

REGULARITIES IN THE TEMPERATURE-PROGRAMMED DESORPTION SPECTRA OF CO₂ AND CO FROM ACTIVATED CARBONS

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Introduction

Temperature-Programmed Desorption (TPD) of CO and CO₂ has been widely used to study superficial oxygen groups of carbons. In principle, This technique allows the different oxygen groups to be evidenced and the amount of each group to be determined. Nevertheless, TPD spectra are very poorly resolved, apparently because the species involved are too numerous to be separated by this technique. Another possible reason is that the decomposition of oxygen groups could take place within a continuous range of activation energies of desorption because of interactions between neighboring species on the surface of carbon. Besides, readsorption of CO or CO₂ during TPD seems possible in some cases, particularly for porous carbons, leading to a supplementary broadening of the corresponding peaks. Difficulties for interpreting TPD spectra has been discussed by Calo [1]. This work presents an endeavor to overcome these difficulties experimentally by means of Intermittent TPD, and also by a close observation of some TPD spectra obtained by the present authors or found in the literature.

Experimental

Samples

Four activated carbons were used in this work. Carbon P is a commercial one, named "Charbon végétal activé", from Prolabo. Carbon A was prepared from almond shells. The raw material was pyrolyzed at 1173 K in an N₂ flow and activated in a steam flow at 1123 K. Carbon V was prepared from olive stones washed with H₂SO₄ and then pyrolysed at 1273 K under an N₂ flow. The activation was carried out at 1113 K under a CO₂ flow. Carbon B was prepared from a Spanish lignite, which was demineralized with HCl and HF and pyrolyzed at 1113 K in an N₂ flow. This sample was activated in a CO₂ flow at 1073 K. Before the TPD experiments, the activated carbons underwent the following treatments. Three samples of Carbon A were treated by HNO₃ (AN), H₂O₂ (AO) and Na₂S₂O₈ (AS),

respectively. Carbon B was treated with H₂O₂ and left to ambient air for two years (BCA). Three samples of Carbon V were oxidized by HNO₃ (VN), NaOCl (VCl) and O₂ (30 Torr, 623 K)(VO), respectively. Parts of the carbons treated by HNO₃ or NaClO were then outgased under vacuum up to 823 K to obtain the corresponding preparations VND and VClD. Carbon P has been studied as recieved.

These carbons from different origins, variously activated and treated, provided a series of samples with different textures and with various grades of oxidation of their surface.

Apparatus

TPD experiments were performed with two apparatuses. The first one works under vacuum (10⁻⁶ mbar) with a heating rate of 5 K/min. In the second one, TPD runs were performed at atmospheric pressure under a He Flow. The evolution of CO and CO₂ was followed by means of a mass spectrometer in both cases. The Intermittent TPD (Differential method) was carried out under vacuum. This method has been described in details elsewhere [2].

Results and Discussion

Figure 1 shows the result of the ITPD of CO₂ from carbon P. It is similar to that previously obtained for Carbon AN [2]. Corresponding apparent activation energies of desorption Ed are shown in Table 1, along with those found for sample AN by the same technique. The values of Ed calculated from a well-resolved spectrum, that presented seven maxima or clear shoulders, are also shown in this table. This spectrum was obtained with carbon BCA at 50 K/min under a He flow [3]. The corresponding values of Ed have been calculated using the preexponential factors provided by ITPD. It can be seen that there is a good agreement between the number of desorption steps and the corresponding values of Ed. This is observed though the carbons have quite different origins and oxidation states.

Tables 2 and 3 give the temperatures of the peaks and

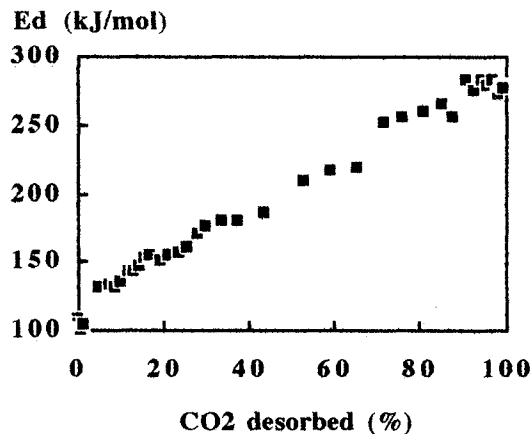


Figure 1. ITPD: Apparent activation energy of CO₂ desorption versus the total amount of CO₂ desorbed.

shoulders found in TPD spectra of carbon V variously oxidized. (These spectra were obtained under vacuum.) It is seen that these temperatures gather around a series of 7 values for CO₂ and 6 values for CO, independently of the oxidizing treatment. Similar observations were made for TPD's under He of carbon A variously oxidized.

Finally, a close look to numerous TPD spectra found in the litterature [4-6] revealed some regularities in the

positions of maxima and shoulders as precedently described .

Conclusions.

Despite the great variety of TPD spectra of CO and CO₂ from activated carbons from different origins and preparations, some regularities appear in the steps of desorption. The TPD spectra may be interpreted by the decomposition of the same oxygen species. The differences are mainly due to different populations of these groups.

References

1. Calo J.M., and Hall, P.J., in *Fundamental issues in control of carbon gasification reactivity*, Ed. J. Lahaye and P. Ehrburger, Kluwer Academic Publisher, the Netherlands, 1991, p.329
2. Joly, J.P., Haydar, S., Perrard, A., Moreno-Castilla, C., Rivera-Utrilla, J. and Ferro-García, M.A., in *Carbon'94 (ext Abstr.)*, Granada, Spain, 1994, pp. 346-3347
3. Carrasco-Marín, F., Rivera-Utrilla, J., Joly, J.P. and Moreno-Castilla, C., *J. Chem. Soc., Faraday Trans.*, 1996, 92(15), 2779
4. Tremblay, G., Vastola, F.J., Walker Jr., P.L., *Carbon*, 1978, 16, 35.
5. Linares-Solano, A., Salinas-Martinez de Lecea, C., Cazorla-Amoros, D., Joly, J.P. and Charcosset, H., *Energy and Fuels*, 1990, 4, 467.
6. Otakc, Y. and Jenkins, R.G., *Carbon*, 1993, 31, 109.

Carbon P (DTPI)(5K/min)		Carbon AN (DTPI)(5K/min)		Carbon BCA (DTP)(50 K/min)	
Ed (kJ/mol)	T range (K)	Ed (kJ/mol)	T range (K)	Ed (kJ/mol)	T (K)
105	341-376	117	370-380	121	450
134	411-454	134	400-435	142	530
155	485-575	155	442-518	159	600
180	589-690	176	540-588	180	700
218	736-775	201	645-737	197	830
259	800-877	255	769-885	259	970
280	900-1120	322	934-1120	318	1130

Table 1. Apparent activation energies of desorption found by ITPD under vacuum and by TPD under Helium for three different carbons

Carbon	V	VN	VND	VCI	VCID	VO
T (K)	490	500	500	490	510	
	626	650	640		630	620
		720		720		
		900	900			
	925	950	950	1025	1000	975
	1060	1050	1050	1100		1100
	1140	1130	1140			1140

Table 2. Temperatures of the peaks and shoulders in the TPD spectra of CO₂ from Carbon V variously oxidized

Carbon	V	VN	VND	VCI	VCID	VO
T (K)	400	470	485	450		400
	510	500	550	490	500	500
	610	650		620	600	
			730			710
	790	825	810		830	780
	910					

Table 3. Temperatures of the peaks and shoulders in the TPD spectra of CO from Carbon V variously oxidized