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OXIDATION OF SULPHUR SPECIES ON ACTIVE CARBONS: THE SUGGESTED MECHANISM

Raisa Nastas, Vasile Rusu, Tudor Lupascu

Institute of Chemistry of Academy of Sciences of Moldova, 3 Academiei, MD-2028, Chisinau, ichem@asm.md, nastasraisa@yahoo.com, Republic of Moldova

Abstract

The oxidation of sulphur (II) species with oxygen in the absence of catalysts is very slow, due to the unfavourable symmetry of the spin state resulting from the different electronic configurations of the reactants. Among the efficient catalysts for the oxidation of sulphur (II) species the activated carbons are indicated, being able to change the electronic configuration of the reactants (S(II) or O₂).

The type of the products and intermediates formed during the oxidation process with oxygen depends largely on pH, reagents concentrations (S(II), oxygen), and the type of the activated carbon (as catalyst).

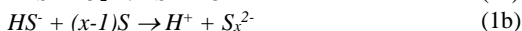
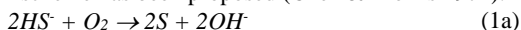
In this work the experimental results were corroborated with literature data, and plausible mechanism or reaction scheme was suggested for each case of active carbon used.

Keywords: *active carbon, mechanism, oxidation, sulphide ion*

Introduction

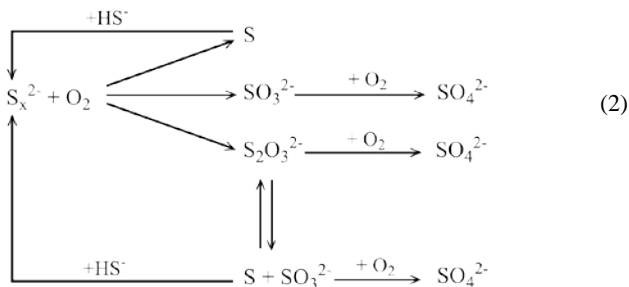
Oxidation of sulphur (II) species has a complex stoichiometry because of the broad spectrum of products and meta-stable intermediates produced during the reaction, including colloidal sulphur S_n, octarhombic elemental sulphur S₈, thiosulphate ions S₂O₃²⁻, sulphite ions SO₃²⁻, poly-sulphides S₄²⁻, S₅²⁻, tetrathionate ions S₄O₆²⁻, sulphate ions SO₄²⁻ (Alferova & Titova 1969, Chen & Morris 1972, Hoffman 1977, O'Brien & Birkner 1977, Kotronarou & Hoffman 1991, Dalai et al 1999, Avrahami & Golding 1968, Lefers et al 1978). The reaction mechanism of oxidation of sulphur (II) species in water by oxygen and the nature of the products strongly depend on the pH of the solution according to literature data (Alferova & Titova 1969, Chen & Morris 1972, O'Brien & Birkner 1977, Kotronarou & Hoffman 1991, Dalai et al 1999, Avrahami & Golding 1968).

For the oxidation of sulphur (II) species in neutral, weakly alkaline and weakly acid solutions the following reaction scheme has been proposed (Chen & Morris 1972):

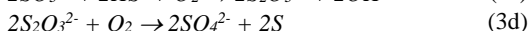


where S denotes the colloidal sulphur.

The formed polysulphide (S_x²⁻) can react with oxygen to produce several products (Chen and Morris 1972):



For $\text{pH} > 11$ the following reaction scheme was proposed (Avrahami & Golding 1968):



Thiosulphate ions are very stable at this pH value and oxidation to sulphate ions is very slow (Avrahami & Golding 1968).

Overall, the oxidation of sulphur (II) species with oxygen in the absence of catalysts is very slow, due to the unfavourable symmetry of the spin state resulting from the different electronic configurations of the reactants (Alferova & Titova 1969, Chen & Morris 1972, Hoffman 1977, O'Brien & Birkner 1977, Kotronarou & Hoffman 1991, Dalai et al 1999, Avrahami & Golding 1968, Lefers et al 1978).

Among the efficient catalysts for the oxidation of sulphur (II) species the activated carbons are indicated, being able to change the electronic configuration of the reactants (S(II) or O_2) (Steijns & Mars 1974, Adib et al 1999, Mikhailovsky & Zaitsev 1997, Primavera et al 1998, Klein & Henning 1984, Katoh et al 1995, Cariaso & Walker 1975, Bagreev et al 2001, Lupascu & Cater 1997, Choi et al 2008, Li et al 2008, Bandosz, 2006).

The type of the products and intermediates formed during the oxidation process with oxygen depends largely on pH, reagents concentrations (S(II), oxygen), and the type of the activated carbon (as catalyst).

Generally, it is considered that on the surface of active carbon the hydrogen sulphide can be oxidized to elemental sulphur and/or sulphur dioxide. In the presence of activated carbons as catalysts, the sulphur is frequently shown as the major product, especially when the pH of the active carbon surface is higher than the hydrogen sulphide dissociation constant (pK_a 7.3) (Alferova & Titova 1969, Dalai et al 1999, Steijns & Mars 1974, Adib et al 1999, Mikhailovsky & Zaitsev 1997, Primavera et al 1998, Bagreev et al 2001, Lupascu & Cater 1997, Steijns et al 1976, Bagreev et al 2000, Adib et al 2000), while the sulphur species S^{4+} and S^{6+} are recorded in smaller amounts (about 30%) (Adib et al. 1999, Mikhailovsky & Zaitsev 1997, Bagreev et al 2001, Adib et al 1999, Bagreev & Bandosz 2001).

The mechanism of formation of elemental sulphur and SO_x species is determined largely by the acid-base properties of activated carbon and their surface pH in

suspension (Adib et al 1999, Bandosz, 2006). It is considered that the first step is the catalytic activation of oxygen on free active centres on the surface of active carbon (Adib et al 1999).

The source of active oxygen on the active carbon surface is considered either the air oxygen (Bagreev et al 2000, Lupascu et al 2014), the functional groups on the surface (Lupascu et al 2014, Mikhalovsky & Zaitsev 1997) or the chemisorbed oxygen (Adib et al 1999, Mikhalovsky & Zaitsev 1997).

The pH value influences the type and quantities of sulphur species formed during oxidation with oxygen in aqueous media (Alferova & Titova 1969). In the pH range 7-14 the main oxidation product is thiosulphate, up to 45-60%. At low pH values poly-thionic acids are formed in small quantities and their content decreases with increasing pH, lacking in solution at pH 8.9. Sulphite ions are formed at pH higher than 8. Overall, it appears that sulphite ions, thiosulphate and sulphate ions are formed in significant quantities at pH>10-11 (Alferova & Titova 1969).

The aim of this work was to corroborate the experimental results with reported literature data, and to suggest a plausible mechanism or reaction scheme for each case of active carbon used.

Materials and Methods

A series of active carbons with different surface chemistry have been used for oxidation of sulphur (II) species in water solutions (Table 1).

Table 1. Characterisation of active carbons

Sample	characterization	pH of suspension
CAP23, initial (R. Moldova)	from peach stones	5.2
CAPO23, oxidized	oxidized with nitric acid	4.6
CAPO23Cu (0.4 meq Cu ²⁺ /g)	impregnated with copper ions	-
CAPO23Fe (0.8 meq Fe ³⁺ /g)	impregnated with iron ions	-
CAP23-NiO (0.5 meq Ni ²⁺ /g)	impregnated with nickel oxide	-
BAU-A, commercial (Russia)	from birch wood	10.0

The experiments were performed by using lab installation provided with an air bubbler and recovery flask for aerated hydrogen sulphide at appropriate parameters, i.e. solid/liquid ratio, aeration flow rate, pH of the medium, initial concentration of sulphur (II) species (Nastas 2006). Elemental sulphur, thiosulphate, sulphite and sulphate ions, and aerated hydrogen sulphide from recovery flask were determined by standard methods (Standard methods for the examination of water and wastewater 1999). All sulphur species were recalculated as H₂S.

Results and Discussion

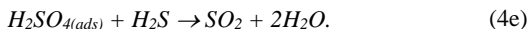
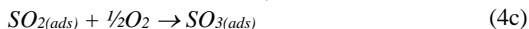
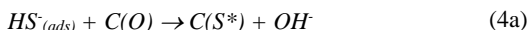
Studies show that as the oxygen content increases on the surface of the active carbons, both by concentration in functional groups and by chemisorbed oxygen (comparison of initial (CAP23) and oxidized (CAPO23) samples), the oxidation of the hydrogen sulphide species is increased and is promoted to higher oxidation degrees of sulphur (Table 1 and 2) (Lupascu et al 2014).

Table 2. Sulphur species formed in the process of oxidation of Sulphur (II) in the presence of activated carbons (Experimental details were reported earlier by Lupascu et al 2014)

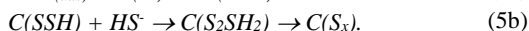
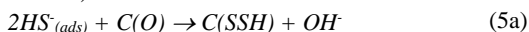
Sample	Sulphur species formed in the process of oxidation, %			
	S ⁰ colloidal	S ₂ O ₃ ²⁻	SO ₃ ²⁻	SO ₄ ²⁻
CAP23	20.4	0	12.5	67.1
CAPO23	6.1	11.7	15.4	65.9
BAU-A	32.9	32.9	4.5	31.2
CAPO23Fe	0	16.1	17.7	66.2
CAPO23Cu	0	9.3	32.7	58.1
CAP23-NiO	95.5	4.8	0	0

To be noted the important role of acid-basic properties of active carbons, influencing dissociation and oxidation of sulphur (II) species onto different species of sulphur (Adib et al 1999). The more acidic is the carbon surface, the greater is the proportion of sulphur oxidized to S⁴⁺ and S⁶⁺ species (Adib et al 1999). For CAP23 and CAPO23 samples the surface pH is acidic, 5.2 and 4.6 respectively, while the surface pH of BAU-A carbon is alkaline, reaching pH 10, which causes different mechanisms of oxidation processes on their surfaces (Table 1). It appears that S(IV) and S(VI) species prevail if the sulphide oxidation is carried out in the presence of oxidized activated carbon (CAPO23) which contains significantly more carboxylic groups on the surface as compared to their quantities on the surface of un-oxidized sample (CAP23) (Table 2) (Lupascu et al 2014).

For acidic surface of active carbons (pH < pKa for H₂S), the content of hydrosulphide ions on the surface is low, *i.e.*, the case of oxidized active carbon CAPO23 (or active carbons obtained by chemical activation method with phosphoric acid). In this case, it is supposed that sulphur is present in the form of free radicals on the surface of active carbon, which are easily oxidized to sulphur oxides (Steijns & Mars 1974, Adib et al 1999, Hoffman 1977), the suggested mechanism being:



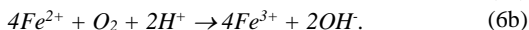
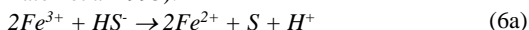
For basic active carbons (pH > pKa for H₂S), *i.e.*, the case of commercially available active carbon BAU-A, the concentration of the hydrosulphide ions on the surface is higher, leading to formation of the stable ortho-rhombic sulphur (colloidal sulphur, S_x) (Adib et al 1999, Steijns et al 1976):



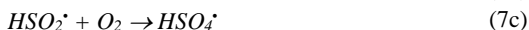
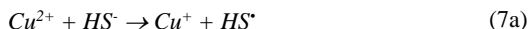
Impregnation of active carbons with transition metals modifies the catalytic properties of samples (Andreev et al 1996, Lupascu et al 2014, Mikhalovsky & Zaitsev 1997, Li et al 2008, Bouzaza et al 2004, Huang et al 2006). Oxidation rate of

sulphur species in the presence of CAP23-NiO active carbon is much higher, being by 2-2.5 times higher than in the presence of other samples (Lupascu et al 2014). However, the major product of the oxidation in the presence of CAP23-NiO is colloidal sulphur (up to 95%, Table 2). In the presence of active carbons CAPO23Fe or CAPO23Cu oxidation products are thiosulphates, sulphites and sulphates (Table 2). To be mentioned that in the presence of these catalysts colloidal sulphur is not formed during oxidation.

In the presence of molecular oxygen, metal ions catalyze the oxidation of hydrogen sulphide in aqueous solutions through redox processes (Chen & Morris 1972, Kotronarou & Hoffman 1991, Katoh et al 1995):

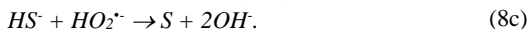


There are reported two possible mechanisms for the catalytic oxidation of hydrogen sulphide species by transition metal ions, (i) either through the formation of free radicals by electron transfer, or (ii) by the formation of metal-sulphide complexes and the precipitation of sulphur (Chen & Morris 1972, Kotronarou & Hoffman 1991). The oxidation process of the hydrogen sulphide species in the presence of $Cu(H_2O)_6^{2+}$ or $Ni(H_2O)_6^{2+}$, is initiated by the transfer of electron from the HS^- ion to the hexaaqua metal ion, forming the HS^\bullet hydrosulphide radical, which is further oxidized by oxygen through the chain reaction (Kotronarou & Hoffman 1991):



The state or the form of immobilized metals on the surface of activated carbon influences significantly the selectivity of formation of sulphur species. The catalyst obtained by impregnation with nickel oxide (CAP23-NiO) exhibits considerably higher catalytic activity and the major oxidation product is colloidal sulphur.

It is considered that catalytic activity of the samples, obtained by modification of active carbons with nickel oxide, is due to the presence of the nickel hydroxide phase (Andreev et al 1996). The reaction mechanism includes activation of the oxygen molecule in the heterogeneous redox transformation process $Ni^{2+} \leftrightarrow Ni^{3+}$ and the formation of HO_2^\bullet radicals:



Conclusions

Studies show that as the oxygen content increases on the surface of the active carbons, both by concentration in functional groups and by chemisorbed oxygen

(case of oxidized sample CAPO23), the oxidation of the hydrogen sulphide species is increased and is promoted to higher oxidation degrees of sulphur.

Is noted the important role of acid-basic properties of active carbons, influencing dissociation and oxidation of hydrogen sulphide to different species of sulphur. Oxidized active carbon, CAPO23, is rich in acidic functional groups on the surface and has a higher catalytic activity, therefore is more efficient compared to commercial activated carbon BAU-A, which is poor in acidic functional groups and has a basic pH of surface.

Active carbons modified with iron(III) and copper(II) ions (samples CAPO23Fe and CAPO23Cu) show higher catalytic activity in the oxidation of sulphur (II) species, compared to CAPO23 sample. Oxidation products are thiosulphate, sulphite and sulphate ions, without the formation of colloidal sulphur, suggesting the mechanism of catalytic oxidation of sulphur (II) species by free radical formation. The process is initiated by the transfer of electrons from the hydrosulphide ion to the metal ion, forming HS^\bullet radicals, which are further oxidized with oxygen through chain reactions.

The state or the form of immobilized metals on the surface of activated carbon influences significantly the selectivity of formation of sulphur species. Impregnated metals in the form of ions favour the formation of sulphur in high oxidation degrees (S^{4+} and S^{6+}) while impregnated metals as oxides favour the oxidation of sulphide ions to elementary sulphur. The catalyst obtained by impregnation with nickel oxide (CAP23-NiO) exhibits considerably higher catalytic activity and the major oxidation product is colloidal sulphur, suggesting the reaction mechanism which includes the activation of oxygen molecule in the heterogeneous redox transformation process ($\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$) and the formation of HO_2^\bullet radicals that convert hydrosulphide ions to colloidal sulphur.

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