ACTIVATED CARBON FIBERS FROM PAN. II: CATALYTIC ACTIVITY FOR SO_2 OXIDATION

I. Martin-Gullon, M. Jagtoyen, G. Kimber and F. Derbyshire.
Center for Applied Energy Research, University of Kentucky
3572 Iron Works Pike, Lexington, KY 40511, United States of America.

Introduction

Environmental regulations have driven research and development to find new processes and materials that can provide cost-effective methods for flue-gas clean-up. In relation to SO_2 removal, attention has been given to adsorption or catalysis by activated carbons. Mochida and co-workers [1] have pioneered a novel approach in which activated carbon fibers (ACF) are used to remove SO_2 by its conversion to sulfuric acid through reaction with oxygen and water vapor at near-ambient temperatures. They have reported that commercial polyacrylonitrile (PAN) based fibers can be used to produce active catalysts. Fei et al (2) also described the preparation of ACF from shale oil which gave higher SO_2 conversion than ACF from either PAN or coal liquids. They speculated that the high nitrogen contents and the nitrogen functionalities present in PAN and oil shale ACF might be responsible for their high activity. Both groups have further shown that heat treatment of ACF can considerably enhance their catalytic properties. Kim et al (3) also found that the activation of PAN fibers using KOH was more effective than steam activation.

In an attempt to explain some of these results and to identify the important catalytic parameters of PAN ACF, a study has been made of the influence of the method of activation on the activity for SO_2 removal. In the first part of this study, we described the preparation of a series of PAN ACF by KOH activation and steam activation (4). In this second part, we describe the catalytic behavior of these materials in the form of fibers and activated carbon fiber composites.

Experimental

The PAN-based ACF used in this work are listed in Table 1, showing fibers that were activated in this laboratory (that were prepared from Milcar90 type PION18 from R.K Carbon Fibers Inc.), and one commercial product (FE300) from Toho Rayon (Japan), that was supplied by courtesy of Professor Mochita at Kyushu University. Samples which exhibited high SO2 conversion activity were further heat treated at 800°C in N2 (10K/min, 1 h soaking time) to examine the effect in their catalytic activity.

Table 1. PAN-based ACF tested in this work.

Sample	Activation	T °C	B.O.* %	S_{BET} m^2/g
SA800	Steam	800	87	670
K-700-1	KOH- 1:1	700	36	1023
K-800-1	KOH- 1:1	800	53	2489
FE-300	Commercial	-	-	994

*Burn-off or weight loss.

Composites were formed from ACF samples K-700-1, K-800-1 and FE300, using methods described elsewhere [-]), and after cured these composites were also heat treated at 800°C before investigating the catalytic behaviour.

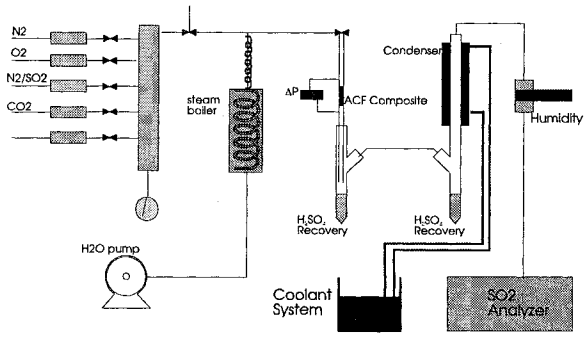

Figure 1. Experimental system.

The experimental apparatus used to determine SO_2 conversion activity is shown in Figure 1. A synthetic flue gas mixture is prepared by mixing metered flows of dry gases. Water is delivered through a syringe pump and is admixed with the other gases after passing through a boiler to ensure its complete evaporation. The gas stream (300 cm^3/min containing 6% O_2, 10% H_2O, 1000 pppm SO_2, with the balance N_2) passes downwards

through a sample of ACF or ACF composite (about 0.75 g) that is maintained at 30°C. Sulfuric acid drains continuously from the bed and is recovered in a flask. Fugitive emissions are trapped using a condenser, that employs a glycol-water mixture to attain a temperature of –5°C. After determining the humidity of the effluent gas stream a humiditymeter (Omega TX50): the humidity measurement is necessary to monitor the extent of water removal and to correct the infrared detector reading for the presence of water vapor. The SO_2 concentration is determined using an infrared detector (Rosemout 880A).

Results

Figure 1 shows the SO_2 breakthrough plots for the as-received ACF. In all cases there is a characteristic lag before SO_2 is detected in the effluent stream. Its concentration then usually rises to some steady state value. However, for the steam activated fibers, the concentration progressively increased with time on stream, and after about 20h there was almost no catalytic activity. For the other ACF, the KOH activated samples showed the highest steady state activity: 55% conversion for K-800-1, and 40% for K-700-1. The commercial ACF (FE-300) produced 30% conversion. The activity follows in proportion to the surface area, and the data for FE-300 is in good agreement with that reported by Kisamori et al [1].

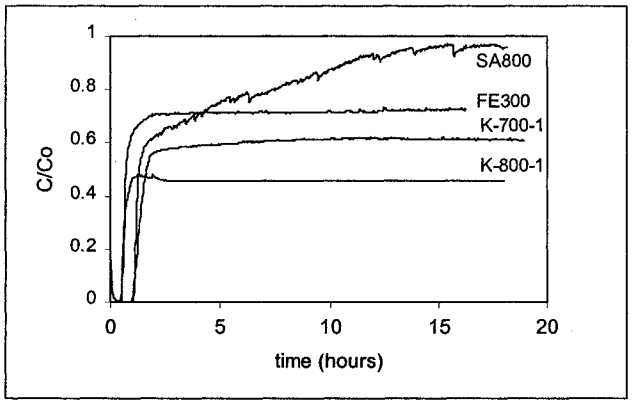

Figure 2. SO2 breakthough plots for as received ACF.

The influence of heat treatment on SO_2 conversion is shown in Figure 3, where steady state activities are compared for the as-recieved fibers, the heat treated fibers, and the (heat treated) composites. Since different masses of catalyst were used in the experiments, a normalized factor F is used to express conversion, where F is mmol of SO_2 converted/$g_{catalyst}$.h. It is apparent that heat treatment significantly increases the catalytic activity, as found by others [1-2]. The greatest increase is for the FE-300 fibers, which could be explained by the effect of heat treatment in eliminating surface oxygen. The oxygen content of the KOH activated fibers is 5-8%, which is much lower than that of the FE-300 fibers (16%). Hence, a greater gain in activity could be anticipated in the latter case. It can also be seen that, generally, the composites exhibit similar activities to those of the corresponmding heat treated fibers.

Conclusion

It has been shown that PAN-based ACF can exhibit good activity for SO2 conversion. Steam activation produced a catalyst whose activity continuously declines, but commercial and KOH activated fibers produce high steady state SO2 conversions.

It is also apparent that the inclusion of the ACF into a more practical composite form can be achieved without loss of catalytic activity.

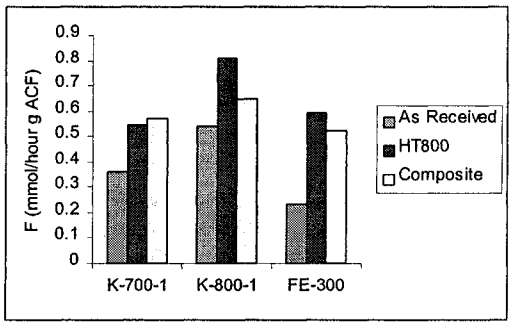

Figure 3. Catalytic activity for as-received ACF, heat-treated 800°C, and ACF composites.

Literature.

1. S. Kisamori, K. Kuroda, S. Kawano, I. Mochida, Y. Matsamura, M. Yoshika. *Energy & Fuels*, 8, 1337, 1994.
2. Y. Fei, Y. Sun., E. Givens, F. Derbyshire. *ACS proc.*, 40(4), 1051, 1995
3. J. Kim, I. Hong, J. Lee. *Carbon'95*, 534, 1995.
4. G. Kimber, F. Derbyshire, M. Jagtoyen, Y. Fei. *Carbon'95*, 518, 1995.
5. I. Martin-Gullon, M. Jagtoyen, F. Derbyshire. This conference.

Acknowledgements. This work was funded by the CAER. Authors thank also Prof. Mochida for suppliyng the Toho Rayon fibers.