Reactive intermediates of the reduction of SO₂ on activated carbon†

Eduardo Humeres,[1]* Maria da Gloria B. Peruch,[1] Regina F. P. M. Moreira[2] and Wido Schreiner[3]

[1]Departamento de Química, Universidade Federal de Santa Catarina, 88040-670 Florianópolis, SC, Brazil
[2]Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina, 88040-670 Florianópolis, SC, Brazil
[3]Departamento de Física, Universidade Federal do Paraná, Centro Politécnico, 81531-970 Curitiba, PR, Brazil

ABSTRACT: The reduction of SO₂ on activated carbon was studied in the range of 600–700 °C in a differential reactor under steady-state conditions and under chemically controlled kinetics. Initial rates of carbon conversion and gas reagent were calculated from the mass balance of the gaseous products. The kinetics was first-order with respect to carbon and first-order with respect to the partial pressure of SO₂. The activation parameters were $\Delta H^{\neq} = 21.5 \, \text{kcal mol}^{-1}$ and $\Delta S^{\neq} = -211 \, \text{cal mol}^{-1} \, \text{K}^{-1}$. The activated carbon was ca. 10^5 times more reactive than graphite, and determined by the enthalpy of activation. The main reaction products were CO₂ and sulfur. CO and COS were produced from consecutive reactions of the primary products. During the pre-steady state, the sulfur content of the carbon increased to a plateau where the reaction reached the steady state condition. This sulfur was shown to be chemically bound to the carbon matrix and represents the stable reactive intermediates of the reduction of SO₂. The XPS spectrum of the residual carbon C(S) showed two forms of sulfur bound to carbon: non-oxidized sulfur (sulfide and/or disulfide) and oxidized sulfur (sulfone, sulfoxide, sulfenate, sulfinate). The sulfur intermediates C(S) reacted with SO₂ at the same rate as pure activated carbon and with CO₂ to produce SO₂ by the reverse reaction. The reaction of C(S) with CO produced COS. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: sulfur dioxide; activated carbon; reactive intermediate; inserted sulfur

INTRODUCTION

Sulfur and nitrogen oxides are perceived as the worst air pollutants, being the precursors of acid rain.[1] Several reactions are used to eliminate SO₂ from flue gases, such as oxidation to SO₃ followed by formation of sulfuric acid, or reduction to elementary sulfur.[2] The reduction to elementary sulfur is an attractive alternative because the product is easy to handle and stock, and has a high commercial value.[3] Several reductants can be used such as hydrogen,[4] carbon monoxide,[5] hydrocarbons[6] and carbons.[6–12]

When heating different carbons with sulfur, hydrogen sulfide, carbon disulfide or sulfur dioxide, highly stable superficial C—S complexes have been observed[13–16] that change the carbon's reactivity.[12] Several mechanistic proposals have assumed the formation of superficial complexes on the carbon that are able to act as intermediates, but without any experimental evidence.[9,11,12,17]

Mechanistic studies of the reduction of SO₂ by carbon have been hampered by deficient experimental techniques that do not allow quantitative measurements of the reactivity and the product distribution. We have studied the C + SO₂ reaction with different carbons under controlled conditions, showing that the reaction is first order with respect to carbon and first order with respect to SO₂.[18] The reactivity increased with decreasing crystallinity and the primary products were CO₂ and sulfur, while CO, COS and CS₂ were end-products formed by consecutive reactions.

The products of the C + SO₂ reaction involve the C—O—S system and there are 21 possible reactions that are thermodynamically possible (Scheme 1).[5a,19] The stoichiometry of these reactions has to be considered in a mechanistic study.
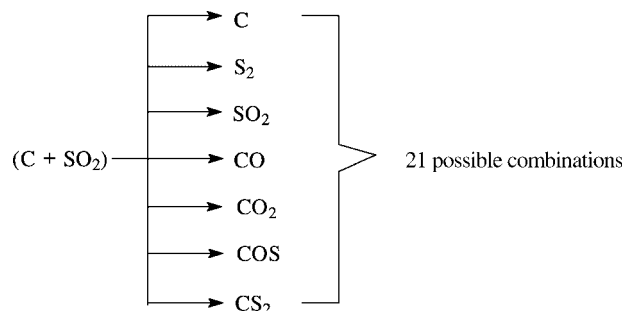
In this work, the mechanism of reduction of SO₂ by activated carbon was studied in a quartz reactor under differential conditions with an SO₂ conversion of less than 20%. Initial rates and product distribution were measured once the reaction reached the steady state condition and the kinetics was chemically controlled.

Scheme 1. Reactions of C + SO$_2$ that are thermodynamically possible

The oxidized surface[20] of activated carbon might be the determinant of its reactivity, and it is important to observe to what extent the reduction occurs by a mechanism similar to that postulated for other carbons.

EXPERIMENTAL

Reagents

Sulfur dioxide, from White & Martins, was 99.9% pure. The activated carbon was from Carbomafra S. A., and had a particle size of 1.68 mm. The X-ray Photoelectron spectra (XPS) were performed in a Perkin-Elmer PHI ESCA 5600 spectrometer, using a MgKα source. The operating pressure was maintained below 10^{-8} Torr using an ion-pump and a Ti-sublimation pump to minimize contributions from contaminants. The calibration was carried out with respect to the main C$_{1s}$ peak at 284.6 eV. The concentration of the elements was calculated using the intensity of an appropriate line and XPS cross-sections. X-ray diffraction analysis and the XPS spectrum in the C$_{1s}$ region showed that the activated carbon was highly amorphous.

The specific surface area was determined by the static method, using CO$_2$ at room temperature as adsorbate. The Dubinin–Polanyi isotherm equation[21] was used to fit the experimental data.

The commercial activated carbon was demineralized with HCl and HF[22] and it was then used as such through-out the experiments. The samples were pre-treated before the kinetic runs at 700 °C for 3 h under a nitrogen atmosphere. The chemical characteristics of the samples are presented in Table 1. The analysis of a sample after a reaction at 630 °C is given as an example of the changes of composition due to the reaction with SO$_2$.

The FTIR spectrum of the demineralized carbon showed a band at 1561 cm^{-1} (lactone and/or quinone) and a second band at 1107 cm^{-1} that can be attributed to a C—O—C bond.[23]

Reaction system

The reaction was studied in the same system as that described in previous work.[18] The carbon samples were placed in a tubular quartz reactor fitted with a temperature controller and heated by an electric oven. The total flow and the partial pressure of SO$_2$ diluted in nitrogen were controlled by two flowmeters and the gas mixture was pre-heated in a gas mixer before entering the reactor. The reaction products were allowed to flow through two cooled traps to condense the sulfur, and the gaseous products were analyzed by GLC using Porapak-Q and 5-Å molecular sieve columns.

Kinetics

The samples were dried for 12 h at 110 °C and placed in the reactor which was heated for 3 h at 700 °C under a flow of 80 ml min^{-1} of nitrogen. The temperature of the reactor was then adjusted to the reaction conditions and SO$_2$ diluted in nitrogen was injected into the reactor. The carbon conversion and product distribution were calculated from GLC analyses. The reactor operated under differential conditions with an SO$_2$ conversion of less than 20%. The reaction reached steady state conditions about 1 h after starting the flow of SO$_2$.

When the reaction is not diffusion-controlled, but only chemically controlled, the rate R of disappearance of carbon with time, calculated from the mass balance of the gaseous products, is given by Eqn. (1)

$$R = \frac{1}{1 - x_c}\frac{dx_c}{dt} \qquad (1)$$

Table 1. Characteristics of the carbon samples

	Commercial	Demineralized	Pre-treated[a]	After reaction[b]
C (%)	98.31	97.87	96.87	86.63
H (%)	1.23	1.62	2.53	1.25
N (%)	0.45	0.51	0.60	0.55
S (%)	nil	nil	nil	11.57
Ash (%)[c]	6.50	0.31	0.31	0.31
Surface area (m^2 g^{-1})	420	384	—	—
Apparent specific gravity[d] (g cm^{-3})	1.34	1.16	—	—

[a] At 700 °C, 3 h, N$_2$ atmosphere.
[b] At 630 °C, total flow 95 ml min^{-1}, P_{SO_2} 0.20 atm.
[c] From proximate analysis.
[d] From mercury porosimetry.

where $x_c = 1 - \frac{w_t}{w_0}$ is the carbon conversion and w_t and w_0 are the masses of carbon at times t and $t = 0$, respectively. In the presence of constant excess of SO_2 in the gas flow, and at low carbon conversion, the kinetics becomes pseudo-zero-order and Eqn. (1) becomes the initial rate R_0 as in Eqn. (2)

$$R_0 = \left(\frac{dx_c}{dt}\right)_{x_c \to 0} \quad (2)$$

that can be calculated from the linear plot of carbon conversion x_c versus time. In the absence of catalysis, at constant temperature the rate of reaction is a function of the concentration of reactants:

$$R_0 = kC_c^m P_{SO_2}^n \quad (3)$$

where k is the rate constant, C_c is the concentration of carbon active sites in mol m^{-2}, P_{SO_2} is the partial pressure of SO_2 in atm, and m and n are the orders of the reaction with respect to carbon and SO_2 respectively.

Alternatively, the initial rates were also calculated from the mass balance of the reagent gas (R_G).

RESULTS AND DISCUSSION

Kinetics and reactivity

The reaction was studied at 630 °C and it was found that variation of the total flow in the range of 65–110 ml min^{-1}, maintaining the partial pressure of SO_2 at 0.2 atm, did not change the initial rate, indicating that the reaction was not diffusion-controlled under those conditions. The GLC readings showed that the reaction reached the steady state after 1 h, considering that the product distribution was constant.

The order with respect to carbon was found using the shrinking core model for spherical particles,[24,25] according to Eqn. (4),

$$\frac{t}{\tau} = 1 - (1 - x_C)^{1/3} \quad \text{where} \quad \tau = \frac{\rho r_0}{kC_G} \quad (4)$$
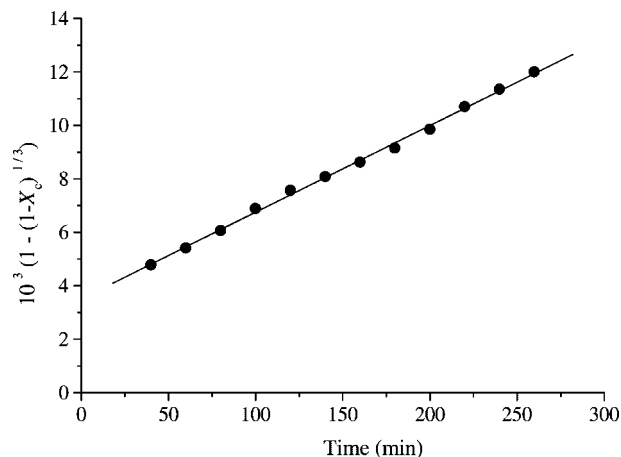

Figure 1. Determination of the order of the reaction with respect to carbon; temperature 630 °C; total pressure 1 atm; total flow 95 ml min^{-1}; P_{SO_2} 0.20 atm; sample 2 g

and where x_C is the carbon conversion, t is the time, ρ is the specific weight, r_0 is the initial radius of the particle, and C_G is the concentration of the gaseous reagent. The linearity of the plot of $[1 - (1 - x_C)^{1/3}]$ versus time indicated that that the reaction was first-order with respect to carbon (Fig. 1). Therefore, $m = 1$ in Eqn. (3).

The dependence of R_0 on the partial pressure of SO_2 was linear in the range of P_{SO_2} 0.11–0.25 atm (Table 2), so consequently the reaction was first-order with respect to SO_2 ($n = 1$) and Eqn. (3) becomes

$$R_0 = k_2 C_C P_{SO_2} \quad (5)$$

A first-order relationship with respect to carbon and SO_2 similar to Eqn. (5) has also been found for different carbons with a wide range of cristallinity.[18]

At total flow of 95 ml min^{-1} and $P_{SO_2} = 0.2$ atm, the reaction could be carried out under differential reactor conditions in the range of temperature 600 to 630 °C. At higher temperatures the carbon conversion during the steady state was too high. The activation parameters obtained are consistent with those of different carbons (Table 3), and show that the reactivity increases with

Table 2. Reduction of SO_2 by activated carbon

t (°C)	P_{SO_2}[a] (atm)	R_0[b] (mol s^{-1}m^{-2})	Molar fraction[c] (%)		
			CO_2	CO	COS
600	0.20	1.6×10^{-10}	100.0	—	—
625	0.20	2.0×10^{-10}	100.0	—	—
630	0.11	1.8×10^{-10}	100.0	—	—
630	0.20	3.6×10^{-10}	60.5	39.5	—
630	0.25	4.6×10^{-10}	58.2	41.8	—
675	0.20	5.1×10^{-9}	52.8	32.8	14.4
700	0.20	1.0×10^{-8}	55.7	25.6	18.7

[a] Total pressure: 1 atm; total flow: 95 ml min^{-1}.
[b] Samples: 2.0 g.
[c] Average molar fraction without considering nitrogen and SO_2.

Table 3. Activation parameters for the reaction C—SO$_2$ for different carbons

Carbon	$k_2{}^a$ (atm^{-1} s^{-1})	$\Delta G^{\neq}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq b}$ (cal mol^{-1} K^{-1})	Reference
Graphite	1.4×10^{-8}	111.1 ± 3	40 ± 1	-240 ± 9	18
Charcoal	$7.7 \times 10^{-4\,c}$	89 ± 4	20.2 ± 0.1	-229 ± 17	18
Activated carbon	$4.8 \times 10^{-3\,c}$	84 ± 2	22 ± 6	-211 ± 19	This work

[a] At 900 °C.
[b] At 25 °C; standard state concentration in mole m^{-2} atm^{-1}.
[c] Calculated from activation parameters.

Table 4. Reactions of activated carbon at 630 °C[a]

Reaction	P^b (atm)	Molar fraction[b] (%)				$10^5 R_G{}^c$ (mol s^{-1} atm^{-1})
		CO$_2$	CO	COS	SO$_2$	
COS[d]	0.2 COS	16	84			2.6
CO + SO$_2$[d]	0.17 CO; 0.17 SO$_2$	100[e]				7.7^{CO}; 2.7^{SO_2}
C + SO$_2$	0.25 SO$_2$	60[e]	40[e]			3.2
C + CO$_2$	1.0 CO$_2$		100			2.8
C + CO	1.0 CO	100[e]				1.1
C + COS	0.2 COS	92	8			2.2
C + CO + SO$_2$	0.12 CO; 0.18 SO$_2$	53[e]		47[e]		8.6^{CO}; 6.3^{SO_2}
C(S)$_{16}{}^f$ + SO$_2$	0.25 SO$_2$	100				3.1
C(S)$_{18}{}^f$ + CO$_2$	1.0 CO$_2$				100	2.0
C(S)$_{17}{}^f$ + CO	1.0 CO	68[e]		32[e,g]		5.0

[a] This work unless indicated. At constant residence time; carbon samples: ca. 2.0 g; total pressure: 1 atm (dilution with N$_2$); total flow: 100 ml min^{-1}.
[b] Average molar fraction without considering nitrogen, reagent gas and sulfur.
[c] Rate of disappearance of the reacting gas.
[d] Without carbon.
[e] Reference 18.
[f] Subscript, %sulfur content after reaction with SO$_2$.
[g] Obtained already during the pre-steady state period.

decreasing crystallinity: activated carbon is as reactive as charcoal and more than 10^5 times more reactive than graphite. In general, the entropy of activation is highly negative and the difference in reactivity between graphite and activated carbon was determined mainly by $\Delta H^{\neq}$.

Product distribution

For different carbons[18] the stoichiometry of the reaction was shown to be

$$SO_2 + C \rightarrow CO_2 + 1/2\,S_2 \qquad (6)$$
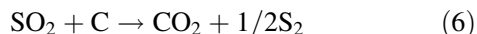
The main reaction product for the reduction of SO$_2$ on activated carbon was CO$_2$ and, depending on the reaction conditions, CO and COS were found as subproducts, always at lower molar fractions than CO$_2$ (Tables 2 and 4). The product distribution depended on whether the reaction was diffusion-controlled or chemically controlled. The CO is not an intermediate and it is formed after CO$_2$ because the Boudouard equilibrium (Eqn. (7))

$$CO_2 + C \overset{K}{\rightleftharpoons} 2\,CO \qquad (7)$$

predicts that the ratio CO:CO$_2$ should be greater than 1, since $K =$ ca. 6 at 630 °C.[26] The reaction C + CO is 2.6 times slower than the C + CO$_2$ reaction, and therefore if CO were formed first it should have accumulated (Table 2 and 4). Sulfur dioxide is also reduced by CO,[5] but the partial pressure of CO is very low and the formation of CO$_2$ from this reaction is not important, as will be discussed below.

As shown in Table 4, at 630 °C, in the gas phase or in the presence of carbon, COS produces CO$_2$ and CO besides elementary sulfur (visually observed). There is no formation of COS from reactions C + SO$_2$ or C + CO + SO$_2$, and COS decomposes on sulfurized carbon slower than SO$_2$ and CO, consequently, it must be an end-product. Therefore, CO and COS were produced from consecutive reactions of the primary products. These results are also consistent with the assumption that CO$_2$ and sulfur are formed through the same path.[5,17,18]

Insertion of sulfur on the carbon matrix

During the reaction of activated carbon with SO$_2$, it was observed that sulfur was rapidly incorporated into the carbon matrix under all reaction conditions (Fig. 2). The increase of sulfur with time followed a saturation curve that reached a plateau at the same time that the system
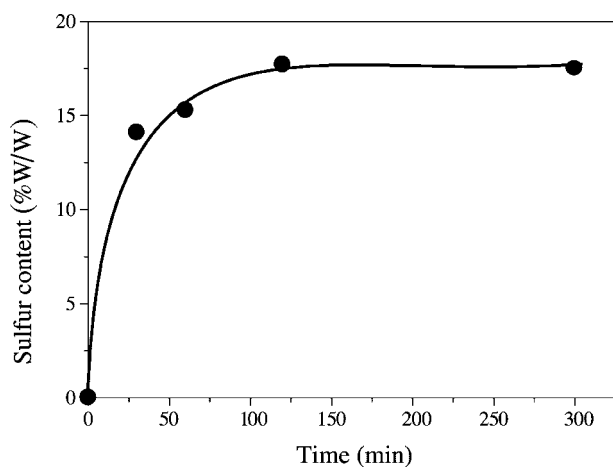
Figure 2. Increase of sulfur content of activated carbon with time at 630 °C. Sample 2.0 g; total flow 87 ml min^{-1}; P_{SO_2} 0.20 atm

reached steady-state conditions. The sulfur content of the residual sample did not change upon intensive extraction with CS_2, indicating that the sulfur was chemically bound to the matrix.

The carbon surface was partially oxidized. Before heating, the FTIR spectra of the sample presented two bands corresponding to a lactone and/or quinone (1561 cm^{-1}) and a C—O—C bond (1107 cm^{-1}). After the reaction with SO_2, the FTIR spectra showed a lactone and/or quinone band (1555 cm^{-1}) and a new band at 1150 cm^{-1} that can be attributed to a C=S or/and S=O group.[23]

The XPS spectra of the residual carbon after the reaction showed in the S_{2p} region that sulfur was bound to the matrix by two different bondings (Fig. 3). The constant sulfur content during the steady-state condition of the reaction strongly suggests that the forms of inserted sulfur in the carbon matrix are reactive intermediates in the mechanism (Scheme 2). The band at 162.5 eV was assigned to a sulfide ($x = 1$) and/or disulfide ($x = 2$), and the band at 166.8 eV was related to an oxidized sulfur S=O$_x$: sulfone ($x = 2$), sulfoxide ($x = 1$), or O—SO$_x$: sulfenate ($x = 0$), sulfinate ($x = 1$).[27]

In fact, the initial rate of carbon with SO_2 in the steady-state, measured as R_{SO_2}, is the same as the rate of the
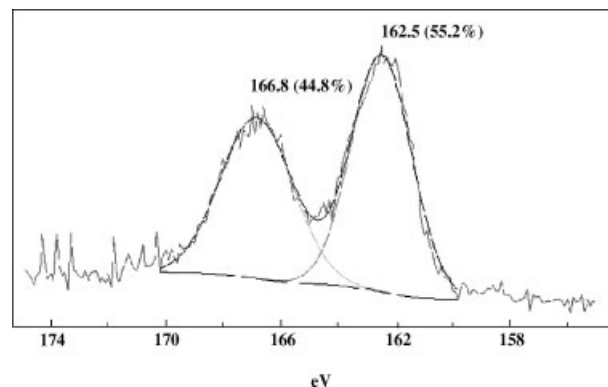

Figure 3. XPS spectrum in the S_{2p} region of a carbon sample after the reaction with SO_2. Sample 2 g; temperature 630 °C; total flow 95.0 ml min^{-1}; P_{SO_2} 0.2 atm

residual carbon C(S) (Table 4). The reaction of C(S) with CO produced CO_2 and COS even during the pre-steady-state time, supporting the assumption that COS is an end product formed through a consecutive reaction of CO with the complexed sulfur.

The reaction of C(S) with CO_2 did not produce COS but only SO_2, demonstrating that the reaction proceeds through the sulfur intermediates as shown in Scheme 1, according to Eqn. (6) that consequently is reversible (Fig. 4). It also shows that CO_2 is indeed the primary product of the inverse reaction.

The rate R_{SO_2} of disappearance of SO_2 of the reaction C + CO + SO_2 is equal to the addition of R_{SO_2} for C + SO_2 and CO + SO_2 (Table 4). However, since no CO was formed for the reaction C(S) + SO_2 and only SO_2 was observed for C(S) + CO_2, it can be concluded again that CO_2 is the primary product, although some CO reacts with SO_2 to produce CO_2. Consequently, the initial rate of carbon conversion R_0 should be slower than R_{SO_2}, as was experimentally observed.

From these results it is possible to postulate a mechanism for the reduction of SO_2 by activated carbon (Scheme 3). Adsorption of SO_2 on site C_A leads to intermediates C(S) and thereafter to the main products CO_2 and S_x (represented as S_2). Consecutively, CO_2 can undergo reduction to CO on site $C_B(CO_2)$ through the Boudouard reaction. The sulfur complexed on site $C_A(S)$
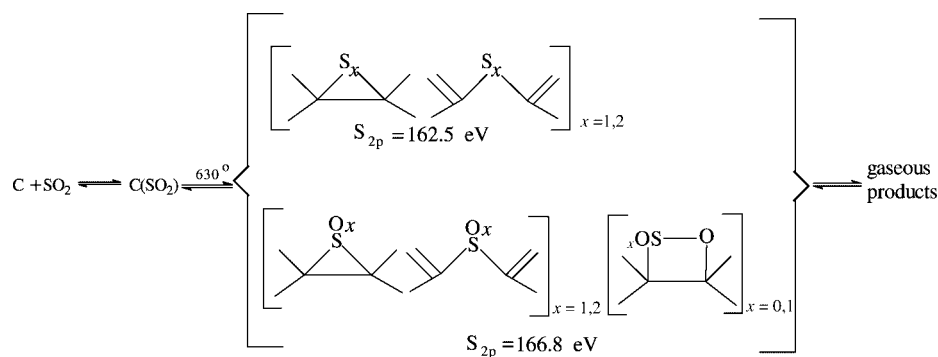
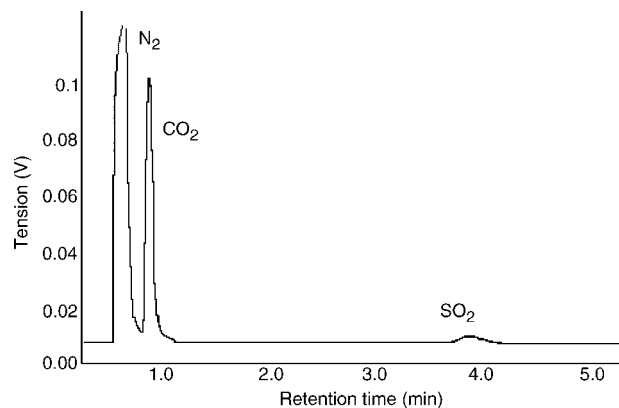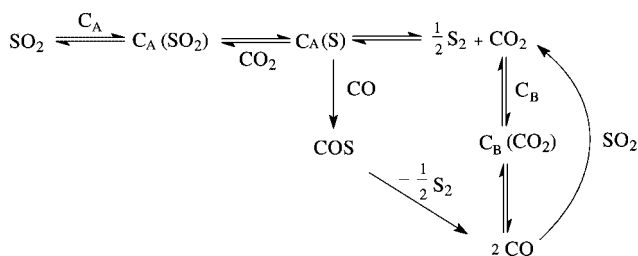**Scheme 2.** Mechanism of the reaction on the carbon matrix

Figure 4. GLC chromatogram of the reaction C(S)$_{18}$ + CO$_2$ → SO$_2$ at 630 °C; sample (residual carbon): 1.65 g; total flow: 75 ml min^{-1}; P_{CO_2} =1.0 atm. Reaction time: 25 min

Scheme 3. Overall mechanism for the reduction of SO$_2$ by activated carbon

reacts with CO to form COS, and with CO$_2$ to retro-form SO$_2$.

For the C—S$_x$ reaction with different carbons, like graphite and charcoal, it was shown that sulfur was chemically bound to the carbon matrix as a sulfide or/ and disulfide. These intermediates are involved in the formation of CS$_2$ and the total inhibition of the reaction.[13] Sulfurized graphite was able to reduce SO$_2$, but more slowly than pure graphite although with the same product distribution.[18]

The reactivity of these different forms of sulfur inserted in a carbon matrix deserves a more detailed study related to the change of the chemical and physical properties of the modified carbon.

CONCLUSIONS

The kinetics of the reduction of SO$_2$ on activated carbon was first-order with respect to carbon and first-order with respect to the partial pressure of SO$_2$. The reactivity of activated carbon was similar to charcoal and ca. 10^5 times higher than graphite, as determined by the enthalpy of activation.

Under differential reactor conditions and chemical control the primary steady-state products were CO$_2$ and sulfur. CO and COS were produced from consecutive reactions of the primary products.

During the pre-steady-state the sulfur content of the carbon increased to a plateau when the reaction reached steady-state conditions. This sulfur, C(S), was shown to be chemically bound to the carbon matrix and represent the stable reactive intermediates of the reduction of SO$_2$. The C(S) sulfur was bound to carbon as non-oxidized sulfur (sulfide and/or disulfide), and oxidized sulfur (sulfone, sulfoxide, sulfenate, sulfinate). The sulfur intermediates C(S) reacted with SO$_2$ at the same rate as pure activated carbon, and with CO$_2$ to produce SO$_2$ by the reverse reaction. The reaction of C(S) with CO produced COS.

REFERENCES

1. (a) Wiltowski TS, O'Brien WS. *Inter. Conf. Environ. Energy and Society.* USA: Schaumburg, Illinois, 1994; (b) Graedel TE, Allemby BR. *Industrial Ecology.* Prentice Hall: New Jersey, 1995.
2. Akhmedov MM, Ibragimov AA, Kasumova NM. *Russian J. Appl. Chem.* 1996; **69**: 999–1001.
3. Kohl AL, Nielsen R. In *Gas Purification*, Marsh H, Heintz EA, Rodriguez-Reinoso F (eds). Gulf Publishing Company: Houston, 1997.
4. Paik SC, Kim H, Chung JS. *Catalysis Today* 1997; **38**: 193–198.
5. (a) Lepsoe R. *Ind. Eng. Chem.* 1940; **32**: 910–918; (b) Liu W, Saronfim AF, Flytzani-Stephanopoulos M. *Appl. Catal. B* 1994; **4**; (c) Ma J, Fang M, Lau NT. *J. Catal.* 1996; **158**: 271–278.
6. Wiltowski TS, Sangster K, O'Brien WS. *J. Chem. Tech. Biotechnol.* 1996; **67**: 204–212.
7. Macák J, Pick P. *Erdoel Erdgas Kohle—Petrochemie.* 1973; **26**: 345–350.
8. Blackwood JD, McCarthy DJ. *Proc. Austral. Inst. Min. Metall.* 1974; **249**: 25–31.
9. Abramowitz H, Insinga R, Rao YK. *Carbon* 1976; **14**: 84–86.
10. Blomster K, Taskinnen P, Myyri J. *Trans. Inst. Min. Metall. Section C.* 1977; **86**: C142–C152.
11. Ratcliffe CT, Pap G. *Fuel* 1980; **59**: 237–243.
12. Panagiotidis T. *Sci. Tech.* 1988; **41**: 239–246.
13. Humeres E, Moreira RFPM, Castro SC. *J. Braz. Chem. Soc.* 1994; **5**: 69–76.
14. Chang CH. *Carbon* 1981; **19**: 175–186.
15. Panagiotidis T, Richter E, Jüntgen H. *Carbon* 1988; **26**: 89–95.
16. Blayden HE, Patrick JW. *Carbon* 1971; **5**: 533–544.
17. Macák J, Pick P. *Erdöl und Kohle Erdgas-Petrochemie* 1975; **26**: 345–350.
18. Humeres E, Moreira RFPM, Peruch MGB. *Carbon* 2002; **40**: 751–760.
19. (a) Siller CW. *Ind. Eng. Chem.* 1948; **40**: 1227–1233; (b) Kellog HH. *Metall. Trans.* 1970; **2**: 2161–2169; (c) Owen AJ, Sykes KW, Thomas DJD. *Trans. Faraday Soc.* 1951; **47**: 419–428.
20. Rodríguez-Reinoso F. In *Introduction to Carbon Technologies*, Marsh H, Heintz EA, Rodriguez-Reinoso F (eds). Secretariado de Publicaciones: Alicante, 1997.
21. Karr C, Jr. *Analytical Methods for Coal and Coal Products.* Academic Press: New York, 1978.
22. Bimer J. *Fuel* 1998; **77**: 519–525.
23. (a) Barton SS, Harrison BH. *Carbon.* 1975; **13**: 283; (b) Silverstein RM, Bassler GC, Morrill TC. *Spectrometric Identification of Organic Compounds*, 5th edn. Wiley: New York, 1991; (c) Fanning PE, Vannice MA. *Carbon* 1993; **31**: 721–730.

24. Hshieh FY, Richards EN. *Combustion & Flame*. 1989; **76**: 37–47.
25. Levenspiel O. *Engenharia das Reações Químicas*. Edgard Blüchter SA, 1976; **2**: 298–309.
26. Bale CW, Pelon AD, *Facility Anal. Chem. Thermodynamics*, http: www.crct.polymtl.ca/fact
27. (a) Suoninen EJ, Thomas TD, Anderson SE, Runyan MT, Ungier L. *J. Electron Spect. Rel. Phen*. 1985; **35**: 259–272; (b) Kelemen SR, Gorbaty ML, George GN, Kwiatek PJ. *Amer. Chem. Soc. Div. Fuel Chem*. 1992; **36**: 1213–1216; (c) Reucroft PJ, Kim JY. *Amer. Chem. Soc. Div. Fuel Chem*. 1992; **37**: 756–763; (d) Hittle L, Sharkey AG, Honalla M, Proctor A, Hercules DM, Morsi BI. *Fuel* 1993; **72**: 771–773; (e) Wilson K, Hardacre C, Baddeley CJ, Lüdecke J, Woodruff DP, Lambert RM. *Surface Sci*. 1997; **372**: 279–288; (f) Moulder JF, Stickle WF, Sobol PE, Bomben KD. *Handbook of X-ray Photoelectron Spectroscopy*. Physical Electronics: Minnesota, 1993.