

Thermoanalytical and XPS surface characterization of oxidized chars

F. Cerciello*, O. Senneca*, A. Coppola**, P. Salatino**

francesca.cerciello@unina.it

*Istituto di Ricerche sulla Combustione, C.N.R., Naples, Italy

**DICMAPI Università degli Studi di Napoli Federico II, Napoli, Italy

Abstract

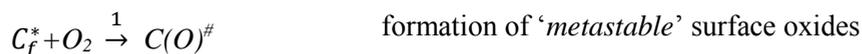
The chemical nature of the carbon–oxygen complexes on the surface of solid carbons was investigated with reference to a char from medium-rank coal (South African). Chars have been pre-oxidized in air at temperature $573 \text{ K} \leq T \leq 1073 \text{ K}$. The carbon oxides that populate the char surface and their evolution have then been investigated combining thermal analysis with core-level XPS Spectra, acquired at high-resolution using Synchrotron radiation. TPDs show that the amount of surface oxides is maximum after exposure to oxygen at 723 K, in correspondence to a carbon conversion degree of $\approx 20\%$. It decreases for higher temperature of oxidation and carbon burnoff. XPS show formation of epoxy functionalities at low temperature and their evolution into more stable oxides (carbonyl and ether-hydroxy) afterwards. The relative abundance of carbonyl/epoxy and ether-hydroxyl/epoxy on the carbon surface is in fact maximum for an oxidation temperature of 723 K and carbon burnoff of $\approx 20\%$. Results are analysed in the light of the semi-lumped kinetic models of carbon oxidation with a focus on the role and nature of surface oxides as intermediates in carbon gasification.

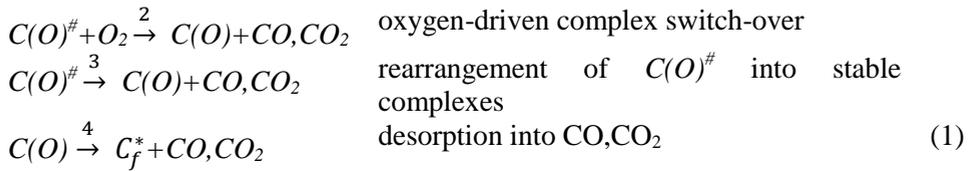
1. Introduction

The mechanism of carbon oxidation is a subject that, after extensive literature published [1-11], still raises great interest in a variety of research fields such as carbon combustion, oxidation of carbon-based materials, self-oxidation and safety issues in storage of carbons. Various reaction mechanisms and kinetic models have been proposed to explain the characteristics of consumption of O_2 , and formation of oxidation products in the gas and solid phases [1,4,6].

In the four-step mechanism proposed by Haynes [6] (eq.1), oxygen is firstly chemisorbed (non dissociatively) on a free carbon active site forming oxygen-carbon complexes (step 1) which can further on be released as CO and CO_2 (step 4).

The mechanism introduces the so called “switch over reaction” which describes the evolution of C-O complex from a less stable to a more stable one under the action of molecular oxygen (step 2). Alternatively, metastable oxides can be rearranged or isomerized into more energetically favourable forms (step 3). In the Haynes’ scheme all the reaction steps produce CO and CO_2 ,





Larciprete et al. [7-8] employed high resolution XPS spectroscopy (HR-XPS) with ab initio calculations and found that in the early stages of oxidation, epoxy is the dominant surface species, while ethers and C=O bonds become more abundant in the later stages of oxidation. Furthermore, they suggested that aligned epoxy groups tend to unzip into ethers due to the cumulative cleaving force exerted on the underlying C–C bonds. They found also that ether-epoxy pairs attract the diffusing epoxides and convert in lactone-ether pairs promoting the desorption of CO-CO₂. The role of epoxy interaction with surface oxides has been pointed out also by Montoya et al. [9] investigating the effect of neighbouring surface oxygen groups on the desorption of the CO molecule from carbonyl. They found different possible and energetically feasible CO desorption pathways as a consequence of surface oxides interactions.

Recently, Senneca et al. [10-11] underlined the key role of epoxy groups as metastable intermediates in the heterogeneous oxidation of coal, and investigated the thermicity of reactions occurring during oxidation (600-800 K) and during TPD experiments of char coal. Thermoanalytical methods (DTG, DSC, TPD) were used to identify the key reactive steps (chemisorption, structural rearrangement and switch-over of surface oxides, desorption) and their energetics.

In the present study, temperature programmed desorption experiments are supported by X-ray photoelectron spectroscopy (XPS) of oxidized char samples in order to highlight the distribution of functional groups formed upon coal char oxidation at different temperatures.

2. Experimental description

2.1 Oxidation and Desorption treatments in Thermobalance

South African char was used for the present study. Char samples were subjected to pre-oxidation treatments at $573 \text{ K} \leq T \leq 973 \text{ K}$ for times ranging from 10 to 45 minutes and Temperature Programmed Desorption (TPD) with analysis of evolved gas. Experiments were performed using NETSCH 409 CD apparatus connected with a NDIR CO and CO₂ analyser (ABB AO2020 Uras 14). In the pre-oxidation step the sample (20 mg) was heated to T_{ox} at the heating rate of 20 K/min in N₂ (250 mL/min) and held at this temperature for 5 min before switch in a flow of synthetic air (250 mL/min) for a time t_{ox} . The TPD experiment was performed heating the sample from up 473 K to 1573 K in nitrogen at the heating rate of 20 K/min and was held at temperature for 40 min. TPD gas evolution was worked out to obtain the CO-CO₂ released as a function of time/temperature. The amount of CO and CO₂ released has been normalized for w_0 .

2.1 Samples preparation for XPS

Oxidation treatments of char in the form of slabs were performed by heating up in electric oven under a flux of air to the temperatures $573 \text{ K} \leq T_{ox} \leq 1073 \text{ K}$. The treatments were carried out for t_{ox} ranging from 1 to 120 min. For comparison, isothermal combustion tests were carried out at the same combustion temperature T_{ox} . In this case, the sample was loaded in the TGA (Netzsch STA 409CD) in and heated up to T_{ox} in a flow of nitrogen (200 mL/min) at the heating rate of 20 K/min. Once the desired temperature was reached, the gas was switched over from nitrogen to air and the sample was held at T_{ox} for time t_{ox} . This procedure allows to estimate the carbon burnoff level.

2.2 Spectra acquisition of oxidized char samples

The XPS experiments were performed in the ultra high vacuum chamber (UHV) (base pressure 8×10^{-11} mbar) of the SuperESCA beamline at the Elettra synchrotron radiation facility (Trieste, Italy). Samples were in the form of slab of about 6 mm of diameter.

*Cl*s and *O*1s core level spectra were measured at photon energies of 400 and 650 eV, with energy resolutions of 80 and 150 meV, respectively. For each spectrum the binding energy position was calibrated by measuring the Fermi level of the Au reference sample.

To separate the contribution to the intensity of the inelastically scattered electrons and make a comparison of the individual spectra possible, the Shirley background was removed from each of them. Background subtraction was performed with the software *IGOR Pro* version 6.12A. Spectra were fitted, after background removal, with Doniach–Sunjic function convoluted with Gaussians [12]. Band assignment was carried out following the procedure used in [10-11].

3. Results

The following graph in Fig.1A shows as example the deconvolution of the *O*1s spectrum of the char oxidized at 573K. To highlight the influence of oxidation temperature on the nature of functional groups, the bar graph histogram in Fig.2A reports the calculated relative intensities of the components of the *O*1s according to eq.2. The intensity of each component of the *O*1s spectrum has been normalized for the Oxygen/Carbon content of the samples as detected by the XPS measurements. This procedure allows to take into account the different oxidation degrees. The qualitative analysis of the *O*1s spectra was carried out to better visualize and interpret the evolution of the carbon-oxygen functionalities during the oxidation process.

$$\%Intensity O_i = \frac{Area_{o_i}}{\sum_i Area_{o_i}} \cdot \left(\frac{\sum_i Area_{o_i}}{\sum_i Area_{C_i}} \right) \cdot 100; \quad \frac{\sum_i Area_{o_i}}{\sum_i Area_{C_i}} \cong \frac{[O]}{[C]} \quad (2)$$

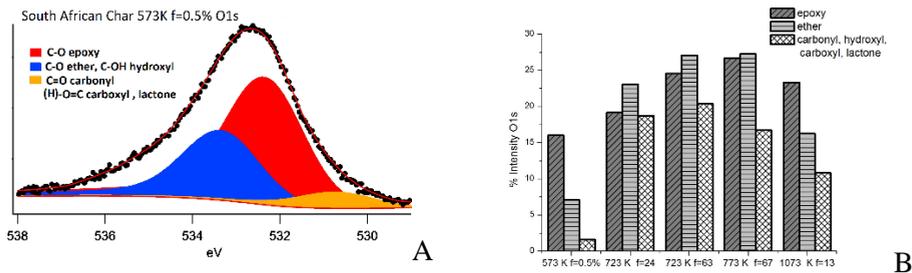


Figure 1. A) Oxygen functionalities obtained by deconvolution of O1s spectrum of char samples oxidized at 573 K. B) Intensities of the components of the O1s spectra of the different samples. The carbon burnoff level %of is also reported.

As can be seen from the O1s spectrum of the char oxidized at 573K, the main component, at about 532.2 eV, is due to epoxy groups. It follows that more than 15% of the oxygen present on the char surface is in the form of epoxides. The remained oxygen forms ethers-hydroxyls (7%), and carbonyls (2%). Their components are at 533.4 and 530.8 eV respectively.

Upon oxidation at 723-773 K the O1s spectrum clearly shows that extensive uptake of oxygen is taking place. In fact, a sharp rise in the intensity of the O1s signal is evident. An increase in the ratio of the intensity for all the species is observed. Reasonably, rearrangement of epoxides towards ether and carbonyl groups is the predominant event taking place on the surface of this sample. However, at 773 K, the O1s spectrum does not show further chemisorption of oxygen compared oxidation at 723 K. In particular the peak of ethers (27%) almost equals that of epoxy component (26%) with a decrease of the component at 530.8 eV (17%). Results suggest that structural rearrangement of epoxides towards ethers and carbonyls upon extensive oxidation promotes also the desorption of labile species. Upon oxidation at 1073 K the O1s spectrum still reveals the existence of the main component with epoxy group as predominant species, followed by ether and carbonyl component. Reasonably, due to the high temperature, desorption of labile species is the predominant event taking place on the surface of this sample.

Fig.2A-B show the ratio of ether-hydroxyl (533.4 eV)/epoxy (532 eV) and carbonyl-carboxyl (530.8 eV)/epoxy (532 eV) estimated from O1s spectra deconvolution. Fig.2C reports the total amount of gas released ($wCO+CO_2$)/ w_0 in the TPD experiments as function of pre-oxidation temperature. Notably the value of carbon conversion reached on the pre-oxidation step is also reported.

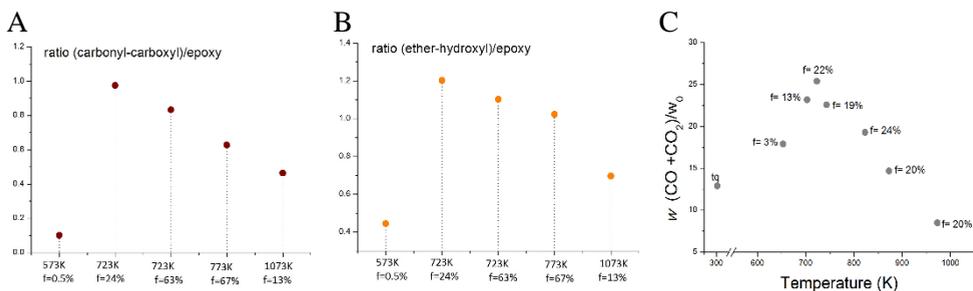


Figure 2. A) Ratio of (ether-hydroxyl)/epoxy and B) ratio of (carbonyl-carboxyl)/epoxy estimated from *O1s* spectra deconvolution. C) Gas released in TPDs as function of pre-oxidation temperature of char samples. The carbon burnoff level %*f* is also reported.

The plot in Fig 2C shows a progressive increase of surface oxide complexes with temperature of oxidation, up to 723 K, and with conversion, up to $\approx 20\%$. In the experiments at higher oxidation temperature roughly same carbon burnoff level is reached but the percentage of total gas released decreases. Notably, similar results have been suggested by the plots in Fig 2A-B. In fact, the plots show an increasing ratio of (ether-hydroxyl)/epoxy and (carbonyl-carboxyl)/epoxy from 573 to 723 K (reaching carbon burnoff of 24%), followed by a decrease for higher carbon burnoff and high temperature. This result confirms the high interaction between carbonyl/epoxy and ether-hydroxyl/epoxy groups upon oxidation at mild temperature and could explain the origin but also the different percentage of CO/CO₂ in TPDs.

4. Discussion and Conclusion

Correlating thermoanalytical and structural (XPS) characterization, suggests the effect of temperature of oxidation on the nature of the carbon–oxygen complexes. In particular, deconvolution of the *O1s* spectra provides valuable clues on epoxidation as being the prevalent type of oxygen functionalization when oxidation is performed at low temperature (early stage of oxidation). TPDs show that the amount of surface oxides is maximum after exposure to oxygen at 723 K, in correspondence to a carbon conversion degree of $\approx 20\%$. At the same time, *O1s* spectra show a more pronounced increase in the number of ether and carbonyl bonds. Experimental results are in substantial agreement with semiglobal reaction scheme that was assumed as the reference [11] and provide additional insight into the role of the individual reaction steps. Altogether TPD and XPS results suggest that the “metastable” oxides may prevalently consist of epoxy functionalities, whereas the more stable oxides would be composed by ether and carbonyl moieties. At higher temperatures, and upon extensive oxidation (in particular: $T \approx 723$ K, $f \approx 20$), “metastable” surface oxides (epoxy) evolve into more stable carbon–oxygen complexes (ether, carbonyl). Results underline the importance of evolution of the “metastable” oxides into more stable

oxides by complex-switch-over driven by molecular oxygen, and their interaction as being the reason of the enhanced CO-CO₂ released.

References

- [1] Hurt, R.H., Calo, J.M., “Semi-global intrinsic kinetics for char combustion modelling”, *Combust. Flame*. 125:1138-1149 (2001).
- [2] Du, Z., Sarofim, A.F., Longwell, J.P., “Kinetic Measurement and Modeling of Carbon Oxidation”, *Energy Fuels*. 5:214-221 (1991).
- [3] Wang, H., Dlugogorski, B.Z., Kennedy, E.M., “Analysis of the mechanism of the low-temperature oxidation of coal”, *Combust. Flam.* 134:107–117 (2003).
- [4] Wang, H., Dlugogorski, B.Z., Kennedy, E.M., “Coal oxidation at low temperatures: oxygen consumption, oxidation products, reaction mechanism and kinetic modelling”. *Prog. Energy Combust. Sci.* 29:487–513 (2003).
- [5] Zhuang, Q., Kyotani, T., Tomita, A., “Dynamics of Surface Oxygen Complexes during Carbon Gasification with Oxygen”. *Energy Fuels* 9:630-634 (1995).
- [6] Lear, A.E., Brown, T.C., Haynes, B.S., “Formation of metastable oxide complexes during the oxidation of carbons at low temperatures”. *Twenty-Third Symposium (International) on Combustion/The Combustion Institute* 23:1191–1197 (1991).
- [7] Larciprete, R., Fabris, S., Sun, T., Lacovig, P., Baraldi, A., Lizzit, S., “Dual Path Mechanism in the Thermal Reduction of Graphene Oxide”. *J. Am. Chem. Soc.* 133:17315–17321 (2011).
- [8] Larciprete, R., Lacovig, P., Gardonio, S., Baraldi, A., Lizzit, S., “Atomic Oxygen on Graphite: Chemical Characterization and Thermal Reduction”. *J. Phys. Chem.* 116:9900–9908 (2012).
- [9] Montoya, A., Truong, T., Mondragon, F., Truong, T.N., “CO Desorption from Oxygen Species on Carbonaceous Surface: 1. Effects of the Local Structure of the Active Site and the Surface Coverage”. *J. Phys. Chem. A* 105:6757–6764 (2001).
- [10] Levi, G., Senneca, O., Causà, M., Salatino, P., Lacovig, P., Lizzit, S., “Probing the chemical nature of surface oxides during coal char oxidation by high-resolution XPS”. *Carbon* 90:181–196 (2015).
- [11] Levi, G., Causà, M., Lacovig, P., Salatino, P., Senneca, O., “Mechanism and thermochemistry of coal char oxidation and desorption of surface oxides”. *Energy Fuels* 31:2308–2316 (2017).
- [12] Doniach, S., Šunjić, M., “Many-electron singularity in X-ray photoemission and X-ray line spectra from metals”. *J. Phys. C: Solid State Phys.* 3:285-291 (1970).