CO_2 REACTION WITH ACTIVATED CARBON

Sónia A. Carabineiro[a], F. Brás Fernandes[b], Ana M. Ramos[a], Joaquim S. Vital[a], Isabel F. Silva[a]

[a]*Departamento de Química, C.Q. F. B.,* [b]*Departamento de Ciência dos Materiais, CENIMAT, Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, 2825-114 Caparica, Portugal*

Introduction

CO_2 is a major source for the so called greenhouse effect, leading possibly to changes in climate. To reduce the emission of CO_2 carbon gasification can be used as an important process in producing clean fuels and chemical feed stocks [1-7]. All carbonaceous materials can be gasified in CO_2 to produce CO, which is a useful product. The use of catalysts was proposed for low temperature gasification to overcome slow reaction with CO_2 [1, 3-5, 7]. The aim of the present work is to study the behaviour of several metal catalysts and their binary mixtures supported in activated carbon and carbon itself as a catalyst for C/CO_2 reaction.

Experimental

Kinetics and adsorption studies were carried out using Charcoal Activated GR MERCK impregnated with 4%wt of a precursor salts of Mg, Mn, Ba, Pb, Cu, V, Ni, Fe and Co. Conversion was studied using a fixed bed reactor and a GC/MS apparatus with sample heating at 2°C/min (TPR). Catalyst active phases were identified by *in-situ* XRD. Further details of experimental procedure are described elsewhere [8, 9].

Results and Discussion

CO_2 adsorption capacity is increased by adding a catalyst, when compared with the sample without catalyst. The best catalysts were Fe and Mg, adsorbing 4887 and 3078 μmol CO_2/gC, respectively. Binary mixtures showed no synergetic effects for CO_2 adsorption.

Figure 1 shows the Arrhenius plots for CO_2 reaction for samples doped with 4%Ba, 4%Fe and 4%Ba+4%Fe. A substantial decrease in activation energy for the Ba catalysed reaction compared to the uncatalysed is observed (290 to 117 $kJmol^{-1}$).

Figure 2 shows the catalysed program temperature reaction profile for CO_2 conversion. The analysis of the reaction products for the reaction with CO_2 using a GC/MS on line show the presence of CO together with some unreacted CO_2. Active phases play also an important role on the catalytic conversion of CO_2.

Figures 3, 4 and 5 shows *in situ* XRD patterns obtained in CO_2 at several temperatures for carbon doped with 4%Fe, 4%Ba and 4%Ba+4%Fe. The peaks show shifts to 2θ with increasing temperature, which reflects expansion of the crystal lattices. Pt peaks appear in the spectra resulting from exposure of the sample holder to the X-ray beam as carbon burned away.

In situ XRD shows clearly that catalyst is reduced to lower oxidation states such as $BaCO_3$/BaO/Ba and Fe_2O_3/Fe_3O_4. The catalytic effect observed for the CO_2 conversion can be explained by the occurrence of redox processes in which the oxides particles are reduced by reaction with the carbon at points of contact with the carbon substrate to form lower oxides according to a redox mechanism. Ba in the carbon surface seems to increase carbon reactivity at low temperatures.

In situ XRD experiments carried out in nitrogen, the peak attributed to BaO is only clearly visible after sample cooling. These observations suggest that BaO is present as a melted phase.

Melting of the catalysts improves wetting of the carbon surface promoting catalyst/carbon interaction [10-12]. Catalysts seem to act as an oxygen acceptor from CO_2, transferring it to the carbon surface and recovering reduced state. Similar behaviour has been reported by several authors [1, 7, 13-18].

Conclusions

In the C-CO_2 reaction a reduced catalyst surface is required to CO_2 conversion. The ability of the catalyst to chemisorb the gases going through redox transference of oxygen to the carbon reactive sites seems to explain catalytic activity.

Acknowledgements

Sónia Carabineiro acknowledges finantial support from Fundação para a Ciência e Tecnologia (Grant BD1275/95).

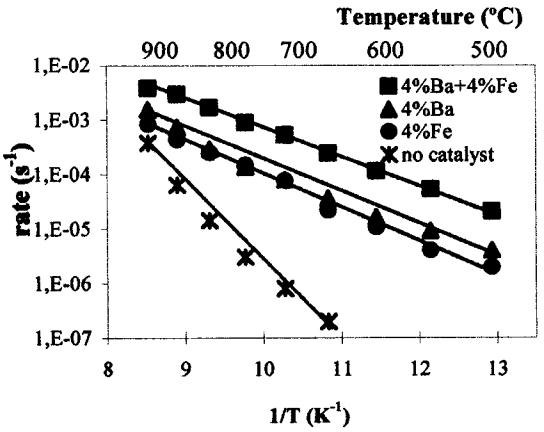

Figure 1 - Arrhenius plots for carbon gasification in CO_2 for samples doped with Ba, Fe and Ba+Fe.

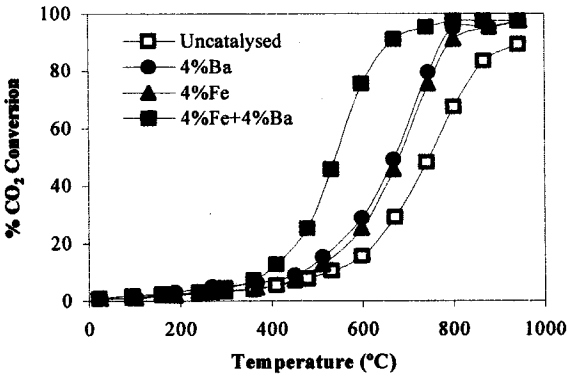

Figure 2 - CO_2 conversion as a function of temperature for samples doped with Ba, Fe and Ba+Fe.

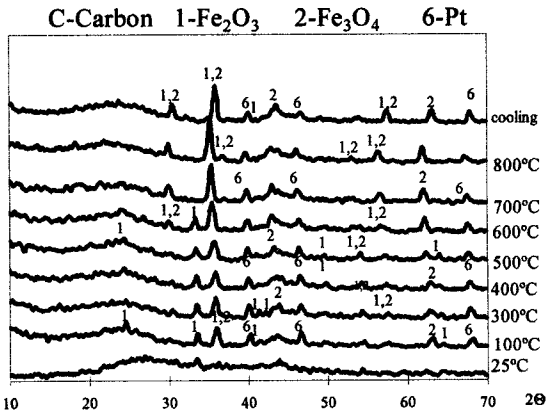

Figure 3 – *In situ* XRD data obtained on heating Fe-Carbon in CO_2 at various temperatures.

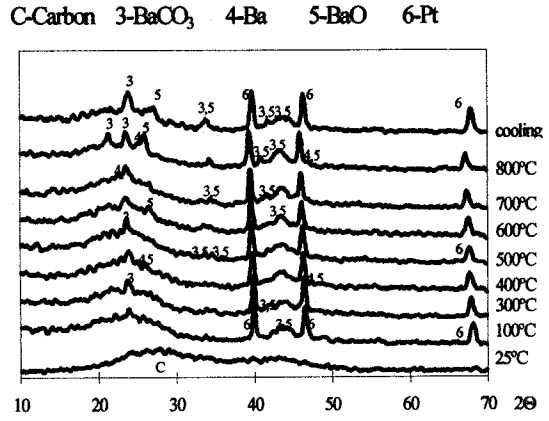

Figure 4 - *In situ* XRD data obtained on heating Ba-Carbon in CO_2 at various temperatures.

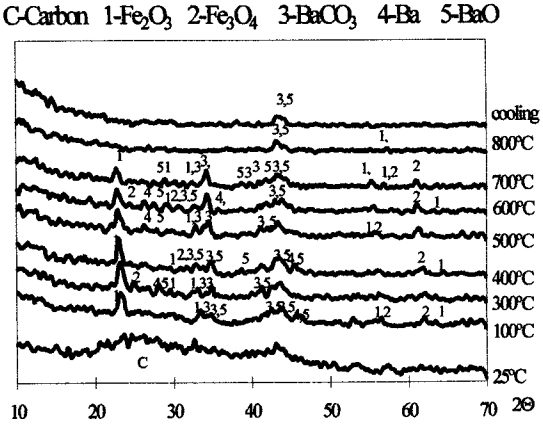

Figure 5 - *In situ* XRD data obtained on heating Ba+Fe- Carbon in CO_2 at various temperatures.

References

1. Mckee, D. *Carbon*, 1970, 8, 623.
2. Wood, B. J. and Sancier, K. M., *Catal.Rev.-Sci.Eng*, 1984, 26, 2, 233.
3. Meijer, R., Weeda, M., Kapteijn, F. and Moulijn, J., *Carbon*, 1991, 29, 929.
4. Perez-Florindo, A., Cazorla-Amorós, D. and Linares-Solano, A., *Carbon*, 1993, 31, 493.
5. Cazorla-Amorós, D., Linares-Solano, A., Salinas-Martinez de Lecea, C. and Kapteijn, F., *Carbon*, 1994, 32, 423.
6. Xianding, X. and Moulijn, J.A., *Ener. Fuels*, 1996, 10, 2, 305.
7. Ohme, H. and Suzuki, T., *Ener.Fuels*, 1996, 10, 4, 980.
8. Carabineiro, S., Silva, I.F., Fernandes, F.B., *Proc. 9th Int. Conf. Coal Sci.*, Ed. ª Ziegler, K. van Heek, J. Klein. W.Wanzl, DGMK, Vol I (1997), 1103-1106.
9. S. Carabineiro, I.F. Silva, F.B. Fernandes, A.M. Ramos, J.S.Vital, *Proc. Eurocabon 98*, Strasbourg, France, 5-9 July 1998, Vol. I, 411.
10. Baker, R.T.K., Lund, C.R.F., Chlundzinski Jr, J.J., *J.Cat*, 87 (1984) 255.
11. Silva, I.F. and L.S. Lobo, *J.Cat*, 1990, 126, 489.
12. Silva, I.F., Mckee, D. and L.S. Lobo, *J.Cat*, 1997, 170, 54.
13. Illán-Gomez, M.J., Linares-Solano, A., Radovic, L. and Salinas-Martinez de Lecea, C, *Ener. Fuels*, 1995, 9, 97.
14. Illán-Gomez, M.J., Linares-Solano, A., Radovic, L. and Salinas-Martinez de Lecea, C, *Ener. Fuels*, 1995, 9, 540.
15. Illán-Gomez, M.J., Linares-Solano, A. and Salinas-Martinez de Lecea, C., *Ener. Fuels*, 1995, 9, 976.
16. Illán-Gomez, M.J., Linares-Solano, A., Radovic, L. and Salinas-Martinez de Lecea, C., *Ener. Fuels*, 1995, 10, 158.
17. Marquez-Alvarez, C., Rodriguez-Ramos, I. and Guerrero-Ruiz, A., *Carbon*, 1996, 34, 339.
18. Mehardjeive, D., Khristova, M., and Bekyarova, E., *Carbon*, 1996, 34, 757.