted to that obtained during the decomposition of methanol. The result supports the fact that these compounds are formed because of methanol partial oxidation and not from direct methanol decomposition and/or from carbon catalyst gasification. The selectivity to carbon-based products as a function of TOS at 350 ºC on ACP2800 in air shown in Figure S2. Steady state conditions are reached after approximately 60 min.

Table 2. Steady-state methanol conversion and selectivity to carbon-based products at different reaction temperatures for reaction in air and He (P_{MeOH}=0.02 atm, W/F_{MeOH}=0.1 g·s/μmol).

T (ºC) - Atmosphere	**X_{MeOH} (%)**	**Selectivity (%)**							
		CH_3OCH_3	**CO_2**	**CO**	**$(CH_3O)_2CH_2$**	**$HCOOCH_3$**	**C_3H_6**	**C_2H_4**	**CH_4**

275-Air	11.7	94.2	2.0	2.6	0.3	0.3	0.4	-	-
300-Air	20.2	93.3	2.9	2.7	0.3	0.5	0.3	-	-
325-Air	29.6	91.1	3.8	3.2	1.2	0.5	0.2	-	-
350-Air	43.0	88.0	5.3	3.9	2.8	0.5	0.1	-	-
350-He	5.7	96.9	-	-	-	-	1.0	0.1	2.0
350-He	42.1[a]	96.0	0.4	0.3	0.04	0.04	0.8	0.1	2.1
350-He	11.5[a]	96.4	0.4	0.3	0.04	0.05	0.6	0.1	1.9

[a] Non steady-state methanol conversion.

Formaldehyde, which is a commonly observed product in the methanol oxidation reaction, was not detected. Formaldehyde is considered an intermediate in the formation of DMM, MF and carbon oxides [55]. Therefore, the increasing selectivity to CO_x with reaction temperature can be due to the oxidation of these intermediate products, and also to the presence of stronger acid sites on this activated carbon, which are able to retain the reaction intermediates products for longer time, allowing further oxidation of the intermediates. Nevertheless, the steady state selectivity to CO_2 and CO is in all the cases very low (never exceeding a value of 5.3%).

Figure 3a and 3b represents the steady-state methanol conversion and selectivity to main products as a function of the methanol partial pressure (from 0.010 to 0.04 atm) and as a function of TOS at an inlet methanol partial pressure of 0.02 atm, respectively, at a reaction temperature of 300 ºC. A significant increment in methanol conversion with increasing methanol partial pressure can be noticed, with the selectivity to DME remaining very high and practically constant. Almost no change in MeOH conversion (from 22 to 19 %), and selectivity to DME (from 94 to 92 %) is observed for the catalysts after 23 h on stream (Figure 3b). This result suggests that the catalyst does not suffer significant deactivation at longer reaction times at temperatures up to 300 ºC and under the experimental conditions used in this study, indicating a high stability of the available surface acid sites.

Higher reaction temperatures (>300 ºC) resulted in a slight decrease of methanol conversion at longer reaction times. These results seems to be related to the interaction of oxygen with the P-surface groups, forming C-O-P type groups, water and other OSG of lower thermal stability, which may decompose to CO and CO_2 under the reaction temperature studied and produce a slight gasification of the carbonaceous substrate with time.

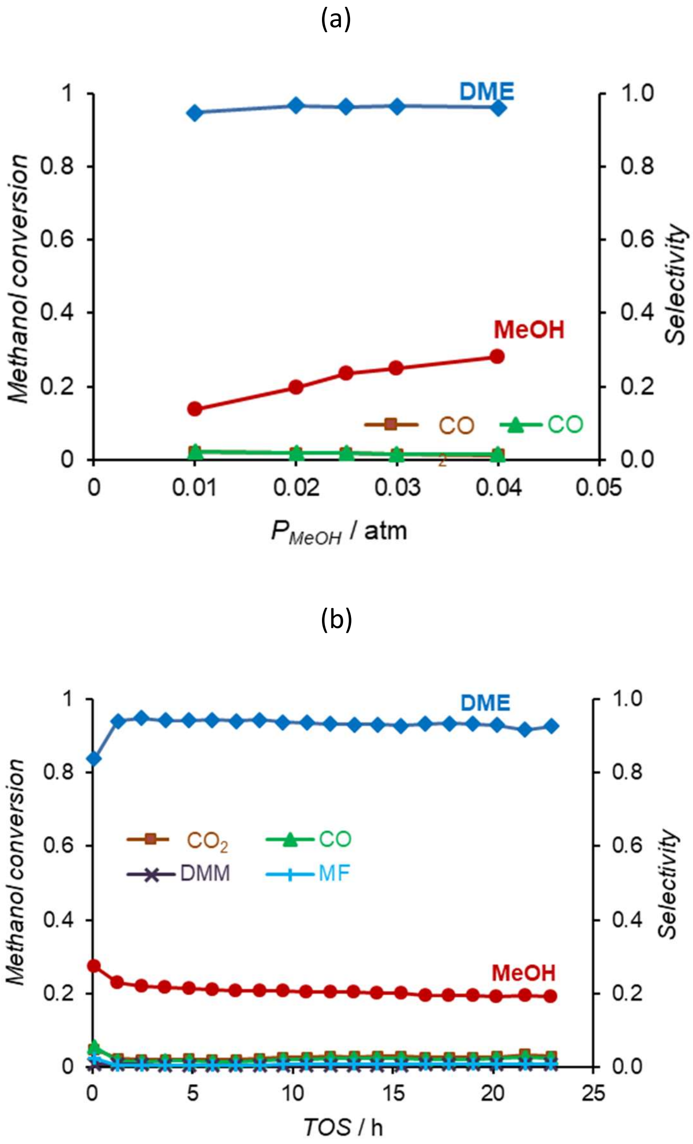

Figure 3. a) Steady-state methanol conversion as a function of the methanol partial pressure (W/F_{MeOH} = 0.1g·s/µmol), at a reaction temperature of 300 ºC. b) Conversion of methanol and selectivity to

carbon-based products as a function of TOS, at 300 ºC in air atmosphere (P_{MeOH} = 0.02atm, W/F_{MeOH} = 0.1g·s/µmol).

Having knowledge of the influence of the water vapor concentration in the inlet stream on methanol conversion and selectivity is of primary importance to investigate the ability of these carbon materials to catalyze the dehydration of methanol, given that water is usually found with methanol in the reactor feed during the industrial scale production of DME. Figure 4 shows the methanol steady state conversion and selectivity to DME, CO_2 and CO_2 for different inlet partial pressures of water vapor ($P_{H2O,}$ 0.01-0.06 atm) at 300 ºC in air. Both MeOH conversion and selectivity to DME decreased progressively from 20 to 11% and from 98 to 85%, respectively, when the water vapor content in the feed was raised to 0.04 atm. For higher concentrations of water vapor in the inlet gas, both the MeOH conversion and the DME selectivity did not suffer any further change, remaining constant at values of 11 and 85 %, respectively. The decrease of the methanol dehydration activity in the presence of water vapor has previously been reported in literature [56, 57]. Water is supposed to block the methanol dehydration active sites owing to a competitive adsorption with methanol on the catalyst surface [1]. However, the presence of water in the inlet stream shifted the equilibrium of the DME formation. Therefore, part of the observed decrease of the methanol conversion with the water vapor content up to 0.04 atm in the feed may be associated to thermodynamic reasons (see equilibrium conversions in Figure S3 in the absence and presence of water vapor). In addition to this, the fact that methanol could form hydrogen bonds with water molecules might also inhibit the rate of ether formation. Taqvi *et al.* [58] reported that the ability of methanol to form hydrogen bonds enhanced water and methanol adsorption on activated carbons. Rodríguez-Mirasol *et al.* [59] also found that methanol adsorption on activated carbons was enhanced in the presence of water and ascribed the increased methanol uptake to the formation of water clusters, which were supposed to appear around the chemisorption sites and act as additional adsorption sites. The formation of these clusters might avoid the reaction between a methanol molecule adsorbed on the active sites and a methanol molecule in the gas phase. The slight reduction of methanol conversion and selectivity to DME with water vapor may be due to a strong interaction between water molecules and isolated Brönsted acid active site, of P-OH type. The low influence of water vapor on the conversion of methanol and selectivity to DME observed at higher water vapor concentrations suggests a weak interaction between the water vapor and the surface active sites of less strong or moderate acidity, like those of the C-O-P type.

The influence of oxygen concentration in the inlet gas on the catalytic dehydration of methanol was also studied. Figure 5 shows the steady-state conversion of methanol as a function of temperature for different inlet oxygen concentrations. As it can be observed, the methanol conversion significantly increased with oxygen concentration in the gas phase from a methanol conversion of 5 % in He atmosphere to *c.a.* 20 % in air atmosphere at 300 ºC. Moreover, in the presence of 10 % oxygen, the catalyst was no longer deactivated and showed a conversion and selectivity behavior similar to the one observed for air in Figure 3 (data not shown). Therefore, a continuous supply and an excess of oxygen seem to be necessary to maintain the catalyst active, i.e., without deactivation.

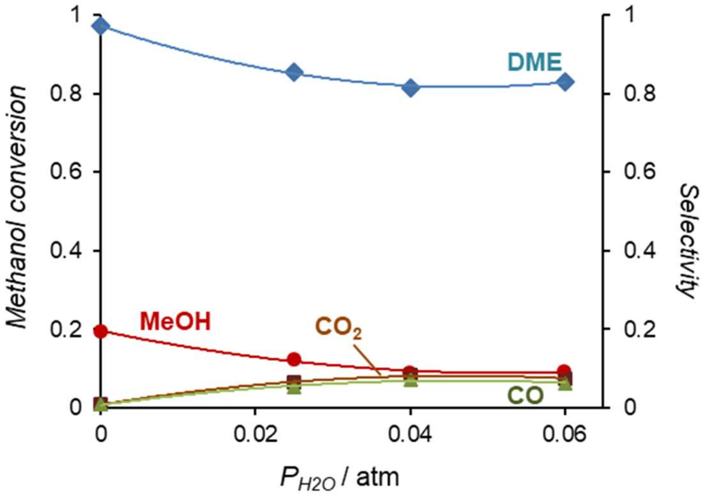

Figure 4. Evolution of the steady-state methanol conversion and selectivity to main products as a function of the inlet water vapor partial pressure at 300 ºC (P_{MeOH} = 0.020atm, W/F_{MeOH} = 0.10g·s/µmol).

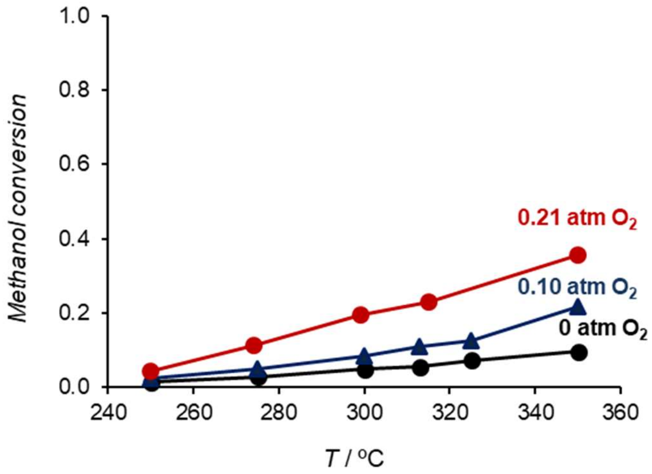

Figure 5. Evolution of the steady-state methanol conversion as a function of temperature and different oxygen partial pressures (P_{MeOH} = 0.020atm, W/F_{MeOH} = 0.10g·s/µmol).

All these results proved that the catalytic performance of ACP2800 for methanol dehydration is strongly influenced by the reaction atmosphere. Therefore, oxygen is most likely to actively intervene in the mechanism of this catalytic process inhibiting the deactivation of the catalyst, either by reacting with certain intermediate species or by interacting with the catalyst surface. In this sense, the used catalysts resulting from methanol decomposition in the presence and absence of oxygen are analyzed in detail in the following section, in order to elucidate the role of oxygen in the decomposition reaction of methanol on phosphoric acid activated carbons.

3.3. Role of oxygen on the catalyst activity

3.3.1. Characterization of used catalysts

The surface chemistry of the carbon catalyst was characterized after methanol decomposition using both He (ACP2800-RH) and air (ACP2800-RA) in the reaction gas mixtures and at a reaction temperature of 350 ºC for 2 h. ACP2800-O350 sample obtained after air oxidation of ACP2800 at 350 ºC for 2 h is also presented for comparison. Table 3 summarizes the mass surface concentration of the used catalysts. The amount of surface P decreases from 3.5 wt. % for the fresh carbon catalyst to 2.1 and 1.7 wt. % for the catalyst after reaction in both air and He atmospheres, respectively. Moreover, when using He as the reaction gas carrier, the carbon content increases significantly due to carbon species deposition, whereas in air the amount of surface carbon remains constant and the surface oxygen content increases, as a result of the carbon surface oxidation.

Table 3. XPS mass surface concentration (%) and phosphorous surface groups distribution (%) on ACP2800 before and after reaction in air and in He (350 ºC, 2h, P_{MeOH} = 0.02 atm; W/F_{MeOH} = 0.1 g·s/µmol).

	XPS (% wt)			**P_{2p} deconvolution**		
Sample	**C_{1s}**	**O_{1s}**	**P_{2p}**	**C–OPO_3**	**C–PO_3 and C_2PO_2**	**C_3PO**
ACP2800	87.1	9.2	3.5	33.3	49.5	17.2
ACP2800-O350	82.8	12.8	3.8	38.8	44.7	16.4
ACP2800-RA	85.6	11.8	2.1	35.2	49.6	15.1
ACP2800-RH	91.3	6.6	1.7	24.3	47.4	24.3

Figure 6 represents the P_{2p} zone of the XPS for the fresh carbon and for the used samples after methanol decomposition using air and He as carrier of the reaction gas, whereas the amount of the different surface P functional groups, obtained by the deconvolution of the different P_{2p} XPS spectra, are compiled at the last columns of Table 3. In general, the P_{2p} spectra of the samples show the main peak at a binding energy of about 133.7 eV, which is characteristic of pentavalent tetracoordinated phosphorus (PO_4) as in phosphates and/or polyphosphates[38, 40]. In the presence of He, the signal intensity clearly decreases with respect to that for the fresh sample and the P_{2p} peak shifts to lower binding energies, probably associated to the deposition of carbon species over the surface P acid species (P-OH of C–O–

PO_3 and C–PO_3 type groups) and to the reduction of the most oxygenated P groups (of C–O–P type) to C–PO_3, C_2PO_2 and/or C_3PO types, respectively. However, when the reaction takes place in the presence of air, in addition to a lower decrease of the signal intensity, the P_{2p} peak shifts to higher binding energies, characteristic of more oxygenated phosphorus compounds. The values reported in Table 3 confirm the higher amount of C–O–PO_3 type surface groups for ACP2800-RA with respect to those for ACP2800-RH and ACP2800.

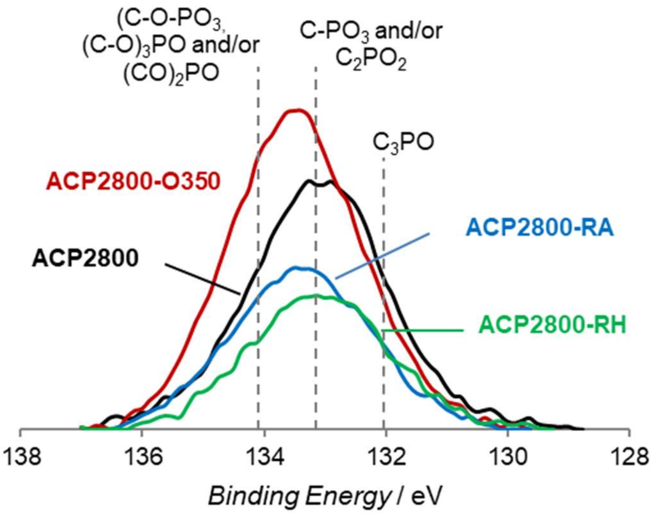

Figure 6. Normalized XPS spectra of ACP2800 before (black line) and after reaction (350 ºC, 2h) in air (blue line) and in He (green line) atmospheres.

To understand the distribution of surface acidity and strength of acid sites, the samples were further characterized by NH_3-TPD. Figure 7 shows the NH_3-TPD profiles for pristine ACP2800 and for the wasted catalysts used in oxidative and inert reaction atmospheres. The most intense desorption peaks can be observed *c.a.* 150 ºC (I) and 250 ºC (II). The first one is associated to the adsorbed NH_3 molecules on weak or moderate strength acidic surface groups; those groups of C–O–P type of the phosphate formed on the carbon surface during the activation process [34]. The peak observed at 250 ºC and the broad desorption peak at higher temperatures (III) may be due to the P-OH acidity of these phosphate groups, which confers to the carbon surface strong Brönsted acid sites [22, 33]. The population of surface acid sites differs considerably when the catalyst is used under different reaction atmospheres at 350 ºC. The total acidity, expressed as the total amount of NH_3 desorbed during the TPD, and the acid strength distribution obtained by integrating the area of the three NH_3-TPD peaks achieved by deconvolution of the curves are reported in Table 4. Reaction under inert atmosphere (see ACP2800-RH) significantly reduces the total surface acidity. Only a small amount of acid surface sites of less strength seems to be present on the surface of the carbon catalyst after deactivation in He atmosphere. This is an expected result, since strong acid-sites are known to promote the polymerization of olefins and thereby increase the rate of coke formation, thus being the main cause of catalysts deactivation in methanol decomposition reactions [10]. It has also been reported that deactivation by coke deposition can occur from adsorbed DME though condensation reactions [60, 61]. On the other hand, the catalyst after being used in air atmosphere (see ACP2800-RA in Fig. 7) is able to retain most of the surface acidity of (weak or) moderate strength and only strong Brönsted acid sites seem to be eliminated (deactivated) in such reaction conditions. This result reveals that the most important role played by oxygen is avoiding the deactivation of (weak or) moderate acid sites, which contributes to maintain the dehydration activity of the catalyst for long reaction times (see Figure 1).

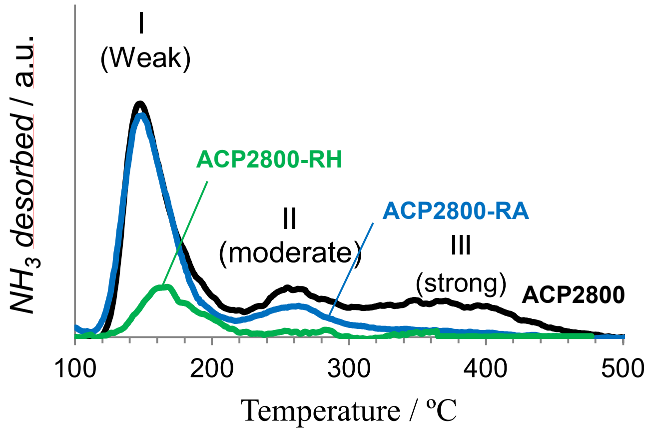

Figure 7. NH_3-TPD profiles of the catalyst before and after reaction in air and in He (350 ºC, 2h, $P_{MeOH} = 0.02$ atm; $W/F_{MeOH} = 0.1$ g·s/µmol).

Table 4. Estimation of the total acidity and acid strength obtained from NH_3-TPD

	Surface acidity (µmol NH_3/g_{cat})			
Sample	**Total**	**Weak**	**Moderate**	**Strong**
ACP2800	152	82	32	38
ACP2800-RA	104	79	19	6
ACP2800-RH	40	40	0	0

Figure 8 depicts the CO and CO_2 profiles obtained in TPD experiments for the fresh carbon catalysts and those used for methanol dehydration in the absence and presence of air at a reaction temperature of 350 ºC, whereas the total amounts of CO and CO_2 evolved and the total oxygen concentration are presented in Table 5. The samples show a significant CO (and to a lesser extent CO_2) evolution at temperatures higher than 750 ºC, which has been ascribed to the decomposition of stable C–O–P bonds of C–O–PO_3 (and O=CO–PO_3) surface groups, producing gaseous CO and C'–PO_3 surface groups [27, 34]. Here C' represent a new (or nascent) carbon site. Moreover, the fresh carbon, ACP2800, desorbs a small amount of CO_2 in the low temperature region, indicating the presence of carboxylic moieties, though in insignificant amounts.

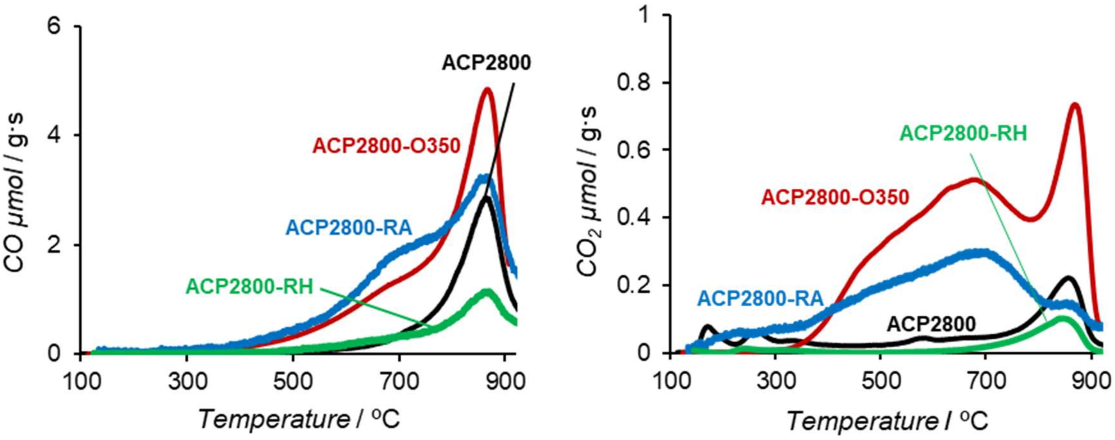

Figure 8. CO and CO_2 evolution during the TPD experiment of ACP2800 before and after reaction in air and in He (350ºC, 2h, P_{MeOH} = 0.02 atm; W/F_{MeOH} = 0.1 g·s/µmol); and after air oxidation of ACP2800 at 350 ºC, for 2h (ACP2800-O350).

Table 5. Total amount of CO and CO_2 produced in the TPD experiments for the fresh, oxidized and used activated carbons and total oxygen concentrations.

Sample	**CO** (µmol/g)	**CO_2** (µmol/g)	**O(TPD)**[a] % wt
ACP2800	2735	305	5.4
ACP2800-O350	5139	1321	12.5
ACP2800-RA	4700	740	9.9
ACP2800-RH[b]	1114	32	2.8

[a] Total oxygen calculated from the amounts of CO and CO_2 produced during the TPD

[b] The sample was exposed to ambient air before the TPD experiment

The amount of oxygen surface groups (OSG) decreased drastically when the methanol dehydration was carried out in He, in agreement with the results obtained from the XPS analyses. However, the total amount of CO and CO_2 evolved in the TPD for the case of the carbon used in reaction under air atmosphere increased with respect to that of the fresh sample (see also Table 5). This behavior is in agreement with previous results reported by our group [34], where we investigated the oxidation evolution of ACP2800 carbon surface in air at different temperatures (120-350 ºC). For comparison purpose, TPD of ACP2800 after air oxidation at 350 ºC for 2 h (ACP2800-O350) is also represented in Figure 8. We found that only after air oxidation at temperatures higher than 300 ºC, all the P surface groups with C–P bonds were completely oxidized to C–O–P ones. Other OSG that decomposes as CO or CO_2 at lower temperature (300-750ºC) were subsequently formed, such as phenolic, ether, anhydride and carbonyl groups (as CO) and lactone and anhydride groups (as CO_2) (see Fig. 8 for ACP2800-O350) [34]. These results suggested that these oxygen-containing P groups may facilitate the transfer of spillover oxygen on the activated carbon surface [62], which would explain the formation of other oxygen groups of lower thermal stability on the carbon surface once P surface groups are saturated with oxygen. The TPD profiles of ACP2800-RA revealed the same formation of OSG of lower thermal stability, whilst the CO desorption peak at 860 ºC did not reached the value of that obtained in the case of ACP2800-O350 (Figure 8). This fact together with the observed huge decrease in the amount of CO desorbed for ACP2800-RH suggest that the active sites are indeed the oxidized P surface groups (phosphate and/or polyphosphate) that decompose at around 860 ºC in the TPD experiment. These P surface groups are practically reduced by the products (or intermediates) of methanol dehydration reaction, producing the deactivation of the catalyst, in the case that oxygen is not present in the reaction mixture.

According to these results, there seems to be two (or probably three) different acid surface active sites. Those of higher acid strength (of P-OH type) that present the higher activity for methanol dehydration but are promptly deactivated. Those of moderate acid strength (of C-O-P type) that are less prompt to deactivation, but finally deactivate at longer TOS in the absence of oxygen in the gas phase. Finally, the fact that the reaction of methanol on ACP2800 in He atmosphere presents a residual methanol steady state conversion of about 8 % at 350 ºC (Figures 2 and 9) suggests the presence of a third type of active sites of weak acidity that are not easily deactivated in the absence of molecular oxygen in the reaction gas mixture. These active sites may be oxygen surface group of weak acid character, but of relatively high thermal stability, such as lactone, anhydride, phenol and/or ether type. The evolution of, particularly, CO_2 and also CO in the TPD profile for ACP2800 catalyst at temperatures lower than 750 ºC confirms the presence of these oxygen group on its surface.

The carbon catalyst presented in this work shows a good catalytic behavior for the methanol dehydration reaction if compared to that of other catalysts reported in the literature under similar operation conditions, with the noticeable advantage of having been obtained from an inexpensive industrial waste. The steady-state methanol conversion and reaction rate values (assuming differential reactor behavior, for conversion values lower than 0.15) obtained for ACP2800 in this work at 275 ºC in air (Figure 3) is 11.7 $mol_{MeOH}\cdot g_{cat}^{-1}\cdot s^{-1}$. This value is significantly higher than those obtained for SAPO-5 and $Cs_2HPW_{12}O_{40}$ (2.73 and 3.07 $mol_{MeOH}\cdot g_{cat}^{-1}\cdot s^{-1}$, respectively) at the same reaction temperature and similar to that reported for HY zeolite [17], despite the fact that lower space time values (almost 3 times lower) were used in the present work. Much higher values for methanol conversion were reported for alumina and HZSM-5 zeolite at 275 ºC (and higher space times). However, the selectivity to DME is drastically reduced over HZSM-5-based zeolites when the temperature is increased above 275 ºC under helium and/or air atmospheres, due to the strong acid character in this type of catalysts [17].

3.3.2. Catalyst stability and regeneration

To analyze the stability of carbon species (or coke) deposited on the catalyst active sites after the methanol reaction and the possible recovery of the activity of the catalyst (or regeneration of the active sites), a series of reactions in air-He-air (or regeneration in air) have been carried out. Figure 9 displays the evolution of the methanol conversion at 350 ºC (red marker, ○) and the selectivity to DME (red marker, ●) for the ACP2800 catalyst, in three successive reaction stages, using first methanol in air, later methanol in helium and finally, methanol in air again. Results for regeneration of the catalyst in air between the second and third reaction stages have also been included. The selectivity to all carbon-based products is depicted in Figure S4.

The results of the first stage of the experiment, in the presence of oxygen in the reaction gas, indicate that the catalyst is partially deactivated after 60 min of reaction. According to the NH_3-TPD results, only the moderate and weak acid sites seem to be stable enough at longer reaction times, at this temperature.

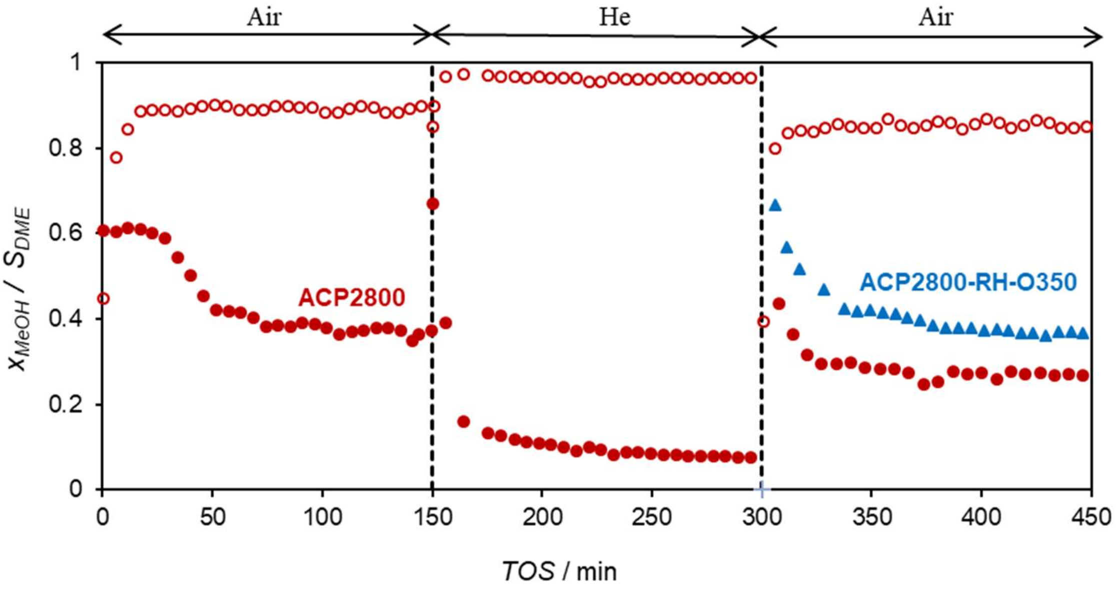

Figure 9. Methanol conversion and selectivity to DME as a function of TOS using first air (ACP2800 (X_{MeOH} ●, S_{DME} ○)), then He (ACP2800 (X_{MeOH} ●, S_{DME} ○)), and finally air as reaction gas (ACP2800-RH (X_{MeOH} ●, S_{DME} ○), ACP2800-RH-O350 (X_{MeOH} ▲)). (T=350 ºC, P_{MeOH} = 0.020 atm, W/F_{MeOH} = 0.10 g·s/μmol).

In the second stage of the experiment, where the reaction gas mixture was shifted to He, suppressing the oxygen supply, the methanol conversion decreased to a low value (8%, approximately), probably due to carbon species (C_xH_y) depositions on strong and moderate-strength acid sites, which are blocking and/or reducing those of P-OH and of C–O–P type groups, as it was revealed by the XPS and TPD results (Figure 6 and 8, respectively). In line with previous observations [34], phosphoric acid-activated carbons with a high relative concentration of C–P type surface groups presented a significantly lower acidity than those with a high concentration of C–O–P groups[34]. On the other hand, it seems that a small amount of weak acid surface sites that remained on the almost deactivated ACP2800 catalyst after reaction in He atmosphere, revealed by the NH_3-TPD for ACP2800-RH, produced a residual steady state conversion of methanol of approximately 8 %, with a selectivity to DME of almost 100 %.

After the deactivation of ACP2800 by methanol dehydration in a He flow for 150 min (second step), air was immediately introduced again in the last stage of the experiment. As it can be observed (Fig. 9, red symbols), the activity was almost restored and the steady state methanol conversion increased from 8 to 27 %, suggesting that oxygen can eliminate the carbonaceous deposits on the moderate acid sites in the reaction operation conditions. The selectivity to DME was also reestablished to the initial value, of about 90%.

Trying to completely restore the activity of the catalyst previously deactivated in He atmosphere, sample ACP2800-RH was afterwards oxidized in air for 2 h at 350 ºC, obtaining sample ACP2800-RH-O350. Subsequently, the methanol dehydration in air atmosphere on this carbon catalyst was studied again (Figure 9, blue marker, ▲, third stage). The catalyst recovered its activity, showing similar steady state methanol conversion (37 %) than the fresh ACP2800 catalyst. Nevertheless, the initial methanol conversion of about 60 % observed for ACP2800 within the first 40 min of reaction of stage 1 was not reached again. This loss of activity at short reaction times could be associated to the blockage of strong Brönsted type (P-OH) active sites by stable (more oxidation resistance) coke deposits, given that the regeneration process by oxidation in air at 350 ºC only seemed to (re)generate the active sites of C-O-P type.

All P surface groups seem to be of the CO_3PO type after regeneration in air, as derived from the large amount of CO evolved above 750 ºC in the TPD experiment (ACP2800-O350 in Fig. 8). During the regeneration of the deactivated catalysts, traces of H_2O, CO_2, CO and, in a lower extent, MeOH were detected in the gas outlet stream. Figure S5 compares the products detected as a function of time during the thermal treatment performed on the deactivated ACP2800-RH under air atmosphere with those of an experiment performed under He atmosphere. These results seem to support the fact that deposition of a light coke on the moderate acid active sites takes place, which is oxidized to CO_2 (CO and H_2O) in air atmosphere, under the reaction conditions used for regeneration. No desorption of adsorbed reaction products was detected. The oxidation of these carbonaceous deposits could be favored by the spillover of oxygen by P-surface groups, which seems to be more efficient than direct regeneration with gaseous oxygen [18]. On this question, Benito *et al.* [63] proved that deposited coke on a H-ZSM-5 catalyst in the temperature range between 300 and 400 ºC by methanol decomposition was very unstable (formed by alkylated aromatics and oligomers) and that it was possible to eliminate it by a degasification step (under vacuum of 10^{-4} mmHg at 300 ºC). They also pointed out that H-ZSM-5 catalyst under the conditions of the MTG process (350 - 450ºC) completely recuperated its activity only after a coke combustion step with air at high temperatures, 550 ºC [64].

In summary, from the catalytic and catalyst characterization results, it can be concluded that methanol decomposition over the surface of ACP2800 in air may be seen as the C-O-P type surface groups being reduced by methanol to produce DME and reduced P surface groups, which are (re)oxidized back to the C–O–P type groups by oxygen, producing water. Moreover, the spillover of oxygen by P-surface groups prevents these active surface sites from deactivation by carbonaceous deposits. This behavior would explain the higher CO desorption amount observed for the TPD profile of ACP2800-RA at around 860 ºC (ascribed to decomposition of C-O-P type surface groups) when compared to the one for ACP2800-RH (Figure 8). On the other hand, the (re)oxidation of the reduced P surface groups (in the presence of air) seems to be favored by oxygen spillover on the carbon surface, producing oxygen surface groups of weak acidity that could present some activity for the conversion of methanol to DME. In this sense, the greater production of CO (500-800 ºC) and CO_2 (200-800 ºC) observed for the TPD profile of ACP2800-RA in relation to those observed for ACP2800 and ACP2800-RH suggests that acid oxygen surface groups of a different nature have been formed on ACP2800 upon reaction with methanol in air.

4. CONCLUSION

A carbon catalyst prepared by chemical activation of olive stone waste with phosphoric acid at an impregnation ratio of 2/1 (weight of H_3PO_4 per weight of olive stone) and an activation temperature of 800 ºC has shown to be effective for the selective methanol dehydration to dimethyl ether. XPS analysis of this carbon catalyst demonstrated the presence of P in form of C–O–PO_3 and C–PO_3 surface groups, which confer to the carbon surface acid and redox sites, as it was also confirmed by MeOH-TPRS and NH_3-TPD.

The catalytic results evidenced that the atmosphere in which the reaction proceeded (air or helium) influences the catalyst behavior. Under helium atmosphere, the catalyst experimented a gradual deactivation, which is associated, on the one hand, to coke deposition formed on the strong Brönsted acid sites (P-OH), as determined from XPS and NH_3-TPD results of the used catalysts and, on the other hand, to the reduction of the carbon P surface groups of C–O–P type, determined by TPD experiments. Nevertheless, in the presence of oxygen in the reaction gas, the carbon surface is modified due to oxygen spillover (favored by the presence of surface P groups) on the carbon surface, preventing the carbon catalyst from deactivation and allowing the steady state methanol conversion to be reached. Methanol conversion and selectivity to DME were not very much affected when water vapor was added to the inlet stream of the reactor, showing the high stability of this catalyst under the reaction conditions studied.

ASSOCIATED CONTENT

Supporting Information

Figure S1-S5.

AUTHOR INFORMATION

Corresponding Author

*E-mail Address: mirasol@uma.es. Phone: +34 951952385. Fax Number: +34 951952385

ORCID

M. J. Valero-Romero: 0000-0003-0372-471X

R. Ruiz-Rosas: 0000-0001-8433-1808

J. Rodríguez-Mirasol: 0000-0003-3122-1220

T. Cordero: 0000-0002-3557-881X

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