

Influence of Metallic Oxides on Oxidative Stability and Electrical Properties of Fullerene C₆₀

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Abstract. The results of examinations on the influence of three different metal oxides on the oxidative stability and electrical conductivity of fullerene C₆₀ are presented. Observed increased oxidation stability of C₆₀ in presence of ZrO₂ can be explained only by Long and Sykes electron transfer theory. Activity of metal oxides, i.e. thermal stability of MeO/C₆₀ samples is in functional liaison with electrical conductivity of samples, which gives additional support to the theory of electron transfer between carbon and metallic oxide.

Introduction

Process of carbon oxidation is still of great interest not only because of coal combustion [1], diesel soot [2] etc., but also because of need for increased oxidative stability of many carbon based materials such as carbon/carbon composites. Ideal material for this type of investigations is fullerene C₆₀ because of his closed cage structure, i.e. all of its carbon bonds are saturated with another carbon atom and no heteroatoms are bonded to his surface. This also makes it especially suitable for examination of the influence of different additives on carbon oxidation process. Catalytic influence of many additives on carbon oxidation process is well known. Inhibitory effect is less often observed [3,4], and usually, it can be explained only by Long and Sykes electron-transfer theory [5,6]. Metallic oxides, especially the oxides of transitional metals, are additives that are extensively studied not only in carbon oxidation reactions, but also in a variety of industrially applicable chemical reactions [6,7]. It is found that their catalytic activity or inactivity depends on the electronic structure of corresponding metal ion. For many different oxidation reactions [7,8], activity maximum appears for oxides having metal ions with partially filled d-orbital (d¹-d⁴, d⁶-d⁹) and activity minimum or total inactivity for those having d-orbital completely filled (d¹⁰) or empty (d⁰ i.e. p⁶, s²). Activity of those that possess half-filled d-orbital (d⁵) is usually in between these two main groups. Yamaguchi et al. [3], in their DTA study, observed both catalytic and inhibitory effect of several refractory oxides on oxidation of graphite, and explained it by well-known electron transfer theory postulated by Long and Sykes. This theory postulates that the additives which are acceptors of electrons will behave as catalyst and those which are donors will behave as inhibitors during carbon oxidation reaction. Acceptors will facilitate the evolution of CO, while donors will make evolution of CO more difficult.

The results of examinations on the influence of three different metal oxides on the oxidative stability and electrical conductivity of fullerene C₆₀ are presented in this paper. Oxides examined in this study are usually found to be the most active (Co₂O₃), medium

active (Fe_2O_3) and neutral or inhibitor (ZrO_2) for oxidation reactions of many organic molecules, graphite, soot etc. [1-3,7,8].

Experimental

All materials used in this study were of p.a. purity. Metallic oxides (MeO) and C_{60} powders are mixed in an agate mortar in wt% ratio 50:50 for the purpose of TGA analysis (non-isothermal: heating rate 15 K/min; atmosphere of flowing air, 40 cm^3/min). Electrical conductivity was measured on pellets with 1:1 molar ratio for C_{60} and corresponding metal ion (Me^{+n}) present in oxide (atmosphere of static air).

Results

Results of TGA analysis of MeO/ C_{60} mixtures and C_{60} alone are given in Table 1. Activity of oxides can be seen through several parameters which are defined as follow: $T_{3\%}$ - temperature where mass loss due to C_{60} oxidation reaches 3 wt%, (i.e. temperature where oxidation reaction begins); T_{max} - temperature where reaction rate has a maximum value (obtained from DTG curve); V_{max} - maximum value for the reaction rate (obtained from DTG-curve).

Table 1. Parameters obtained from TGA and DTG curves of MeO/ C_{60} mixtures.

Sample	$T_{3\%}$ (K)	T_{max} (K)	V_{max} (wt%/min)
$\text{ZrO}_2/\text{C}_{60}$	750	784	16
$\text{Fe}_2\text{O}_3/\text{C}_{60}$	675	698	190
$\text{Co}_2\text{O}_3/\text{C}_{60}$	560	585	200
C_{60}	713	757	137

The relative activity of oxides is in good agreement with the literature data: Co_2O_3 (d^6) is the most active, $\text{Fe}_2\text{O}_3/\text{C}_{60}$ (d^5) shows medium activity, while ZrO_2 (p^6 i.e. d^0) has an inhibitory influence on C_{60} oxidation compared with the values for pure C_{60} . Catalytic activity for Co_2O_3 and Fe_2O_3 can be explained by electron transfer theory, but it can be also explained by modified cyclo-redox theory [2], i.e. by the surface-redox process wherein the surface layer of metallic oxide is reduced by carbon and then oxidized again in reaction with gaseous oxygen. However, the inhibitory effect of ZrO_2 can be explained only by Long and Sykes electron transfer theory. According to the literature, oxides with partly filled d-orbital of cations are expected to be electron acceptors, while those with filled d-orbital (or without d-orbital) are expected to be electron donors [3, 7-10]. Activity of metal oxides observed in the literature and in this work, strongly supports electron transfer theory, at least when oxidation of C_{60} and graphite is considered.

By our best knowledge, none of the literature studies concerning influence of metallic oxides on oxidation of graphite and similar materials examine the possible changes in electrical conductivity of carbon specimen, which should occur due to electron transfers from or to metallic oxide, according to Long and Sykes theory. Considering these facts, we decided to measure the electrical conductivity of C_{60} pellet and pellets made of MeO/ C_{60} mixtures, which contain only a small amount of oxides (10-15 wt% i.e. 3.5 - 5 vol % of MeO) in order to avoid formation of undesirable continuous oxide paths through the pellet but large enough (1 mol of kation Me^{+n} per 1 mol of C_{60}) to produce measurable changes in conductivity of crystalline C_{60} . Temperature dependence of electrical conductivity (χ) for these samples is presented in Fig 1.

From Fig. 1a one can see that all samples show almost perfect semiconductor-like exponential conductivity growth with temperature, except Co₂O₃/C₆₀ sample having an anomaly around 420 K. It is also obvious that conductivity values for different mixtures measured at the same temperature follow the same pattern as the activity of oxides observed in TGA experiment. In general, conductivities decrease in the following order: Co₂O₃/C₆₀ > Fe₂O₃/C₆₀ > C₆₀ > ZrO₂/C₆₀, and similar order can be obtained by comparing values of V_{max} or T_{3%} or T_{max} (Table 1). From this point of view, it is evident that the activity of oxides, i.e. thermal stability of MeO/C₆₀ mixtures is in functional liaison with their conductivity, supporting the theory of electron transfer between carbon and metallic oxide. Problems arise from the fact that acceptors (Co₂O₃, Fe₂O₃) should decrease conductivity of C₆₀ if electrons are transferred from C₆₀ to oxide. Because C₆₀ is an n-type semiconductor [11], reducing the number of free electrons means that number of carriers decreases, and, consequently, conductivity should be expected to decrease. This was observed when conductivity of crystalline C₆₀ was measured in vacuum and in air [11]: conductivity values in air are much lower because oxygen adsorbed on C₆₀ accepts electrons and thus reduces the conductivity of C₆₀. The same point of view may be applied when conductivity of ZrO₂/C₆₀ mixture is considered: if zirconium oxide really transfers electrons to C₆₀, conductivity of C₆₀ should increase. Thus, the obtained results for changes of electrical conductivity of C₆₀ were opposite than expected. The reason for this behavior may be due to two possible reasons: 1) mechanism for electrical conductivity of C₆₀ is still not well understood [11], and some anomalous effects are lacking the proper explanation; 2) although simple explanations presented in Long and Sykes theory may be useful in predicting the influence of metallic oxides on carbon oxidation, this may not be completely a true picture of how acceptors or donors influence the mechanism of carbon oxidation.

Applying the well-known equations apparent activation energy (E_a) can be calculated from the linear portions of curves shown in Fig. 1b:

$$\chi = \chi_0 \exp(-E_a/RT) \quad (1)$$

$$\log \chi = \log \chi_0 - (E_a/2.303RT) \quad (2)$$

where R is universal gas constant (8.314 J/molK) and T is absolute temperature (K). Therefore, the plot of $\log \chi$ versus $1/T$ gives a straight line and the magnitude of the slope gives E_a i.e. conduction energy gap. Apparent activation energies for C₆₀, Fe₂O₃/C₆₀, ZrO₂/C₆₀ and Co₂O₃/C₆₀ samples are presented in Table 2. Linear portions of curves used for determination of E_a for C₆₀, Fe₂O₃/C₆₀ and ZrO₂/C₆₀ samples lie in the temperature interval 365-475 K, while Co₂O₃/C₆₀ sample show two linear regions: 315-410 K and 430-475 K.

E_a values for C₆₀ and ZrO₂/C₆₀ samples are almost equal (within the limits of the standard deviation), while value for Fe₂O₃/C₆₀ is lower. The E_a values for Co₂O₃/C₆₀ sample are significantly lower than for other samples and only a value obtained for high temperature region (60 kJ/mol; 430-475 K) can be to a certain degree compared with E_a values for other samples, because low temperature value (27.5 kJ/mol; 315-410 K) cannot be compared with other samples since their curves are not linear in that temperature region. E_a values follow nearly the same pattern of order previously obtained for values of χ , T_{3%}, T_{max} and V_{max}. E_a values decrease in the following order: C₆₀ ≥ ZrO₂/C₆₀ > Fe₂O₃/C₆₀ > Co₂O₃/C₆₀. As we previously stated, lower value for E_a means that electrons require less energy to overcome the band gap and jump into the conduction band. This can be interpreted as follows. If we assume, that due to the addition of Co₂O₃ or Fe₂O₃ whose kations possess partly filled d-orbitals (3d⁶ and 3d⁵ respectively) and empty 4s orbitals,

acceptor levels are introduced into the band gap of pristine C_{60} . Since Zr^{+4} kation in ZrO_2 possesses completely filled $4p^6$ orbital, first available empty orbital is $5s$ which is substantially higher than $3d$ and $4s$ orbitals and acceptor levels introduced by ZrO_2 are positioned higher than those introduced by Co_2O_3/C_{60} and Fe_2O_3/C_{60} . This may be a way to understand why E_a values for Co_2O_3/C_{60} , Fe_2O_3/C_{60} and ZrO_2/C_{60} lie in the observed order, and especially the reason for higher conductivities of Co_2O_3/C_{60} and Fe_2O_3/C_{60} samples than C_{60} sample, bearing in mind that $\chi \sim 1/E_a$ (Eq. 1). However, this cannot explain the lower conductivity value of ZrO_2/C_{60} sample compared to C_{60} sample. Even if we assume that $4p^6$ orbitals of Zr^{+4} introduce the donor levels into the band gap of pristine C_{60} , it still cannot explain this phenomenon.

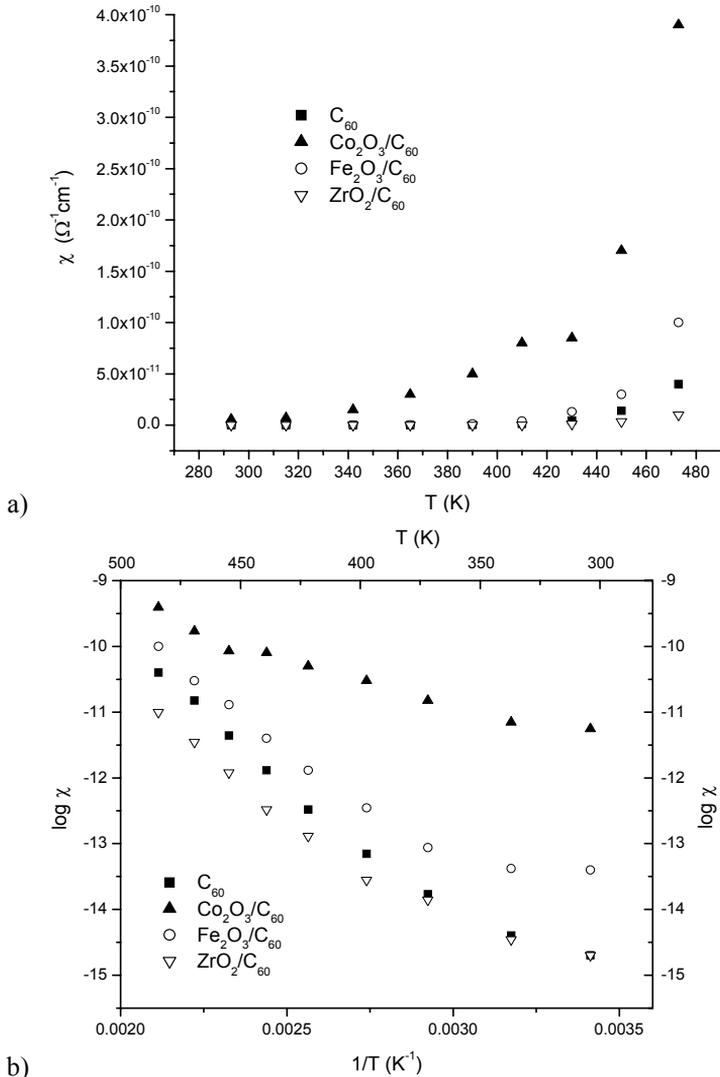


Fig. 1. Temperature dependence of electrical conductivity (χ) for C_{60} and MeO/C_{60} samples.

Table 2. *Values of activation energies calculated from Fig. 1b.*

Sample	Ea (kJ/mol)	Energy gap (eV)
ZrO ₂ /C ₆₀	79 ± 3	0.82
Fe ₂ O ₃ /C ₆₀	72 ± 2	0.75
Co ₂ O ₃ /C ₆₀	27.5 ± 0.5	0.29
	60 ± 2	0.62
C ₆₀	82 ± 3	0.85

For more complete picture it will be necessary to perform some quantum mechanics modelling, which will treat the problem in a more exact way, i.e. considering both MeO and C₆₀ as a whole. This will give a picture on the molecular orbitals (bands) distributed in that entity in respect of energy spectrum, and more importantly, on electrons distribution in these bands (i.e. HOMO-LUMO gap). This task will be additionally complicated when oxygen adsorbed on MeO and C₆₀ is included in order to simulate the real experimental conditions. However, by our opinion, it is the only way to reveal how these oxides influence the mechanism of C₆₀ oxidation.

Considering all these facts, it is obvious that more detailed studies are needed to reveal the true mechanism on the influence of additives on carbon oxidation.

Summary

For the first time, functional liaison between electrical properties and catalytic influence of additives on reaction of carbon (i.e. C₆₀) oxidation is proved. Although the electron transfer theory proposed by Long and Sykes, is still useful for predicting catalytic influence of metallic oxides on carbon oxidation, some inconsistencies appeared and opened new problems which will be a guidelines for further investigations.

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