

ROLE OF OXYGEN AND NITROGEN FUNCTIONAL GROUPS IN THE PERFORMANCE OF CARBON GASIFICATION CATALYSTS

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Introduction

In recent years sufficient evidence has been gathered in the open literature to confirm the importance of carbon surface chemistry on metal adsorption, catalyst dispersion and catalyzed gasification reactivity of solid carbons [1-5]. In spite of the general guidelines available to tailor the preparation and the subsequent performance of carbon-supported metal catalysts, much remains to be done to resolve the specific details that control the behaviour of specific metal-carbon combinations. This contribution presents selected results of a comprehensive study aimed at developing a better understanding of the specific factors that control the performance of four carbon-supported metals as catalysts: copper, molybdenum, vanadium and lead, with the latter in particular having been found to act as an effective catalyst for NO_x conversion [2].

Experimental

An acid-washed commercial activated carbon (BDH) with 0.1% ash content was subjected to a series of pretreatments in order to modify its surface chemistry. The pretreatments, described in detail elsewhere [1,2], essentially involved subjecting portions of carbon BDH to oxidation in nitric acid, flowing ammonia, or both, at different temperatures, concentrations, and exposure times. The three carbons chosen for the present discussion were prepared as follows: (i) sample BDH, as received; (ii) sample H0.2N, prepared by oxidizing a portion of BDH with 0.2 M HNO₃ at its boiling point for 18 hours; and (iii) sample N400, prepared by flowing dry ammonia gas over a portion of BDH at 673 K for 3 hours. The isoelectric point (IEP), point of zero charge (PZC), BET surface area (SA) and micropore volume (MPV) of these three materials were determined using standard methods outlined elsewhere [2]. X-ray photoelectron spectroscopy (XPS) spectra of the C_{1s}, O_{1s} and N_{1s} peaks of these samples were obtained and deconvoluted on an Escalab 200A analyzer equipped with MgK_α radiation [2].

Results and Discussion

Selected properties of the carbon supports investigated are presented in Table 1. The trends induced by the pretreatments

applied are in general consistent with literature reports [1-4]. Oxidation in HNO₃ lowers the IEP but not the PZC, as expected of a diffusion-limited reaction [3-5]. In contrast, NH₃ increases the PZC substantially in comparison with the IEP, as a combined result of the loss of primarily acidic oxygen groups and the gain of basic nitrogen groups [3]. Neither the surface area nor the micropore volume are substantially modified by these treatments. Hence, differences in the performance of metal catalysts supported on these carbons could be attributed to surface or solution chemistry effects [5].

Table 1. Characteristics of Carbon Supports Investigated.

| Support | %C | %O | %N | IEP | PZC | SA [m ² /g] | MPV [cc/g] |
|---------|------|------|-----|-----|-----|------------------------|------------|
| H0.2N | 85.9 | 14.1 | 0.0 | 2.1 | 2.5 | 1361 | 0.28 |
| BDH | 85.8 | 14.2 | 0.0 | 2.6 | 2.5 | 1288 | 0.27 |
| N400 | 84.1 | 9.7 | 6.2 | 3.8 | 7.5 | 1106 | 0.23 |

To eliminate the influence of solution chemistry on the results, we chose to compare the performance of catalysts prepared at conditions that maximized their precursor adsorption capacity. Using an excess of metal salts as precursors [2] and an equilibrium adsorption method for catalyst preparation [1,2], the metal uptakes by the carbons investigated at pH = 9 for Cu and Pb and at pH = 3 for Mo and V are listed in Table 2.

Table 2. Adsorption Uptakes [wt.%] and Equilibrium Constants (K) for the Carbon Supports Investigated.

| Support | Cu | K _{Cu} | Pb | K _{Pb} | Mo | K _{Mo} | V | K _V |
|---------|-----|-----------------|-----|-----------------|-----|-----------------|-----|----------------|
| H0.2N | 3.4 | 1.9 | 4.8 | 3.4 | 4.4 | 2.8 | 1.4 | 0.4 |
| BDH | 2.0 | 0.7 | 2.9 | 0.9 | 5.0 | 5.1 | 1.7 | 0.5 |
| N400 | 3.1 | 1.5 | 3.9 | 1.7 | 5.4 | 9.3 | 1.3 | 0.3 |

The trends observed in Table 2 are again in general consistent with both literature reports and the expected behaviour of the metal precursors selected [2] in solution at different pH values [4,5]. Carbon BDH shows an enhanced adsorption affinity for

Mo, and a relatively poor affinity for Cu, Pb and V. Oxidation increased the affinity for Cu and Pb cations, and slightly decreased the affinity for Mo and V (primarily anions). Interestingly, nitriding also increased the affinity for Cu, Pb and especially Mo. The peculiar nature of the adsorption of Mo species by carbons has been the subject of numerous research studies [see Ref. 4 and citations therein] and will be addressed separately [6]. For the present purposes it was of interest to determine if the metal adsorption uptakes could be at least qualitatively related to the individual functional groups present on each carbon support tested. To that effect, the XPS O_{1s} spectra were deconvoluted into four peaks tentatively identified as follows [2]: (I) carboxyl groups with binding energies (BE) between 531.0 and 532.1 eV; (II) carbonyl groups with 532.3 ≤ BE ≤ 533.3 eV; (III) phenolic groups with 533.5 ≤ BE ≤ 534.0 eV; and (IV) adsorbed water with 535.5 ≤ BE ≤ 536.1 eV. The deconvoluted values, expressed as a percent of the total oxygen content of each sample, are listed in Table 3.

Table 3. Oxygen Functional Group Content [wt.%] of the Carbon Supports Investigated.

| Support | I | II | III | IV | % Acid | % Basic | Acid/Basic |
|---------|-----|-----|-----|-----|--------|---------|------------|
| H0.2N | 2.4 | 1.1 | 6.4 | 4.2 | 8.8 | 5.4 | 1.6 |
| BDH | 3.0 | 3.6 | 5.5 | 2.1 | 8.5 | 5.7 | 1.5 |
| N400 | 3.7 | 2.5 | 2.6 | 0.9 | 6.3 | 3.4 | 1.9 |

Table 3 suggests that sample BDH is rich in carbonyl groups relative to its treated counterparts. Oxidation appeared to enrich primarily sample BDH's phenolic group content. In contrast, nitriding appeared to reduce the phenolic and carbonyl group content (as expected), but not the carboxyl group content. As a result, the treatment-induced variations in overall acidic (carboxyl plus phenolic) oxygen group contents are consistent with expectations, whereas the estimated basicity of sample N400 is relatively low. These observations suggest that the strengths of carboxyl groups attached to oxidized and nitrated surfaces may differ considerably, thus complicating O_{1s} peak deconvolution assignments in terms of common binding energy ranges for oxygen groups attached to such dissimilar substrates.

The gasification reactivities of the carbon-supported catalysts in flowing air at 673 K are listed in Table 4. As expected [7], the reactivities in air follow the order Cu > Mo > Pb > V. For Cu, both pretreatments increased the gasification reactivity, presumably due to an increase in the dispersion of the catalysts [1,4]. Extrapolation was necessary for sample N400 because the copper appeared to melt and spread more readily on its nitrogen-group (primarily pyridine type) enriched surface [2], thus improving the metal's catalytic activity [7]. In contrast, Mo activity was inversely proportional to the acid/basic ratio of the carbon supports, as reported elsewhere [4].

Table 4. Carbon Gasification Reactivity R [g/s/g Carbon x 10³] for the Supports and Catalysts Investigated.

| Support | R _{Support} | R _{Cu} | R _{Pb} | R _{Mo} | R _V |
|---------|----------------------|---------------------|-----------------|-----------------|----------------|
| H0.2N | 1.8 | 771 | --- | 32.7 | --- |
| BDH | 0.3 | 477 | 27.4 | 61.3 | 6.4 |
| N400 | 1.3 | (2103) ^a | --- | 16.3 | --- |

^a Obtained by extrapolation from lower temperatures.

As a further attempt to decouple the contribution by acidic and basic functional groups to the performance of the gasification catalysts studied, the reactivity data were normalized with respect to the acidic and basic oxygen group contents. The trends (not shown) are similar to those of Table 4 in that the performance of Cu catalysts was increased, and that of Mo catalysts decreased, by applying oxidation or nitriding pretreatments to the original carbon. Work in progress is aimed at elucidating the role of individual oxygen and nitrogen groups on the overall performance of the catalysts investigated [6].

Conclusions

The effects of surface chemistry modifications on the performance of carbons as catalyst supports are not straightforward. In the absence of information specific to a given metal-carbon combination, the effects of different functional groups should be regarded as complementary in nature. Decoupling such effects for any given catalyst is a challenge that demands very careful systematic studies. Work is continuing to gain insights regarding the precursor sorption ability and the gasification performance of carbon-supported Cu, Pb, Mo and V catalysts [2,6].

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