ELSEVIER

Catalysis Today 78 (2003) 203–210

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Adsorption of SO_2 using vanadium and vanadium–copper supported on activated carbon

S.A.C. Carabineiro[a], A.M. Ramos[a], J. Vital[a], J.M. Loureiro[b],
J.J.M. Órfão[c], I.M. Fonseca[a,*]

[a] *Departamento de Química, REQUIMTE, CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa,*
Quinta da Torre, 2825-149 Monte de Caparica, Portugal
[b] *Laboratório de Processos de Separação e Reacção, Departamento de Engenharia Química,*
Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Oporto, Portugal
[c] *Laboratório de Catálise e Materiais, Departamento de Engenharia Química,*
Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Oporto, Portugal

Abstract

Activated carbon impregnated with precursor salts of Ba, Co, Cu, Fe, Mg, Mn, Ni, Pb and V and their binary mixtures was used for adsorption of SO_2 at 20 °C. The most promising materials for SO_2 removal are carbons doped with V, Cu and mainly their binary mixtures, which show a synergetic effect. Kinetic curves and isotherms of SO_2 adsorption were obtained at 20 °C. These isotherms are reasonably well fitted by the Langmuir model and the respective parameters were determined. TPD experiments show that adsorption of SO_2 increases the oxygenated groups on the carbon surface. The sample doped with V, after SO_2 adsorption at 20 °C, presents an increase of basic oxygenated groups, which may be responsible for the observed extra adsorption of SO_2.

Keywords: SO_2 adsorption; Activated carbon; Kinetics; Equilibrium; TPD

1. Introduction

Flue gases from combustion plants contain significant quantities of sulphur dioxide, which together with nitrogen oxides constitute a primary and substantial source of acid rain [1–6]. The deposition of these acidic components is known to be the main cause for the damage of plants, fish and all biological communities due to the pH reduction of ground waters, streams, rivers and lakes and to the impoverishment of agricultural soils due to lixiviation of plant nutrients. Also harmful effects to the human health and degradation of buildings and monuments in urban areas are caused by the acid rain [1,2]. Sulphur and nitrogen oxides are also responsible for the depletion of the ozone layer that has been linked to several illnesses and respiratory diseases [3,6]. The primary sources of SO_2 are combustion of fossil fuels, incineration of solid wastes, coal-fired power plants, automobiles and industrial boilers [3,5].

Carbon based flue gas desulphurisation systems have achieved commercial success and can remove up to 100% of the SO_2 from combustion flue gas streams [5]. An additional advantage of activated carbon processes is that, in addition to SO_2, they also remove nearly every impurity found in combustion flue gas, including particulate material, heavy metals, organic

---

[*] Corresponding author. Fax: +351-21-2948385.
E-mail address: iss@dq.fct.unl.pt (I.M. Fonseca).

0920-5861/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(02)00335-8

materials, NO_x and other air toxics [5]. Thus, several research works have been dedicated to desulphurisation using activated carbons [6–25], many of which with the recovery of the adsorbed SO_2 in sulphuric acid form [3,4,8,9,14,16,20,23,26–29].

Davini [8,9] showed that there are two types of SO_2 adsorbed on the carbon surface, one "weakly bonded" (physically adsorbed), which easily desorbs at 120 °C and another "strongly bonded" (chemically adsorbed), which desorbs only above 350 °C. Other authors observed these two types of SO_2 in their works as well [21,23]. Davini [8] also proposes a mechanism in which there is a fast preliminary adsorption of SO_2 that starts to be physical and then a part of the weakly bonded SO_2 (physically adsorbed) turns slowly with time in the strongly bonded SO_2 (chemically adsorbed) and that the process is related to the chemical nature of the carbon surface.

The quantity of the chemically adsorbed SO_2 seems to be influenced by the surface groups, while the physically adsorbed SO_2 is more closely related to the general physical characteristics of the carbon [8,9]. Other authors mentioned that the oxygen functional groups on the carbon surface are responsible for SO_2 adsorption [3,19,20,30,31] and several others showed that, in SO_2 adsorption, surface chemistry can be more important than surface area and pore structure [18,19,31,32].

Although the oxygen surface groups are stable at temperatures below 200 °C, when a carbon is heated at higher temperatures in inert atmosphere, the oxygen surface groups decompose, yielding carbon dioxide, water and carbon monoxide.

Carbon dioxide starts to evolve at lower temperatures than carbon monoxide. As a general rule, the desorption spectrum of CO_2 shows three peaks with increasing temperature, corresponding to the decomposition of carboxylic acid, carboxylic anhydride and lactone surface groups. On the other hand, CO desorption occurs at higher temperatures from the decomposition of phenol, ether, carbonyl/quinone and pyrone groups [33–36]. If carboxylic anhydrides are present, their decomposition originates CO at the same temperatures as CO_2 [36–38].

The aim of the present work is to study the adsorption of SO_2 in activated carbon loaded with several metal catalysts and their binary mixtures, determining kinetic curves and isotherms of SO_2 adsorption at 20 °C. TPD was used to interpret the role of the oxygen surface groups on the SO_2 adsorption. Textural characterisation of the carbons was performed using N_2 adsorption at 77 K. In situ XRD was used to identify the catalyst phase present after pre-treatment in nitrogen atmosphere.

2. Experimental

Activated charcoal GR Merck (powder) was used to carry out adsorption of SO_2. The textural characterisation of the samples was based on the N_2 adsorption isotherms, determined at 77 K with a Micromeritics ASAP 2010 device. The micropore volumes and mesopore surface areas were determined by the *t*-method, using the standard isotherm for carbon materials proposed by Rodriguez-Reinoso et al. [39]. The adsorption data were also analysed with the Dubinin equation. Since a type IV deviation occurred, two microporous structures were taken into account, and the corresponding volumes, W_{01} and W_{02}, calculated [40]. The Stoeckli equation [41] was used to estimate the average micropore width of the smaller pores, using an affinity coefficient for nitrogen, $\beta = 0.32$.

The activated carbon was impregnated with diluted solutions of acetates of Ba, Co, Cu, Fe, Mg, Mn, Ni, Pb and V (Merck) by the incipient wetness method. The metal loading was 4 wt.%. The same procedure was used to prepare carbons impregnated with binary mixtures of the above referred metal acetates.

A 0.15 g carbon sample was put in a fixed bed reactor, flushed with argon at 100 ml/min to eliminate air traces and heated to 500 °C in flowing Ar to decompose precursor salts and remove volatiles adsorbed on the carbon. The temperature was then lowered to 20 °C and the feed switched to a SO_2 mixture in Ar, at the same flow rate (molar concentrations from 41.6 to 208 $\mu mol/dm^3$). The amounts of adsorbed SO_2 were measured every 15 min by bubbling the outlet gas in 50 ml of a 5% (v/v) H_2O_2 solution and titrating the formed H_2SO_4 with a 0.01 N NaOH solution using "universal liquid pH indicator" (E. Merck) as the end point indicator. This technique was proven to be accurate by Davini [8].

The crystal phases detected by in situ XRD after pre-treatment in inert atmosphere at 500 °C were: $BaCO_3$/BaO/Ba, Co_3O_4/CoO/Co, CuO/Cu, Fe_2O_3/

Fe_3O_4, $MgCO_3/MgO$, Mn_3O_4/MnO_2, NiO/Ni, Pb_3O_4/PbO, and V_2O_5/V_6O_{13} for the samples doped with Ba, Co, Cu, Fe, Mg, Mn, Ni, Pb and V, respectively. Further XRD experiments in inert atmosphere showed the same phases, when the temperature was lowered from 500 °C to the adsorption temperature.

Activated carbons, with and without adsorbed SO_2, were characterised by TPD experiments using a

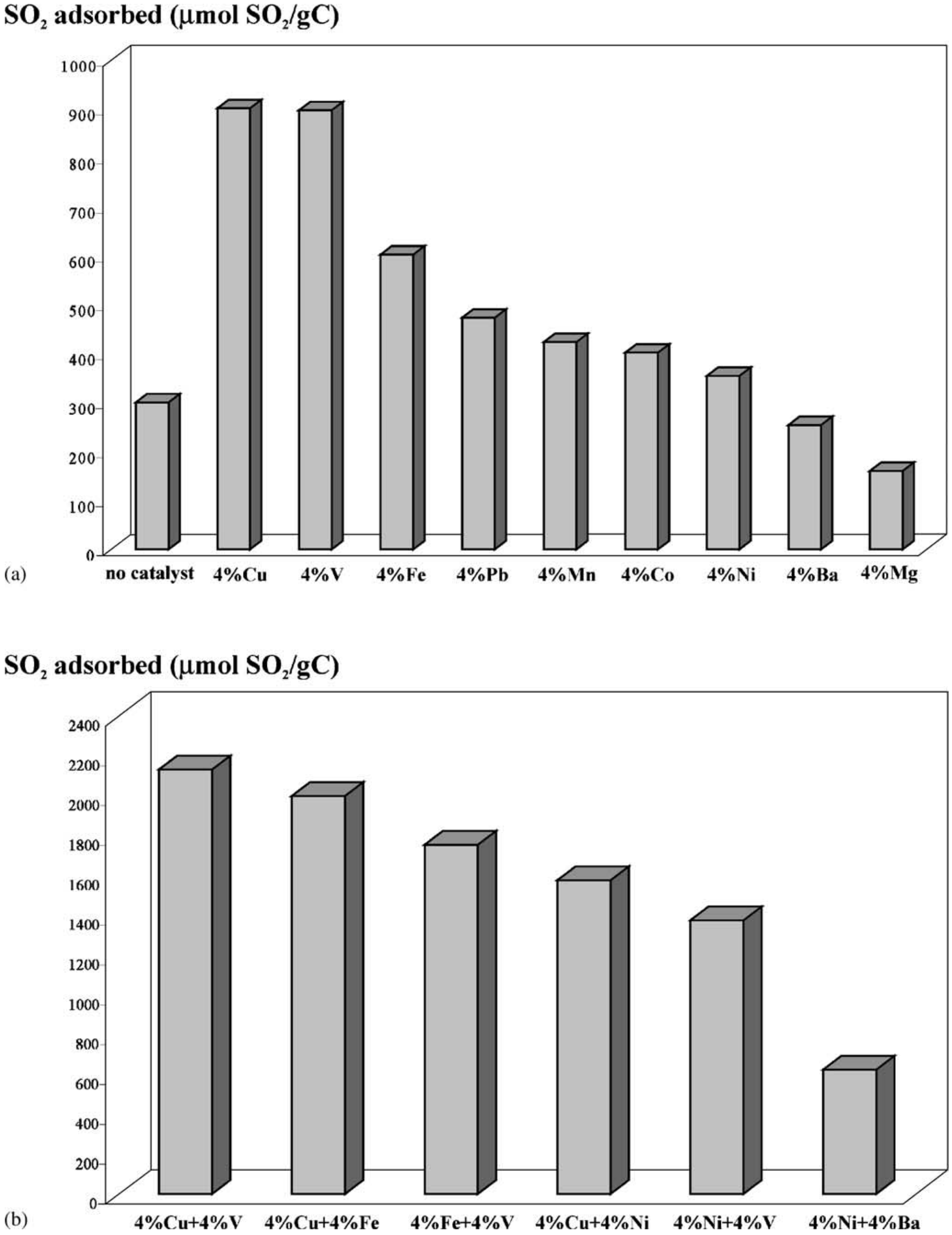

Fig. 1. SO_2 equilibrium uptake for carbon parent sample and samples doped with several additives (a) and several binary mixtures (b) at 20 °C, and under a 208 μmol/dm^3 SO_2 concentration.

quartz micro-reactor. The reactor exit was connected via a capillary tube to a mass spectrometer set-up (Fisons MD800) for continuous analysis of the gases evolved in an MID (multiple ion detection) mode. For experiments, 50 mg of sample was heated under a 350 ml/min He flow and the temperature was linearly increased up to 1100 °C at a rate of 5 °C/min.

3. Results and discussion

Fig. 1 shows the SO_2 equilibrium uptake on the several prepared carbon samples at 20 °C and under a 208 µmol/dm^3 SO_2 concentration. Adding a metal increases the adsorption uptake of the carbon parent sample, except for the samples loaded with Ba and Mg. The best additives are Cu, V and Fe (Fig. 1a). Experiments reported by other authors also showed good SO_2 adsorption results with metals like Co, Ni, Mn, V and Fe [10,11,22]. The values agree relatively well with those reported in the literature [27]. An increase in the adsorption uptake, which becomes larger than the sum of the individual metals, is observed when a mixture of metals is used (Fig. 1b). From these data it can be concluded that the most promising materials for SO_2 removal are carbons doped with V, Cu and

Table 1
Physical characterization of the samples

Sample	S_{BET} (m^2/g)	$S_{mesopores}$ (m^2/g)	$V_{micropores}$ (cm^3/g)	W_{01} (cm^3/g)	L_1 (nm)	$S_{micropores1}$ (m^2/g)	W_{02} (cm^3/g)
Carbon	1077	197	0.389	0.373	1.1	704	0.028
Cu/carbon	829	150	0.302	0.288	1.1	514	0.025
V/carbon	856	127	0.323	0.313	1.0	596	0.016
V–Cu/carbon	691	113	0.258	0.249	1.0	493	0.013

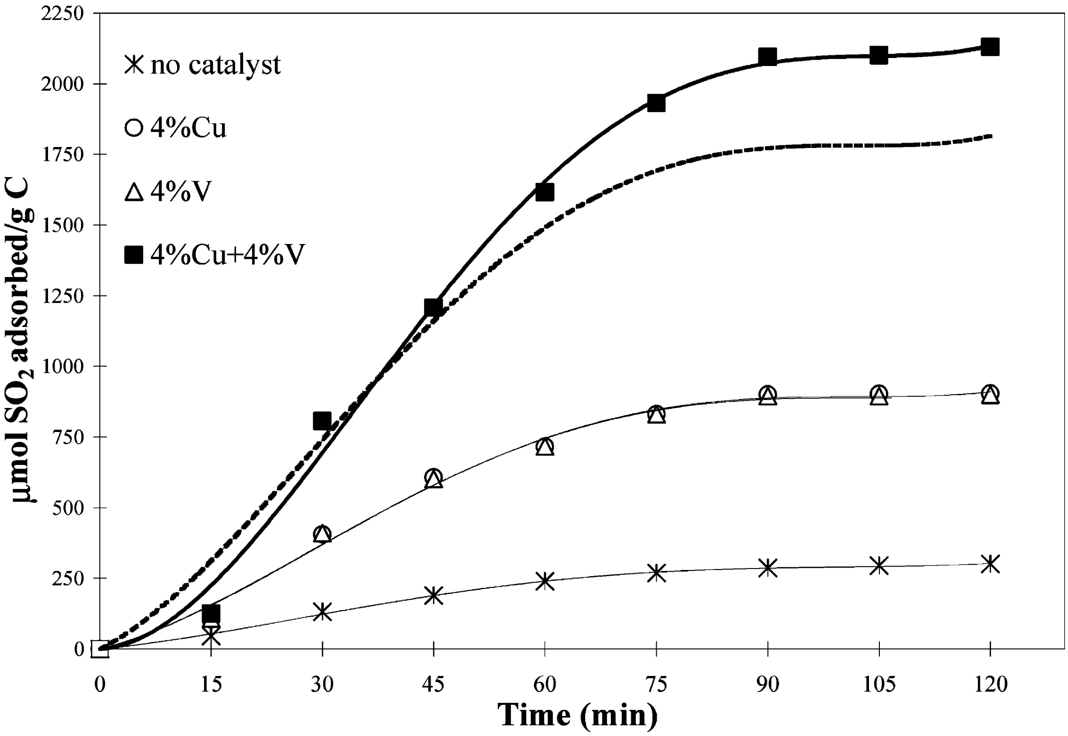

Fig. 2. Evolution with time of the adsorbed SO_2 at 20 °C for an inlet SO_2 concentration of 208 µmol/dm^3, for the carbon parent sample and for samples loaded with Cu, V and Cu + V mixture.

mainly their binary mixture. According to these preliminary results, these systems were selected for further studies.

Table 1 shows the textural characteristics of the carbon parent sample and the samples impregnated with catalysts. It can be seen that both the meso and micropore surfaces, as well as the micropore volume, decrease when the carbon is doped. The decrease in surface area and micropore volume shows that apparently the catalyst is distributed in the pores.

Fig. 2 shows the evolution with time of the adsorbed SO_2 at 20 °C for an inlet SO_2 concentration of 208 μmol/dm^3, for the carbon parent sample and samples loaded with Cu, V and Cu + V mixture. The curves show that after an induction period, the adsorbed amount increases, for all the systems studied, until its equilibrium value, attained in less than 2 h. The dotted line, corresponding to the sum of the Cu and V individual curves, falls below the one for their mixture, showing that a synergetic effect results from their combination, at least after 1 h on stream.

Table 2
Langmuir parameters of the SO_2 adsorption isotherms at 20 °C

Sample	q_m (μmol/g)	K (dm^3/μmol)
Carbon	403	1.48×10^{-2}
Cu/carbon	1380	1.01×10^{-2}
V/carbon	1380	9.99×10^{-3}
V–Cu/carbon	3260	1.04×10^{-2}

The synergy between the V and Cu oxides is probably due to the highly dispersed surface phases on the carbon supports.

This behaviour, also observed with other SO_2 concentrations, will be the subject of further studies.

From the experimental sorption data, adsorption isotherms were plotted, which were reasonably represented by the Langmuir model, as shown in Fig. 3. In Table 2 the Langmuir parameters, q_m (monolayer capacity) and K (equilibrium constant), for the four studied systems are displayed. Apparently the adsorption mechanism is similar for all the doped carbon systems, since the same value of the equilibrium constant is able to represent their isotherms.

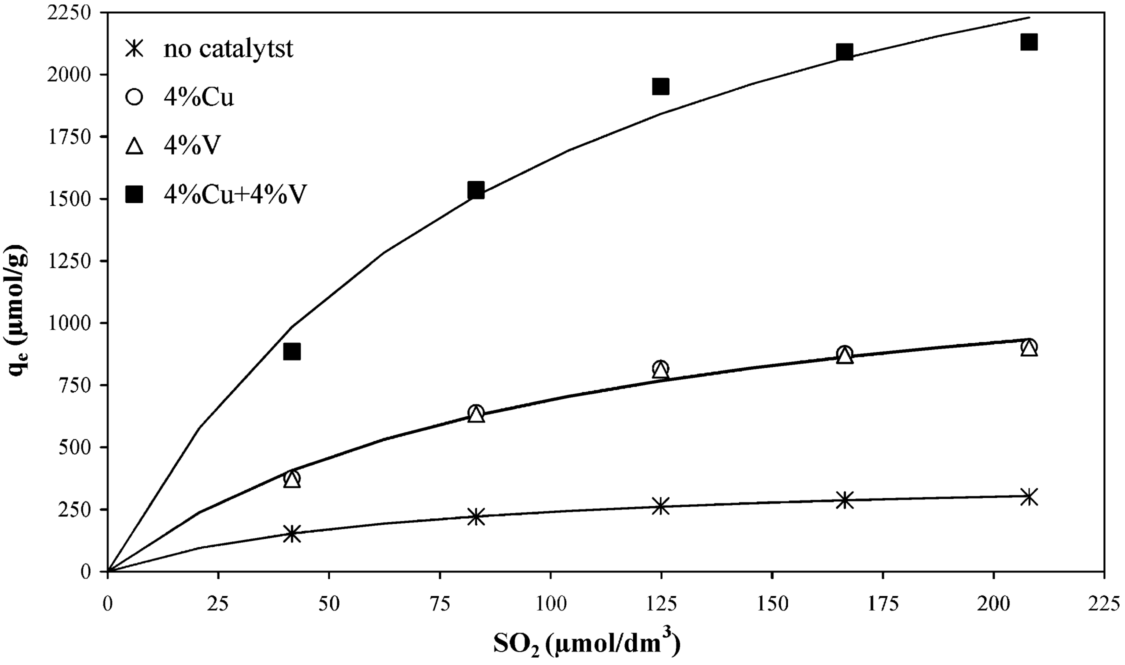

Fig. 3. Adsorption isotherms for the carbon parent sample and samples loaded with Cu, V and Cu + V mixture.

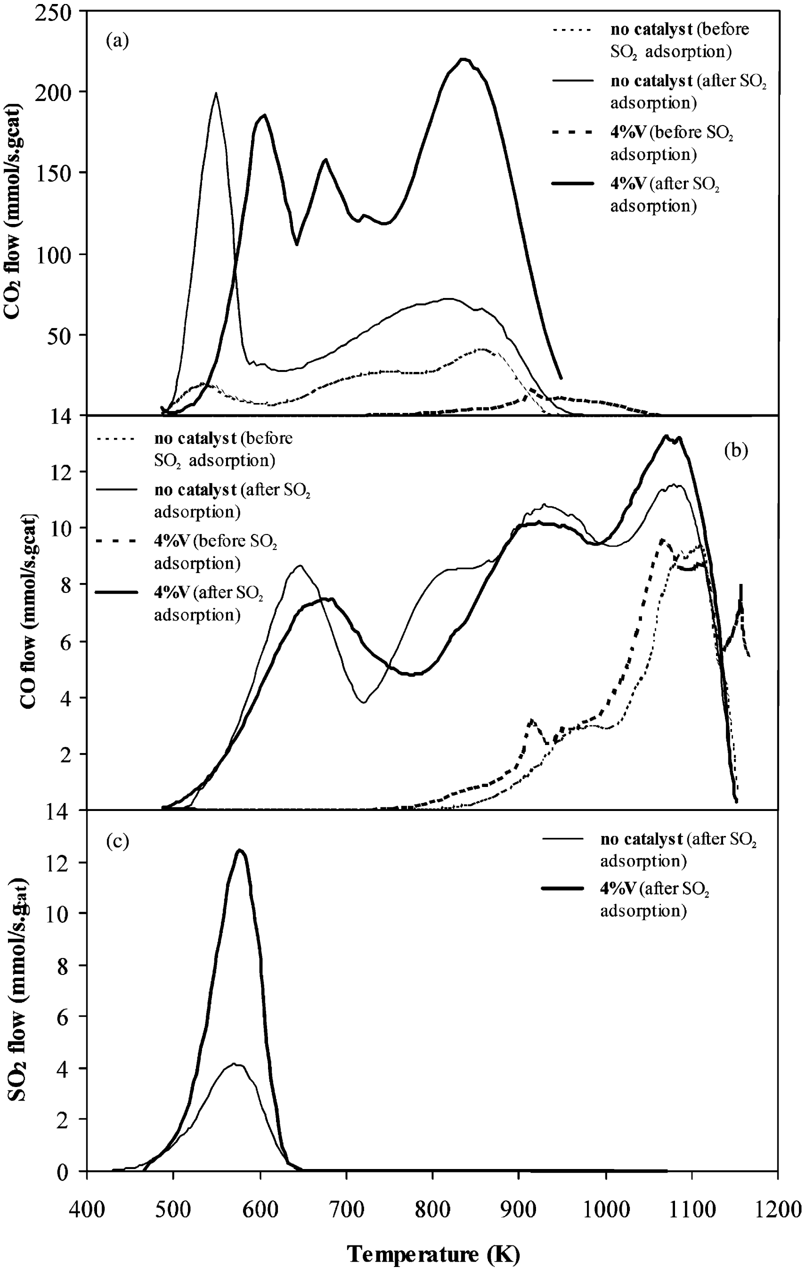

Fig. 4. TPD results for the carbon parent sample and for the V doped sample, before and after SO_2 adsorption. Desorption of CO_2 (a), CO (b) and SO_2 (c) of surface groups are shown.

In Fig. 4, TPD results for the carbon parent sample and V doped one are shown, before and after SO_2 adsorption. The analysis of this figure shows that for the carbon parent sample after adsorption of SO_2 there was an increase of the oxygenated groups, suggesting that the adsorption of SO_2 is dissociative. Comparing the parent and the V doped carbons before SO_2 adsorption, it can be concluded that the doping slightly increases the surface basic groups, probably as a consequence of the preparation process. Even if the sample doped with V suffered a pre-treatment with N_2 at 500 °C, which removes some groups, the fact that its spectrum clearly shows a larger amount of the more basic groups supports the previous conclusion. As was the case for the parent carbon, the V doped one also presents an increase of the oxygenated groups, although showing a much larger presence of basic groups and also of weaker acidic carboxylic groups. Those can be responsible for the extra adsorption of SO_2 observed, since basic groups can enhance SO_2 adsorption as described by several authors [7–9,14,19,25,28,29].

According to the observations of some authors in other systems [42], vanadium oxide is non-stoichiometric, apparently contributing to the adsorption of SO_2 and transferring the surplus oxygen to the carbon surface. Moreover, Davini and Stoppato [11] concluded that V can favour the formation of larger amounts of SO_2–surface oxygen complexes. It seems then that V plays a double role; it contributes to the increase of the surface basic groups during the decomposition of the precursor and to a much larger increase of the same type of groups during the SO_2 adsorption step.

4. Conclusions

Adsorption of SO_2 on activated carbons is enhanced by the impregnation with several metals. The best additives are Cu, V and Fe. When a mixture of Cu and V is supported on the carbon, the adsorption uptake is larger than the sum of the observed with the individual metals, showing that a synergetic effect results from their combination.

The Langmuir model reasonably represents adsorption isotherms. Apparently the adsorption mechanism is similar for all the doped carbons, since the same value of the adsorption equilibrium constant is obtained.

TPD experiments show that the V doped carbon sample, after SO_2 adsorption at 20 °C, presents an increase of the oxygenated groups, showing a much larger presence of basic groups and also weaker acidic carboxylic groups. The former can be responsible for the extra adsorption of SO_2 observed, since they enhance SO_2 adsorption.

Acknowledgements

Sónia Carabineiro acknowledges financial support from Fundação para a Ciência e Tecnologia, grant BD1275/95.

References

[1] M. Freemantle, Chemistry in Action, Macmillan, New York, 1987.
[2] D.C. Anderson, P. Anderson, A.K. Galwey, Fuel 74 (1995) 1018.
[3] M.A. Daley, C.L. Mangun, J.A. DeBarr, S. Riha, A.A. Lizzio, G.L. Donnals, J. Economy, Carbon 35 (1997) 411.
[4] I. Mochida, K. Kuroda, S. Kawano, Y. Matsumura, M. Yoshikawa, Fuel 76 (1997) 533.
[5] J. DeBarr, A.A. Lizzio, Energy Fuels 11 (1997) 267.
[6] J.J.E. Humeres, R.F.P.M. Moreira, Proceedings of the Second World Congress on Environmental Catalysis/AIChE Annual Meeting, 1998, p. 82.
[7] X.S. Zhao, G.Y. Cai, Z.Z. Wang, Q.X. Wang, Y.H. Yang, J.S. Luo, Appl. Catal. B 3 (1994) 229.
[8] P. Davini, Carbon 28 (1990) 565.
[9] P. Davini, Carbon 29 (1991) 321.
[10] J. Klinik, T. Grzybek, Fuel 71 (1992) 1303.
[11] P. Davini, G. Stoppato, Proceedings of the 23rd Biennial Conference on Carbon, vol. I, 1997, p. 316.
[12] J. Rodríguez-Mirasol, T. Cordero, J.J. Rodríguez, Proceedings of the 23rd Biennial Conference on Carbon, vol. I, 1997, p. 376.
[13] C. Moreno-Castilla, F. Carrasco-Marín, J. Riviera-Utrila, E. Utrera-Hidalgo, Proceedings of the 19th Biennial Conference on Carbon, 1989, p. 64.
[14] P. Davini, Carbon 31 (1993) 47.
[15] M.J. Muñoz-Guillena, M.C. Macías-Pérez, C. Salinas-Martínez de Lecea, A. Linares-Solano, Proceedings of the Conference of Carbon'94, 1994, p. 508.
[16] R.V. Vladea, N. Hinrichs, R.R. Hudgins, S. Suppiah, P.L. Silveston, Energy Fuels 11 (1997) 277.
[17] M. Molina-Sabio, M.A. Muñecas, F. Rodriguéz-Reinoso, B. McEnaney, Carbon 33 (1995) 1777.
[18] A.A. Lizzio, J.A. DeBarr, Energy Fuels 11 (1997) 284.
[19] A. Lisovskii, G.E. Shter, R. Semiat, C. Aharoni, Carbon 35 (1997) 1645.
[20] A. Lisovskii, R. Semiat, C. Aharoni, Carbon 35 (1997) 1639.
[21] M.A. Alvarez-Merino, F. Carrasco-Marín, C. Moreno-Castilla, Appl. Catal. B 13 (1997) 229.
[22] P. Davini, Proceedings of the 24th Biennial Conference on Carbon, vol. I, 1999, p. 338.
[23] E. Raymundo-Piñero, D. Cazorla-Amorós, A. Linares-Solano, Proceedings of the 24th Biennial Conference on Carbon, vol. II, 1999, p. 602.

[24] A. Gregório, D. Boavida, I. Gulyurtlu, I. Cabrita, Proceedings of the 24th Biennial Conference on Carbon, vol. II, 1999, p. 752.
[25] P. Davini, Carbon 27 (1999) 1363.
[26] S. Kisamori, I. Mochida, S. Kawano, Proceedings of the 21st Biennial Conference on Carbon, 1993, p. 478.
[27] H. Martyniuk, J. Wieckowska, Fuel 74 (1995) 1716.
[28] J.A. DeBarr, A.A. Lizzio, Proceedings of the 22nd Biennial Conference on Carbon, 1995, p. 562.
[29] I. Mochida, K. Kuroda, S. Miyamoto, C. Sotowa, Y. Korai, S. Kawano, K. Sakanishi, A. Yasutake, M. Yoshikawa, Energy Fuels 11 (1997) 272.
[30] B. Rubio, M.T. Izquierdo, A.M. Mastral, Carbon 36 (1998) 263.
[31] B. Rubio, M.T. Izquierdo, Carbon 35 (1997) 1005.
[32] J. Muñiz, J.E. Herrero, A.B. Fuertes, Appl. Catal. B 18 (1998) 171.
[33] U. Zielke, K.J. Huttinger, W.P. Hoffman, Carbon 34 (1996) 983.
[34] B. Marchon, J. Carrazza, H. Heinemann, G.A. Somorjai, Carbon 26 (1988) 507.
[35] M.C. Román-Martínez, D. Cazorla-Amorós, A. Linares-Solano, C. Salinas-Martínez de Lecea, Carbon 31 (1993) 895.
[36] J.L. Figueiredo, M.F. Pereira, M.M. Freitas, J.J. Órfão, Carbon 37 (1999) 1379.
[37] Q.L. Zhuang, T. Kyotany, A. Tomita, Proceedings of the Conference of Carbon'94, 1994, p. 466.
[38] Y. Otake, R.G. Jenkins, Carbon 31 (1993) 109.
[39] F. Rodriguez-Reinoso, J.M. Martin-Martinez, C. Prado-Burguete, B. McEnaney, J. Phys. Chem. 91 (1987) 515.
[40] A. Linares-Solano, in: J.L. Figueiredo, J.A. Moulijn (Eds.), Carbon and Coal Gasification, Martinus Nijhoff, Dordrecht, The Netherlands, 1986, p. 137.
[41] H.F. Stoeckli, L. Ballerini, S. de Bernardini, Carbon 27 (1989) 501.
[42] S.A.C. Carabineiro, F.B. Fernandes, A.M. Ramos, J. Vital, I.M. Fonseca, Catal. Today 57 (2000) 305.