

HIGH SELECTIVITY ACTIVATED CARBON FOR CO₂/CO SEPARATION

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Introduction

In the transition towards a more sustainable energy economy, fossil fuels are likely to remain the main source of global energy supply for the foreseeable future. However, related CO₂ emissions are a major problem as they contribute to global climate change. Modified combustion techniques cannot reduce CO₂ formation but dependence on fossil fuels over the coming decades can be reconciled with our climate change commitments by developing CO₂ capture and sequestration technologies. Separation techniques for CO₂ are well placed among the competitive solutions.

The major advantage of activated carbons for this application is that they are able to separate gas mixtures at very low concentrations by virtue of their high adsorption capacity. Further exploitation of solid – gas processes has revealed that impregnation of solid adsorbents by metal halides can increase their receptive capacity for adsorbate gases. Activated carbon supported metals are believed to adsorb CO through complex formation between CO and the highly dispersed metal halides on the surface of the adsorbents (*Mohamad, 2000*). Cu(I) can also selectively modify the CO adsorption on porous supports (*Xie, 1996*). As Cu⁺ ions on the surface form coordination bonds with CO and weaken the basicity of the surface, adsorbents displaying greater capacity and selectivity for CO than for CO₂ could be obtained.

The aim of this investigation is to study the CO₂/CO separation efficiency of activated carbons modified in different ways. The samples of well characterized porosity and surface chemistry were tested for the transport dynamics of CO₂ and CO by batch-type frequency resonance (FR) and equilibrium methods.

Characterization of the carbons

GR spherical carbon, prepared from vinyl-pyridine - divinylbenzene co-polymer by carbonization, was used as received and after oxidation (GROX) and also as a support for metal loading.

SAXS measurements indicate that the virgin carbon beads are composed of units of two different characteristic sizes, $d_1=2000$ Å and $d_2=28$ Å. Nitrogen adsorption measurements performed at 77 K (**Figure 1a**) enabled the porosity of these two carbon supports to be determined (**Figure 1b**). The numerical values obtained are compared in **Table 1**.

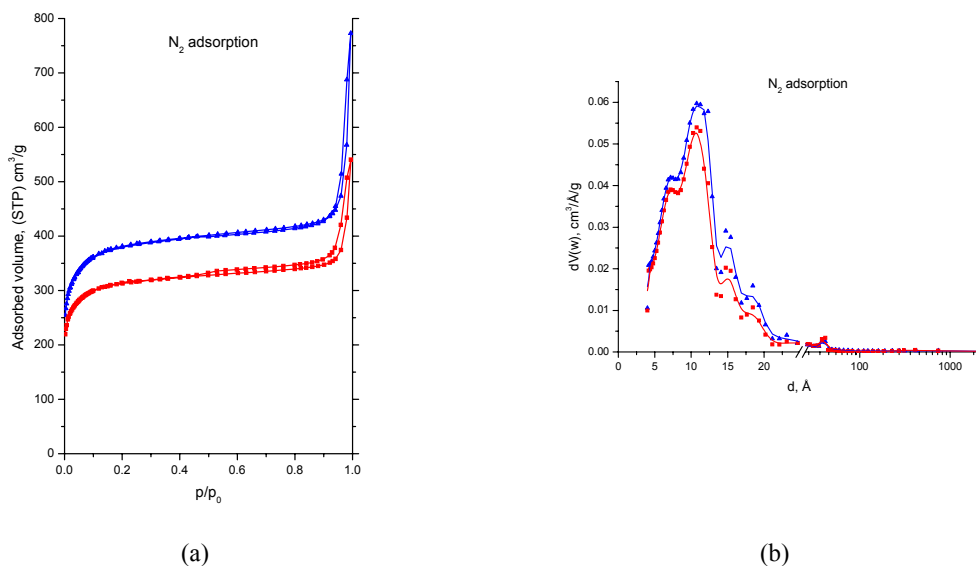


Figure 1. (a) Low Temperature (77 K) Nitrogen Adsorption/Desorption Isotherms; (b) DFT ($d < 25 \text{ \AA}$) and BJH ($d \geq 25 \text{ \AA}$) Pore Size Distributions of GR (\blacktriangle) and GROX (\blacksquare).

Table 1. Morphology Data of the Non-Impregnated Carbons.*

	S_{BET}	V_{TOT}	d_{ave}	W_0	E_0	w	W_0/V_{TOT}
	m^2/g	cm^3/g	\AA	cm^3/g	kJ/mol	\AA	%
GR	1457	0.69	18.9	0.58	14.3	9.1	84
GROX	1191	0.55	18.9	0.46	16.8	7.8	84

* V_{TOT} is the total pore volume at $p/p_0=0.95$, S_{BET} is the BET surface area, d_{ave} is the average pore diameter, W_0 is the volume of the micropores from the Dubinin-Radushkevich method and w is the average width of the micropores.

The surface chemistry of the virgin spherical carbon (GR) was modified in order to increase the acidity of the surface. The sample labelled GROX, which was obtained by treatment with boiling diluted (1:1 w/w) HNO_3 (Soxhlet-apparatus, 1 cycle), followed by thorough washing with water, exhibits the porosity features shown in **Figure 2** and **Table 1**. The acidic treatment does not significantly modify the mainly microporous character of the carbon. The surface chemistry of the virgin and the oxidized carbons are compared in **Table 2**. Although the acidic treatment also results in a higher surface concentration of the nitrogen species, i.e., sources for basic sites, the overall result is increased acidity, as reflected by the pH measured in an aqueous slurry of the beads.

CO_2 adsorption isotherms for GR and GROX, measured in the temperature range 253-283 K, yield for the characteristic heat of adsorption the values 16.5 and 16.8 kJ/mol, respectively. The closeness of these values indicates that the acid treatment does not influence the adsorption interaction with CO_2 .

Table 2. Surface Chemistry of the Virgin and the Oxidized Carbon by XPS.

	C	O	N	O/C	N/C	pH
	atomic %			%		
GR	90.3	7.8	1.9	8.6	2.1	7.9
GROX	85.1	11.8	3.0	13.9	3.5	3.6

Impregnated carbons

Sn(II) and Cu(II) doped samples were prepared by impregnating GR and GROX carbons by soaking in aqueous solutions of various salts and drying them (Adhoum, 2004, Mohamad, 2000). The nature of the anion, the salt concentration, the effect of pH and the mixing ratio were studied systematically. Cu(I) impregnated carbon was also prepared by solid-solid adsorption technique (Xie, 1996). The conditions of preparation and the dynamic selectivity characterized by the ratio of the diffusion constants D_{CO}/D_{CO_2} of selected samples are listed in **Table 3**. It should be commented that the oxidation treatment itself results in a significant increase in the selectivity.

Table 3. Parameters of the Preparation of Selected Metal Loaded Spherical Carbons and their Dynamic Selectivity Performance.*

Nr.	Origin	Metal salt	c mol/l	Liquid/carbon ratio	Drying temperature °C	E_0 kJ/mol	D_{CO}/D_{CO_2}
1	GR	-	-	-	-	16.5	19
2	GROX	-	-	-	100	16.8	33
4	GR	SnCl ₂	0.30	16.0	180	15.3	22
7	GR	Cu(NO ₃) ₂	0.30	16.0	180	16.9	13
12	GROX	Cu(CH ₃ COO) ₂	0.03	16.0	100	14.8	21
14	GROX	Cu(CH ₃ COO) ₂	0.30	16.0	100	14.9	28
21	GR	CuCl	"solid phase adsorption"			13.5	1.7
22	GROX	Cu(CH ₃ COO) ₂	0.52	16.0	100	14.0	33

*c: initial concentration of the aqueous metal ion solution; E_0 : from the Dubinin-Radushkevich plot of the CO₂ isotherm; D_{CO}/D_{CO_2} : ratio of the diffusion coefficients D from the FR response

From the values of the characteristic energy E_0 of CO₂ adsorption (**Table 3**) it can be concluded that impregnation has practically no effect on the interaction energy between CO₂ and the surface. For samples 1-14 in **Table 3**, the average energy is 15.9 ± 1.0 kJ/mol.

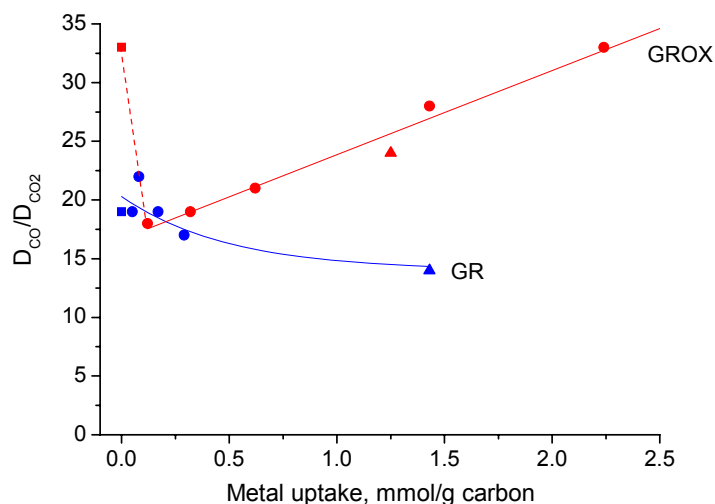


Figure 2. Comparison of the Ratio of the Diffusion Constants D_{CO}/D_{CO_2} on Carbon Samples. Blue: GR Based Samples, Red: GROX Based Samples (■: Non-Impregnated, ●: Cu(II), ▲: Sn(II)).

The ratio of diffusion coefficients D_{CO}/D_{CO_2} , obtained from the FR technique, is a function of metal loading, as shown in **Figure 2**. For all the samples, excluding #21, the trend is independent of all the other preparation parameters, even the metal species. While metal loading reduces this ratio at any uptake in the case of the GR carbon, D_{CO}/D_{CO_2} in GROX, after an initial drop, grows linearly with increasing uptake. The highest value of this ratio ($D_{CO}/D_{CO_2}=33$) was recorded for 0 mmol/g carbon and also for the maximum loading observed experimentally, 2.25 mmol/g carbon. No systematic effect of the anions was noted. The influence of pH is limited, while that of the drying temperature also seems to depend on the metal species. Impregnation reduces the accessible porosity.

Metal uptake was defined by the initial metal salt concentration as well as by the liquid/carbon ratio. The higher the concentration, the greater is the metal uptake. GROX yields significantly better selectivity. Almost all the impregnated samples, however, performed worse than the unimpregnated carbons. The Cu(I) loaded sample displayed poor CO/CO₂ selectivity (**Table 3**), because the metal strongly increased the CO/surface interaction.

The temperature dependence from the equilibrium isotherms with pure CO and CO₂ also allows the selectivity to be determined for GROX and GROX-based samples, #4 and #7 (**Figure 3**).

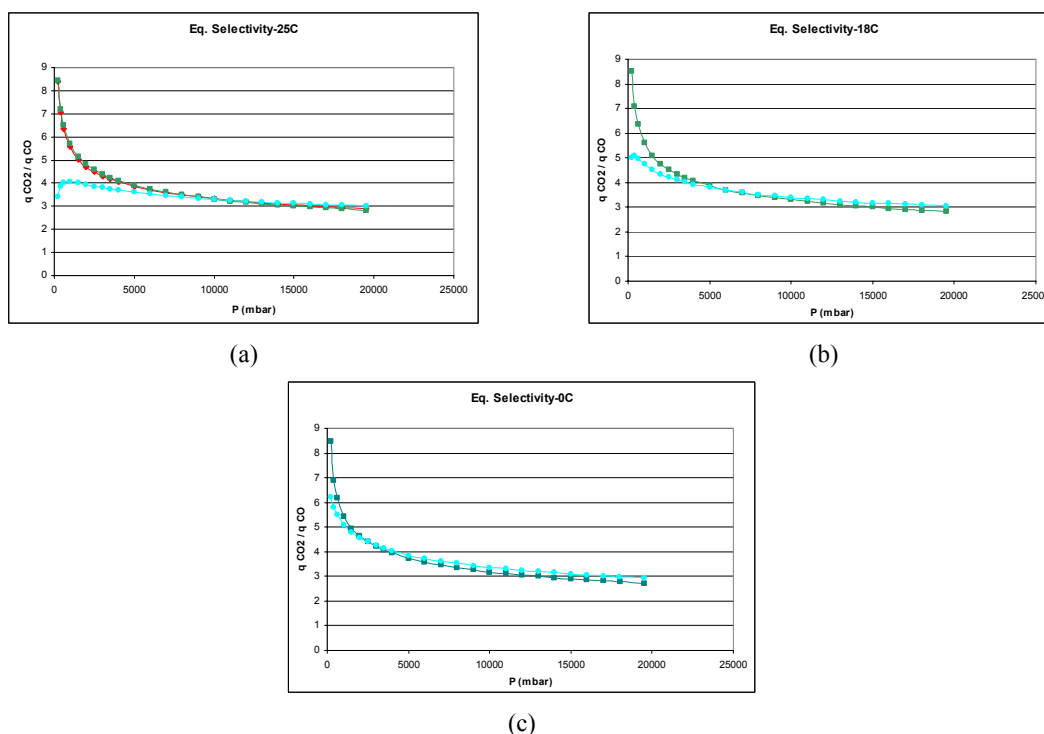


Figure 3. Equilibrium CO/CO₂ Selectivity of GROX (♦), Sn-(■) and Cu-(●) Loaded Spherical Carbon at (a) 25°C, (b) 18°C, (c) 0°C.

It can be seen, that decreasing the temperature, the difference between the two metal loaded carbons is disappeared. While there is no significant margin on the performance of GROX and Sn loaded sample, at 25°C.

Conclusion

In spite of the similar molecular sizes (Webster, 1998) significantly different relaxation time constants are obtained for CO and CO₂ in the two carbons studied here. The best separation factor, 33, was achieved with the oxidized sample. This value exceeds by far the ratio D_{CO}/D_{CO_2} that may be expected from the different mass of these two molecules, namely $(44/28)^{1/2}=1.25$. Impregnation of the carbons influences mainly the CO₂ kinetics, although Sn(II) affects the diffusion properties of both gases. Generally speaking, Cu(II) salts are more effective and GROX is the better substrate.

Acidic conditions during the impregnation have no particular influence. The final properties of the product depend strongly upon the starting material. On impregnating GROX a linear relationship is found between the metal uptake and D_{CO}/D_{CO_2} . The higher the metal uptake, the higher is the ratio of diffusion constants. For the virgin carbon sample, GR, the ratio of the diffusion constants decreases with increasing the metal uptake. Cu(I) selectively increases the affinity for CO, leading to the poorest kinetic separation performance.

Acknowledgements

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References

- Adhoum, N. and Monser, L. 2004. Removal of phthalate on modified activated carbon: application to the treatment of industrial wastewater. *Separation and Purification Technology* 38(3):233-239.
- Czakkel, O., Marthi, K., Geissler, E., László, K. 2005. Influence of Drying on the Morphology of Resorcinol - Formaldehyde-based Carbon Gels. *Microporous and Mesoporous Materials* 86(1-3):124-133
- Iyuke, S. E., Ahmadun, F. 2002. Adsorption and solid catalysed reaction between activated carbon impregnated with SnO₂ and CO at ordinary temperature. *Applied Surface Science* 187(1-2):37-44.
- Jordi R. G., Do D. D. 1993. Analysis of the Frequency-response method for sorption kinetics in bidispersed structured sorbents, *Chemical Engineering Science*, 48(6):1103-1130.
- Mohamad, A. B., Iyuke, S. E., Daud, W. R. W. et al. 2000. Adsorption of carbon monoxide on activated carbon-tin ligand, *Journal of Molecular Structure* 550-551(Sp Iss):511-519.
- Rees L. V. C., Shen D. 1993. Characterization of microporous sorbents by frequency-response methods. *Gas Separation Purification* 7(2):83-89.
- Xie, Y., Zhang, J., Qiu, J., Tong, X., Fu, J., Yang, G., Yan, H., Tangz, Y. 1996. Zeolites modified by CuCl for separating CO from gas mixtures containing CO₂. *Adsorption* 3:27-32.
- Yasuda, Y. 1994. Frequency-response method for investigation of gas-surface dynamic phenomena. *Heterogeneous Chemistry Reviews* 1(2):103-124.
- Webster, C. E., Drago, R. S.; Zerner, M. C. 1998. Molecular dimensions for adsorptives. *Journal of the American Chemical Society* 120(22):5509-5516.