

PREPARATION OF ACTIVATED CHAR FOR COMBINED SO₂/NO_x REMOVAL

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Introduction

Carbon-based processes for flue gas cleanup operating in Europe [1] and Japan [2] today typically use two types of carbons, one to remove SO₂ and the other to remove NO_x with ammonia injection. One of the major impediments to the commercialization of this technology in the U.S. has been the cost of the activated carbon and the fact that there is no commercial carbon on the market today that can simultaneously remove both SO₂ and NO_x from coal combustion flue gas. Such a carbon could find use in traditional fixed-bed as well as (less capital intensive) carbon injection processes. Numerous studies have examined NO_x removal by carbon at 300-600°C, although it is most convenient and economical to remove NO_x from flue gas at lower temperatures (100-150°C). Some studies have not used O₂ when testing their carbons, and nearly all studies have neglected the effect of H₂O on NO_x removal. Whether the same carbon can remove significant amounts of NO_x in the presence of both H₂O and SO₂ remains to be determined. The objective of this study [3, 4] has been to develop a low cost activated char from bituminous coal for simultaneous removal of SO₂ and NO_x from coal combustion flue gas. In this paper, we examine the effect of H₂O and SO₂ on NO_x removal by activated chars shown previously in our laboratory to work well in removing SO₂ from simulated flue gas [5]. We also explore the possibility of adding a catalyst to the char to enhance combined SO₂/NO_x removal.

Experimental

Activated chars were prepared from Illinois bituminous coal (IBC-102). A 2 in. ID batch, fluidized-bed reactor (FBR) was used to pyrolyze 200 g of 48x100 mesh coal (N₂, 900°C, 0.5 h) and activate the resultant char (H₂O, 860°C, 30% conversion). The steam activated char was treated with nitric acid (10 M HNO₃, 80°C, 2 h) and thermally desorbed in N₂ or H₂ at 925°C for 1 h to desorb carbon-oxygen (C-O) complexes. A KOH activated char was prepared by mixing KOH with IBC-102 coal (2:1 KOH/coal) and pyrolyzing in the FBR (N₂, 800°C, 1 h). To prepare catalyzed chars, potassium (acetate) or sodium (carbonate) was added to IBC-102 coal by incipient wetness (IW) and pyrolyzed in N₂ (750°C, 0.5 h); the resultant char was activated in CO₂ (720°C, 2 h). In addition, K or Na was ion-exchanged (IE) onto HNO₃ treated char.

A fixed-bed adsorber (1 cm ID x 30 cm stainless steel tube) connected to a quadrupole mass spectrometer (VG Quadrupoles, Fisons Instruments) was used to obtain SO₂ and NO breakthrough curves. Typically, 6 g of char (8 cm bed height) was placed between two layers of quartz wool and heated to 120°C in flowing He (0.2 L/min). The He flow was switched to 2500 ppm SO₂, 500 ppm NO, 5% O₂ and 7% H₂O, balance He (space velocity = 2000 h⁻¹). The char sample was regenerated in situ by heating to 525-925°C in He.

Results and Discussion

Figure 1 presents NO breakthrough curves for several IBC-102 chars and a commercial carbon catalyst, Centaur carbon (Calgon Carbon). Centaur (B) removed little NO_x at 120°C, whereas the thermally desorbed IBC-102 chars (C-G) performed

better. The air oxidized/thermally desorbed IBC-102 char (D) was slightly better than the KOH activated char (A). Exposure of the char sample to ambient air for 48 h prior to a NO_x removal run had a detrimental effect on performance (compare C and E). Chemisorbed oxygen may poison active sites for NO adsorption/reduction. The absence of adsorbed oxygen enhances SO₂ removal by carbon [5, 6]. Carbon atoms not occupied by adsorbed oxygen atom have valence electrons more available and reactive towards SO₂. These unoccupied or free sites control adsorption of SO₂ [7] and perhaps NO_x. Figure 1 also shows that Sample G (sample E heated to 925°C in H₂ instead of N₂) removed nearly twice as much NO_x as sample E. Treatment of char with H₂ at this temperature serves to gasify the most reactive carbons leaving behind a more stable surface, but one that still contains free sites. The more stable surface adsorbs less O₂ and H₂O at room temperature, which leads to more available sites for reaction with NO_x.

Recent results in the literature seem to suggest that low temperature NO_x removal by activated carbon in the presence of SO₂ is not possible [8]. Figure 2 shows the effect of SO₂ and H₂O on NO_x removal by the IBC-102, HNO₃, 925°C char. The char removes 98% of the NO_x for about 1.5 h, then NO partially breaks through to about 200 ppm. For the next 15 h the [NO] increases from 200 to 300 ppm. Two NO_x removal mechanisms seem to be in effect. One where NO is simply adsorbed on the char surface and the other where the char converts NO to N₂. The catalytic mechanism could account for incomplete breakthrough. When both SO₂ and H₂O are added at t = 17 h, large amounts of NO are desorbed. Figure 2 shows that SO₂ or H₂O (or both) displace adsorbed NO_x. This char also adsorbed the expected amount of SO₂ (111 mg SO₂/g char) even though the char was saturated with NO_x. Note that when SO₂ and H₂O were added, NO₂ was also desorbed from the char. The NO₂ desorption peak appears to coincide with the NO peak. Figure 3 shows the effect of adding H₂O and SO₂ at different times during NO_x removal. Note that the catalytic component of the breakthrough curve (200-500 ppm) no longer persists after H₂O is added. The SO₂ capacities of the IBC-102, HNO₃, 925°C chars in Figures 2 and 3 were quite similar, 111 and 99 mg SO₂/g char, respectively.

Figure 4 shows NO breakthrough curves for char prepared from IBC-102 coal loaded with 6% K by IW. This char has a N₂ BET surface area of only 100 m²/g compared to 500-600 m²/g for the uncatalyzed chars shown in Figures 2 and 3. The NO breakthrough curve (no H₂O) fails to exhibit an initial period of 95-100% NO_x removal. Thermal desorption at 925°C, however, results in a 2 h period of > 98% NO removal. Thermal desorption creates free sites for NO adsorption. Figure 4 shows that this char also removes > 98% NO for about 1 h after 7% H₂O is added. A Na-loaded char prepared in a similar fashion also adsorbed NO_x with H₂O, but not to this extent.

Figure 5 presents NO breakthrough curves with and without H₂O and SO₂ for the same sample of IBC-102, HNO₃, K, IE char thermally desorbed at 525°C or 725°C. Sample A (525°C) removed > 98% of the NO for more than 12 h similar to sample G in Figure 1. With H₂O and SO₂ added at t = 0 h, this char (B) performed very well in removing 98% of the NO_x for 2 h. Regeneration at 725°C (C) reduced its effectiveness, perhaps because K volatilizes at T > 700°C. When H₂O and SO₂ were

again removed from the gas stream (D), NO_x removal performance improved, but not to previous levels (A).

Recent studies [9-11] have shown that K is a good catalyst for NO_x removal (without H₂O or SO₂) at relatively high temperatures (300-600°C). In TPR experiments (5°C/min), K-loaded char appeared to remove some NO_x beginning at 100°C, but it was not clear how much or whether it was even a significant amount [11]. To the best of our knowledge, the results obtained with IBC-102, HNO₃, K, IE char show for the first time that significant amounts of NO_x can be removed by activated char at 120°C in the presence of H₂O and SO₂.

Conclusions

The competitive effects of H₂O and SO₂ on low temperature NO_x removal by activated char was examined. The SO₂ capacity of the char was not affected to any appreciable extent by NO in the flue gas. On the other hand, both H₂O and SO₂ appeared to inhibit NO adsorption by activated char. To minimize these competitive effects and to gain better insight into the mechanism of combined SO₂/NO_x removal by carbon, a series of catalyst promoted chars was prepared and tested. One K-catalyzed char showed exceptional promise since it adsorbed significant amounts of NO even with H₂O and SO₂ in the gas stream. Further work is needed to optimize surface area, number of free sites, and dispersion of catalyst.

Acknowledgments

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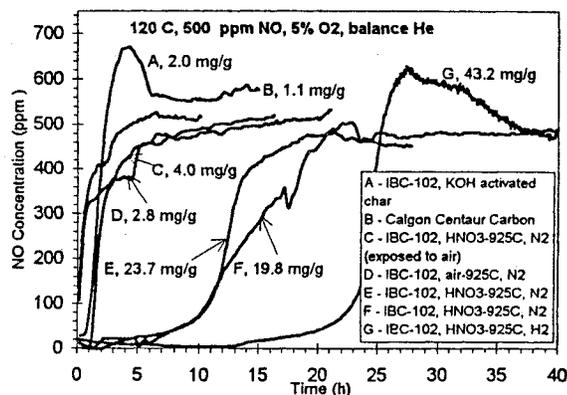


Figure 1. NO breakthrough curves for selected IBC-102 chars and a commercial activated carbon.

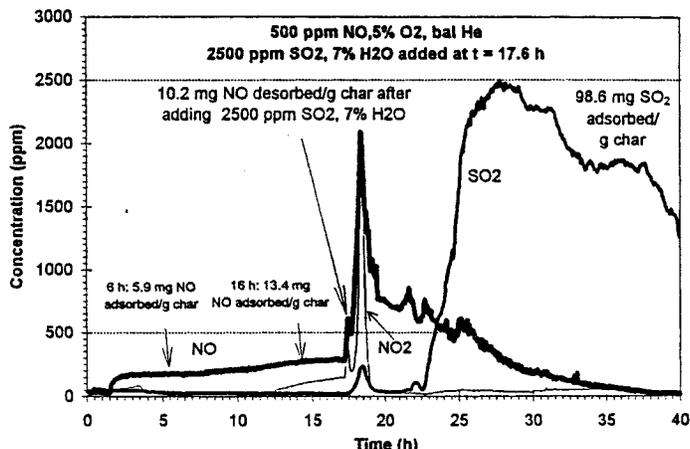


Figure 2. Effect of adding SO₂ and H₂O at the same time on NO_x removal by IBC-102, HNO₃, 925 C char.

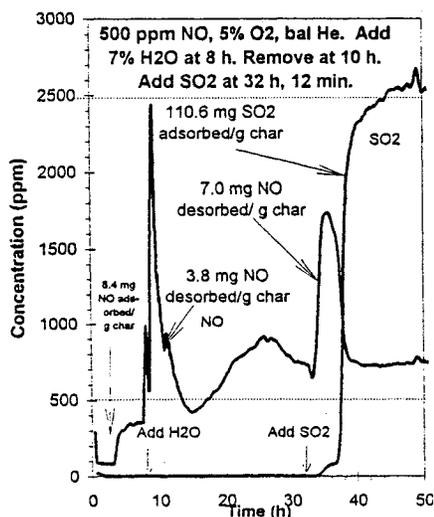


Figure 3. Effect of adding SO₂ and H₂O at different times in NO_x removal by IBC-102, HNO₃, 925 C char.

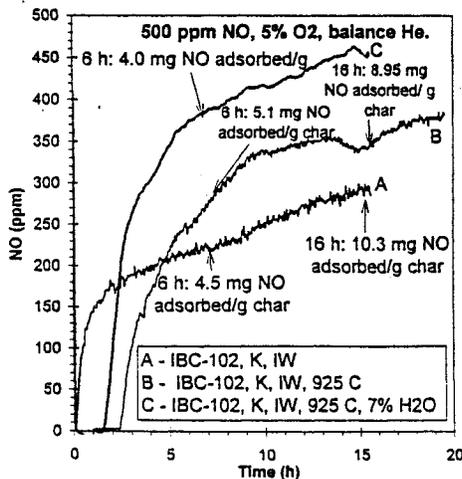


Figure 4. Effect of thermal desorption treatment (925 C) and H₂O on NO_x removal by IBC-102, K, IW char.

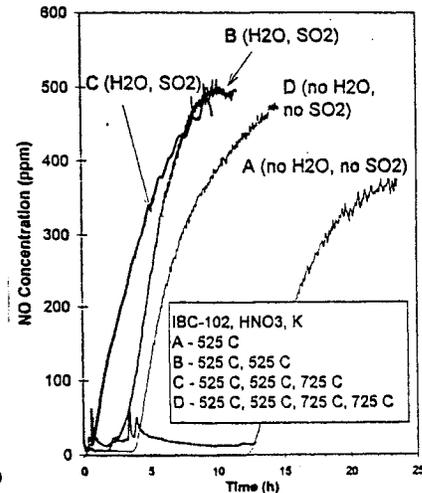


Figure 5. Effect of thermal desorption temperature and H₂O/SO₂ on NO_x removal by IBC-102, HNO₃, K, IE char.