

SELECTIVE ADSORPTION OF NO ON ACTIVATED CARBON TREATED IN HYDROGEN

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Introduction

The primary difficulty with employing carbon for the purpose of NO_x removal at present is a lack of selectivity. Carbon often reacts as readily with oxygen as with NO, yet oxygen is generally present in far higher concentrations (O₂/NO exhaust ratio > 100). Thus, most of the carbon employed as an NO_x removal agent 'burns', rather than performing the function for which it was intended. Is it possible to create a carbon surface with active sites which will selectively react with NO? As discussed below, studies of active site manipulation suggest a possible route.

Experimental

A commercial activated carbon, NORIT C-granular(Nc), was used as the starting material. The adsorption of NO and O₂ on each sample were measured by microcalorimetry carried out in a Calvet-type apparatus which allows *in situ* sample pretreatment [1]. As described in more detail elsewhere [2], samples were prepared either in flowing nitrogen at 950 C (N950), or flowing hydrogen at 950 C (H950). Using this technique, the differential heats of adsorption and the adsorption capacity were acquired simultaneously.

Results and Discussion

In our previous work we demonstrated that it is possible to greatly modify the surface chemistry of carbon, such that the nature of its adsorption properties are dramatically changed. Specifically, microcalorimetry, point of zero charge and isoelectric point studies were all employed to demonstrate that activated carbon treated at high temperatures (ca. 950 C) in hydrogen will not react with oxygen at ambient temperatures, whereas the same carbons treated in an inert gas (e.g. N₂) will react strongly with oxygen at ambient temperatures [2-4]. These differences were traced to differences in the character of active sites. Treatment at high temperatures in any gas will lead to the desorption of oxygen surface functionalities in the form of CO

and/or CO₂. Absent any atom re-arrangement, the desorption of these species will leave highly unsaturated carbon atoms (dangling carbon) on the surface. In an inert gas these dangling carbons will remain, but hydrogen treatments will remove these species. Specifically, hydrogen reacts with any highly unsaturated carbons in the surface to form methane.

All experimental work was completely consistent with the above hypotheses. For example, microcalorimetric studies clearly showed that nitrogen treated samples adsorb a great deal of oxygen at 300 K with very high heats of adsorption. In fact, the heats are consistent with oxygen bonding with nearly 'free' carbon. Heats of this magnitude are consistent with adsorption on 'dangling' (nearly free) carbons. In contrast, only at elevated temperatures (ca. 450 K), did oxygen adsorb, and the measured heat of adsorption were about one-half those found on the nitrogen treated carbon. This is expected for activated oxygen adsorption on mildly unsaturated edge atom sites. Point of zero charge (PZC) measurements also produced results consistent with the above hypotheses. Hydrogen treated carbons retained basic PZC values (>7.0) even after several months of air exposure, indicating that oxygen adsorption, which creates acid sites, did not occur in air. In contrast, the PZC of nitrogen treated carbon became acidic after only minutes of air exposure. Even weight change measures were consistent with the hypotheses. Indeed, carbons treated in hydrogen lost more than twice as much weight (methane formation) as those treated in nitrogen.

The demonstration that it is possible to generate carbon surfaces which do not adsorb oxygen at 300 K naturally suggested a test: Will this same surface adsorb NO at 300 K? Indeed, NO is a stronger oxidant than O₂. Preliminary tests are complete, and it appears that hydrogen treated activated carbon will selectively adsorb NO. As shown in Figure 1, the amount of NO adsorbed on the hydrogen treated sample is significant at 300 K, whereas the amount of oxygen adsorbed on the same material is almost negligible. There are some surprises in the results which suggest the need for further study. For example, the measured heats of

adsorption follow a non-equilibrium pattern. As discussed elsewhere, this can be explained if a linear free energy relationship is not assumed [5]. More NO than oxygen adsorbed on nitrogen treated samples as well (Figure 2). Still, the relative selectivity was not as great as that found for the hydrogen treated sample.

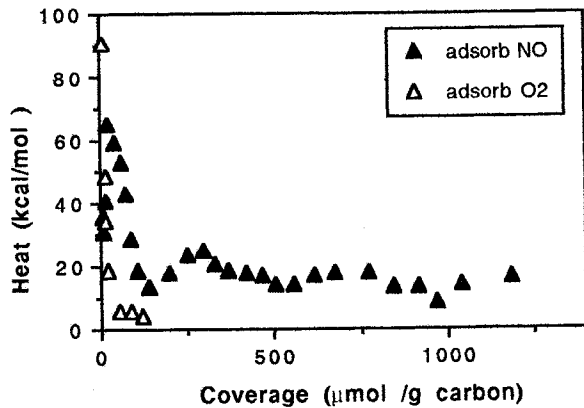


Figure 1. a) The ratio of NO/O₂ strongly adsorbed on H950 is about 10. b) the total NO/O₂ adsorbed ratios about 20.

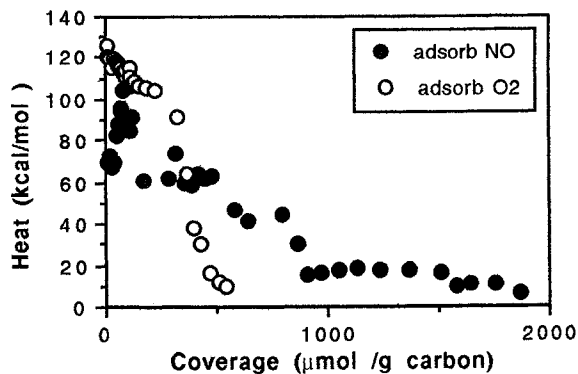


Figure 2. a) The ratio of NO/O₂ strongly adsorbed on N950 is about 2. b) the total NO/O₂ adsorbed ratio is about 3.

Conclusion

In sum, work performed for this study demonstrates that the identity of the treatment gas strongly impacts the surface chemistry of activated carbon. Carbon treated in an inert gas will have dangling carbons on the surface which strongly react with oxygen, and NO, at 300 K. In contrast,

hydrogen treated activated carbon will adsorb very little O₂ at 300 K, but will adsorb significant amounts of NO. The relative selectivity of hydrogen treated carbons toward NO adsorption makes this material a candidate for removal of NO from the exhaust of lean burn combustors.

Acknowledgment

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References

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Table. The amount of O₂ and NO adsorbed at 298K (determined from isotherms)

sample	O ₂ loading (μmol/g)	NO loading (μmol/g)
N950	487	1592
H950	77	1033