

POSTER

AN IMPROVED METHOD FOR EVALUATING THE ACTIVE SURFACE AREA OF SOLID CARBONS

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INTRODUCTION

Ever since its inception [1] the active surface area (ASA) concept has fueled many a debate regarding the number of active sites involved in the gasification of solid carbons [2,3]. The conventional approach to measure ASA involves the following steps: (i) activating the carbon sites by treating the sample under inert gas flow or vacuum at ≥ 1223 K; (ii) cooling down the sample, usually to 373-573 K; (iii) flowing an oxygen-containing gas over the sample to load its active sites with oxygen atoms; (iv) removing all non-chemisorbed oxygen from the sample cell by evacuation or inert gas flow; and (v) monitoring the desorption of CO and CO₂ as the sample is heated back to ≥ 1223 K. The sample's ASA is then calculated by multiplying the number of oxygen atoms desorbed as CO and CO₂ by the surface area presumed to be occupied by each chemisorbed oxygen atom, 0.083 nm² [1]. Unfortunately, the numerous attempts to correlate ASA with carbon gasification reactivity have mostly led to crude or scattered correlations. Different authors have attributed the scatter to either the reactivity measurements (owing to diffusion limitations, catalytic impurities or product inhibition) or the experimental variables that affect ASA measurements (temperatures, oxygen pressures, exposure times, adsorption stoichiometry and the possibility of gasification during chemisorption). The latter aspects have geared modern investigations towards seeking chemical or physical refinements of the ASA concept, such as the reactive surface area (RSA) concept [3c] or fractal geometry interpretations [4]. Yet a third - and seldom explored - possibility is to substantially modify the classical experimental technique by which ASAs are measured. The purpose of this paper is to discuss the advantages of evaluating the ASA of solid carbons by applying an oxygen chemisorption technique known as the "dual isotherm" or "bracketing" method [5,6].

EXPERIMENTAL

The bracketing technique, as applied to the evaluation of the ASA of solid carbons, consists of the following steps: (i) activating the carbon sites by treating the sample under inert gas flow, followed by vacuum, at ≥ 1223 K; (ii) cooling down the sample under vacuum to the chemisorption temperature; (iii) briefly exposing the sample to helium to measure the sample cell's void volume [7]; (iv) introducing incremental doses of gaseous oxygen in order to generate a TOTAL (chemical plus physical) adsorption isotherm; (v) evacuating the sample at the adsorption temperature to

remove the physically adsorbed oxygen; and (vi) reintroducing incremental doses of gaseous oxygen in order to generate a WEAK (physical) adsorption isotherm. A STRONG (chemical) adsorption isotherm can then be constructed by subtracting the reversibly adsorbed WEAK portion from the TOTAL isotherm. The ASA can thus be calculated by extrapolation of the TOTAL isotherm to zero pressure [5] or, alternatively, from the difference between the STRONG and the WEAK isotherm uptakes at a selected pressure [5,6].

All adsorption experiments described below were carried out on a fully automated physisorption-chemisorption analyzer, the AUTOSORB-1-C (Quantachrome Corp.). This commercial instrument features a total of five high resolution pressure transducers (two in the manifold, two in the sample cell itself, and one for continuous P₀ measurements during physisorption tests). Having two dedicated sample cell pressure transducers (10 and 1000 mm Hg) greatly improves the accuracy of pressure measurements by allowing the isolation of the sample cell after a gas dose is made. Monitoring pressure changes in as small a volume as possible is indeed a critical issue when one attempts to measure the small pressure changes associated with generally low chemisorption uptakes. On the other hand, a unique software algorithm allows the unit to produce data points at user-selected target pressures in minimal time. Prior to ASA measurements, representative samples were obtained by riffling selected powders on a Rotary Micro Riffler (Quantachrome Corp.). The AUTOSORB-1-C was then programmed to (i) heat 1 g of sample at 40 K/min to 1273 K in flowing helium; (ii) evacuate at 1273 K for 1 h; (iii) cool down to the adsorption temperature; and (iv) generate TOTAL and WEAK oxygen adsorption isotherms as described above.

RESULTS AND DISCUSSION

The notion that active sites play a role in carbon gasification was a natural extension of earlier theories pertaining to heterogeneous (gas/solid) reactions [8]. Surprisingly, the successful incorporation of the ASA concept into the carbon gasification arena was not followed by the direct importation of active site evaluation techniques developed for, e.g., heterogeneous catalysts. Instead, active sites for carbon gasification were presumed to be covered with reaction intermediates, i.e., oxygen complexes, that could be (a) formed at a temperature low enough to prevent their gasification, and (b) subsequently quantified by thermal desorption. This approach involves a number of fundamental and practical limitations that can be avoided by performing oxygen chemisorption experiments according to the bracketing

technique already described. The advantages of this technique over other ASA evaluation methods are as follows:

1. One has much better control over the degree of coverage of carbon active sites by oxygen. Loading the oxygen in incremental, equilibrated steps avoids uncertainties related to (a) the time needed for complete site coverage in flow methods, and (b) the possibility of a concomitant, pressure-dependent gasification at the adsorption temperature chosen.
2. The bracketing technique avoids ambiguities related to the quantification of oxygen chemisorbed via other methods. In contrast to the bracketing technique, other methods must assume that (a) all the oxygen chemisorbed is desorbed completely and exclusively as CO and CO₂ at ≥ 1223 K, and/or (b) oxygen physisorption, chemisorption heat release, carbon gasification, catalytic impurities and gravimetric buoyancy corrections are relatively unimportant. However, discrepancies between ASA values calculated from TPD and gravimetric [3a] or elemental [4] analyses weaken such assumptions.
3. The results are much more informative. Instead of a single oxygen chemisorption value (STRONG at 1 atm), the bracketing technique yields complete chemisorption and physisorption profiles on the sample as a function of oxygen pressure. This allows one to address fundamental issues such as the progressive filling of different active sites, activated adsorption, oxygen spillover, etc.
4. The bracketing technique is faster, simpler, more accurate and more economical than other methods. With this technique there is no need to spend hours pre-loading the active sites with oxygen and then reheating the samples to desorb surface complexes, or to possess a mass spectrometer/gas chromatograph with which to quantify the desorption products. Modern automated instrumentation can yield accurate, in situ ASA evaluations with minimal operator intervention.

Figure 1 illustrates the kind of results that can be generated with the bracketing technique. The ASA of this sample, calculated by extrapolation of the STRONG isotherms to zero pressure, is 0.0803-0.4371 m²/g in the range 273-373 K. This represents between 0.104% and 0.565% of this sample's BET surface area, also measured on the AUTOSORB-1-C. Interestingly, the ASAs calculated by extrapolation from the TOTAL isotherms to zero pressure yielded similar ASA values (0.437-0.495 m²/g at 273-373 K). This suggests that while the total number of active sites capable of interacting with oxygen at low temperatures is similar, a decreasing fraction of them become labile enough to be desorbed under vacuum as the temperature of oxygen exposure rises. Indeed, the bracketing technique offers potential as a pressure-switching alternative to the gas-switching or temperature-switching attempts currently employed to differentiate between labile (reactive?) and stable carbon gasification intermediates [2,3].

SUMMARY AND CONCLUSIONS

Current ASA evaluation techniques involve a low-temperature exposure of active sites to a flow of an oxygen-containing gas. This particular step leads to uncertainties regarding the extent of oxygen chemisorption and its relationship to carbon active sites. In addition, thermal desorption methods, when employed for ASA evaluation, raise questions regarding active site changes and the true fate of all chemisorbed oxygen atoms. Performing ASA determinations via a static-volumetric technique known as the bracketing method avoids these ambiguities and provides a more thorough and reproducible description of oxygen chemisorption on solid carbons than currently employed ASA evaluation methods. Therefore, the bracketing technique should be the method of choice for ASA measurements.

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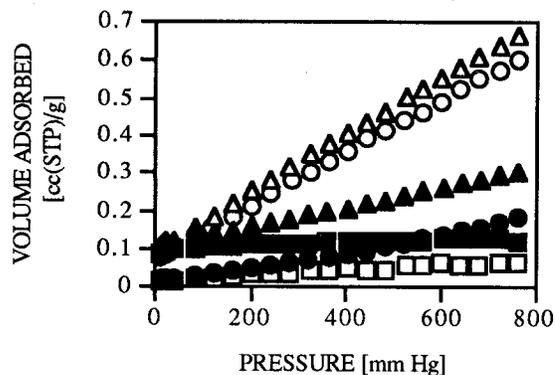


Figure 1. Oxygen Adsorption Isotherms on Carbon Black ASTM-N326. Total (triangles), Weak (circles) and Strong (squares) Isotherms at 0° (open) and 100°C (closed) are shown.