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A STUDY OF METALS SUPPORTED ON ACTIVE CARBON WITH A TEMPERATURE PROGRAMMED REDUCTION (TPR) TECHNIQUE

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Abstract

The influence of active carbon as support on the reducibility of supported metals (Ni, Cu, Cd, Zn) has been studied by means of a temperature programmed reduction (TPR) technique. The TPR profiles indicate that active carbon behaves as a dispersion agent and the supported metal is dispersed in a disordered phase rather than as a stoichiometric compound. The hydrogen consumed in the reduction indicates that the metal residues are present in monovalent and divalent forms. High-temperature reduction peaks were also observed and are explained on the basis of metal - surface interactions and the porosity of the active carbon. Nitrogen adsorption reveals that the active carbon porosity decreases due to progressive closure of the pores when metals are supported on the surface of active carbon.

Keywords: active carbon, temperature programmed reduction technique

Introduction

Active carbon is a structurally heterogeneous carbonaceous material of high porosity, which is important in its use as an adsorbent, catalyst and catalyst support; it is widely used for chemical processes [1–7]. The porosity of solid supports, which originates from both open and closed pores, is a determining factor in the technological application of such materials. In catalytic processes, the internal porosity of the catalyst controls the rate of mass transport of reactants within the grain and hence determines the catalytic activity and selectivity. Efforts have therefore been made in catalyst processing to enlarge the porosity of the support without losing its stability. When the efficiency of active carbon is low, different types of impregnates are added to the carbon lattice to enhance its activity. These impregnates have been found to be generally effective adsorbents [8–11], on which not only adsorption, but also chemical reactions and catalytic decomposition take place. With increasing amount of the dopant, the chemisorption and catalytic activity increase, but the physical adsorption capacity decreases, due to the dispersion of the metals on the support.

The TPR technique has been applied successfully for the characterization of supported metals, and to study the influence of the support material and pretreatment procedures on the reducibility of catalyst surfaces [12]. However, the quantitative evaluation of TPR data relating to supported metals on active carbon supports has scarcely been discussed in the literature. We have studied the reduction of supported metals on active carbon of high surface area. The problem always exists of the assignment of the peaks of a TPR profile to definite chemical species or to the same species located at different sites of the support. This paper describes our attempts to make such assignments by (i) utilizing nitrogen adsorption studies to investigate the pore diameters of active carbon supporting metals; (ii) using TPR in conjunction with XRD.

Experimental

Active carbon supplied by Merck (Cat. No. 2184) was washed by several cycles of immersion in distilled water until there was no change in *pH*. Metal chlorides with purities better than 99% were supplied by Aldrich. The nitrogen gas used for adsorption experiments was 99.99% pure; it was obtained from Masonlite (England) in a break seal storage bulb.

To support the metals on active carbon, a predetermined amount of metal chloride was magnetically stirred in 200 ml of distilled water, and 10 g of active carbon was added to the mixture. The mixture was stirred for 8 h at 373 K until a slurry was formed, and the mixture was then dried under vacuum at 363 K for 3 h. The dried samples were next heated at 735 K for 5 h in nitrogen atmosphere. A blank carbon sample was also prepared by applying the same treatment, except that distilled water was used in place of metal chloride solution.

For the measurement of metal concentration, 1 g of the sample was thoroughly stirred with perchloric acid solution for 4 h at room temperature. The total amount of the metal in solution was then determined by atomic absorption spectroscopy (ZEISS Model FMD 47).

Complete nitrogen adsorption-desorption isotherms were measured at 77 K by using a Quantasorb sorption system, and surface area was calculated by the BET method. Pore size distribution was determined from the nitrogen desorption isotherm by the method of Dollimore *et al.* [13].

The TPR system used for reduction was similar to that described by Karim [14]. The reducing gas, 6% hydrogen in argon, was purified over a Pt/Al_2O_3 catalyst. It was directed (flow rate 40 ml/min) first through the reference compartment of the thermal conductivity cell, then through a U-shaped reactor containing a weighed amount of solid on a silica sinter in one arm, and finally, via a cold trap, through the other compartment of the thermal conductivity cell.

The U-shaped reactor was surrounded by a tubular furnace whose temperature was increased linearly (5 deg·min^{-1}) by using a temperature programmer controlled by a thermocouple in contact with the sample. The amount of hydrogen required for complete reduction was measured by the difference in thermal conductivity of the gas before and after reduction.

The temperature of maximum rate of reduction and the area underneath the profile corresponding to the hydrogen consumption were registered by a microprocessor automated to the TPR system.

After each reduction, the whole system was calibrated by injecting a known volume (0.125 ml) of hydrogen (99.999% pure) into the detector.

Table 1 Adsorption data on active carbon supported metals

Amount of metal mole/100 g	BET surfac earea/ $m^2·g^{-1}$	Metal conc. per unit area / $g·m^{-2}$	Micropore volume DR equation / $cm^3·g^{-1}$	Micropore radii / Å
Carbon				
–	849.2	–	0.3156	7.80
Ni–C				
0.0170	801.1	0.00252	–	–
0.0350	793.2	0.00252	0.2845	7.45
0.0600	773.8	0.00419	0.2804	7.35
0.0800	754.7	0.00528	–	–
0.0130	731.4	0.00675	0.2661	7.27
Cu–C				
0.0160	781.7	0.00124	0.2824	7.31
0.0300	772.7	0.00233	0.2814	7.29
0.0550	763.3	0.00420	0.2599	6.97
0.0800	753.4	0.00609	–	–
0.0950	736.5	0.00710	0.2520	6.90
Zn–C				
0.0150	815.2	0.00120	–	–
0.0300	837.2	0.00239	–	–
0.0550	786.9	0.00429	0.2760	7.04
0.0770	763.3	0.00604	0.2648	6.98
0.0950	746.7	0.00744	0.2573	6.97
Cd–C				
0.0170	763.6	0.00233	0.2880	7.51
0.0300	754.5	0.00409	–	–
0.0375	738.8	0.00494	0.2715	7.44
0.0500	728.9	0.006570	–	–
0.0580	709.6	0.00758	–	–
0.0800	675.1	0.01042	0.2413	7.15

Results and discussion

The relationship between the surface area of the powder and the concentration of the metal is given in Table 1. It is evident that the BET surface area of active carbon decreases with increasing amount of metal. This may be due to the dispersion of metal residues on the surface of the active carbon.

The idea of the presence of metal residues on the surface of active carbon is consistent with the pore size distribution curves (Fig. 1). This is explained in terms of a decrease in the microporosity of doped carbon in the range of approximately 11 Å which may occur in part because of the micropore blockage of active carbon by dispersed metal residues, as confirmed by DR analysis.

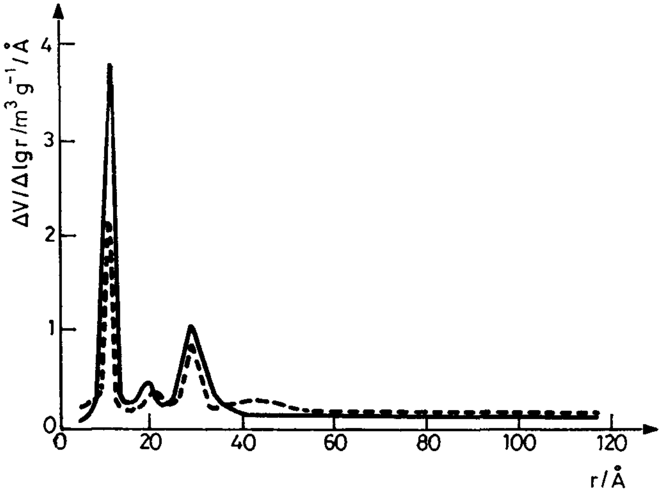

Fig. 1 Pore size distribution in active carbon and active carbon containing 0.0347 mole of nickel per 100 g of active carbon

Figures 2–5 present DR plots of nitrogen adsorption on active carbon and active carbon supporting metals. The DR plot for active carbon exhibits an upward deviation at higher relative pressure, indicating a heterogeneous system of micropores [15]. The DR plots for the supported systems exhibit the same trend, but only a slight upward deviation is observed at higher pressure. This shows that these metal supporting adsorbents have a relatively homogeneous system of micropores and this character increases with increasing amount of metal in the carbon lattice. The micropore volume expressed in cm^3·g^{-1} decreases with increasing metal concentration. This means that the doping of active carbon is accompanied by a diminution in microporosity through the progressive closure of micropores. These results agree with those of Hiria [16], whose X-ray microanalysis showed that Cu(II) chloride is reduced to Cu(I) chloride, which is uniformly distributed on the surface.

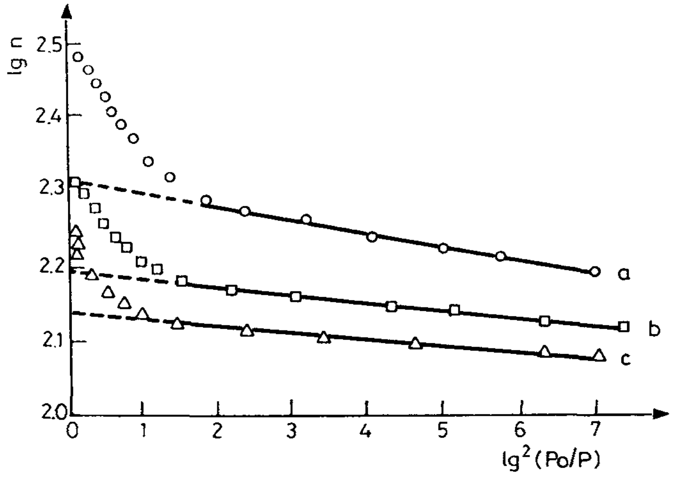

Fig. 2 DR plots for the nitrogen adsorption (a) active carbon and carbon containing nickel, (b) 0.05778 mole, (c) 0.09301 mole

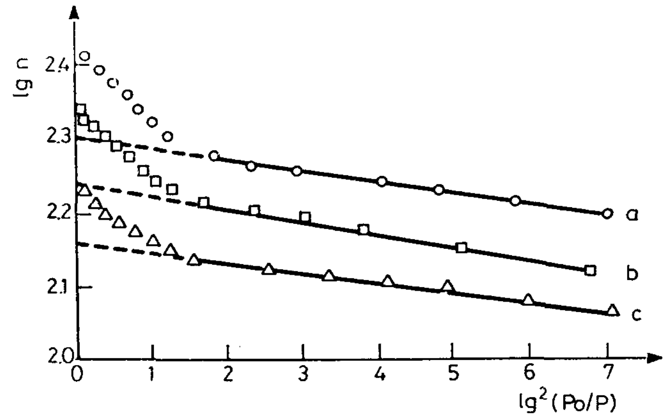

Fig. 3 DR plots of active carbon supported copper (a) 0.0296 mole, (b) 0.0775 mole, (c) 0.0619 mole

The degree of dispersion of supported metals and the influence of the support on their reduction are studied by means of the TPR technique. TPR profiles for supported metals on active carbon of high surface area (containing 5% w/w metal) are given in Fig. 6. The TPR profile for pure active carbon gives no peaks around 773 K and it behaves as an inert material. A broad reduction peak is observed at 923 K, but the hydrogen uptake is negligible, indicating that it may be due to impurities entrapped within the pores of the active carbon. The TPR profiles for zinc and cadmium show one well-defined reduction peak centred at 664 and 592 K, respectively. In the case of cadmium, the quantity of hydrogen consumed corresponds nearly to complete reduction of all the cadmium present and indicates that the reduction of Cd(II) takes place in a single step. In the case of zinc, the value of T_{max} is lower by 60 deg than its bulk value, with a somewhat broader reduction profile, reflecting a disordered phase rather than a stoichiometric compound. The active carbon in this case appears to act as a dispersing agent and promote the reactivity of zinc toward reduction.

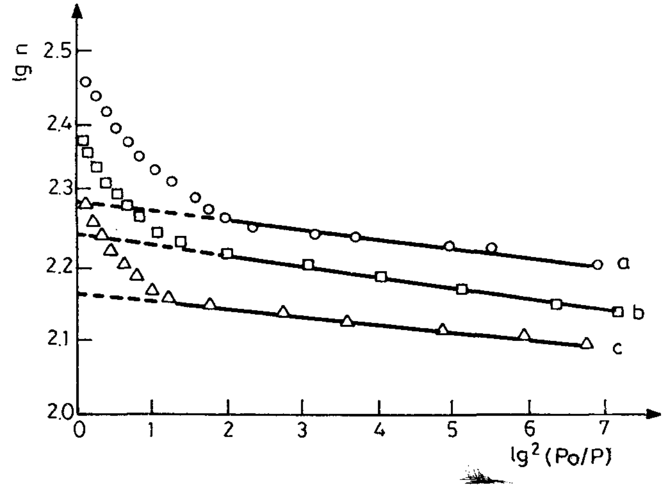

Fig. 4 DR plots of active carbon supported cadmium (a) 0.0168 mole, (b) 0.035 mole, (c) 0.0750 mole

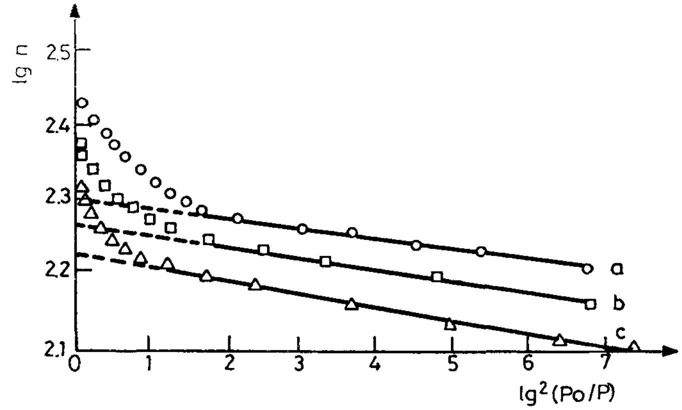

Fig. 5 DR plots of active carbon supported zinc (a) 0.0532 mole, (b) 0.0748 mole, (c) 0.0922 mole

The TPR profile for nickel shows a marked effect of the support in promoting two peaks, one at 621 and the other at 673 K. The low-temperature reduction peak occurs near the reduction temperature of nickel oxide. The second reduction peak is due to a species which is more difficult to reduce. The TPR profile for supported copper shows a typical sharp peak with a shoulder towards high temperature. The main reduction at 668 K contributes more than 80% towards the total reduction. This indicates that in this case the support appears to function purely as a dispersing agent and to promote the reduction of copper. The presence of high-temperature reduction peaks for nickel and a shoulder for copper could be due either to surface – metal interactions or to the presence of active carbon with two different pore size (11.0 and 28 Å). The relation between low-temperature and high-temperature reduction peaks and different pore size

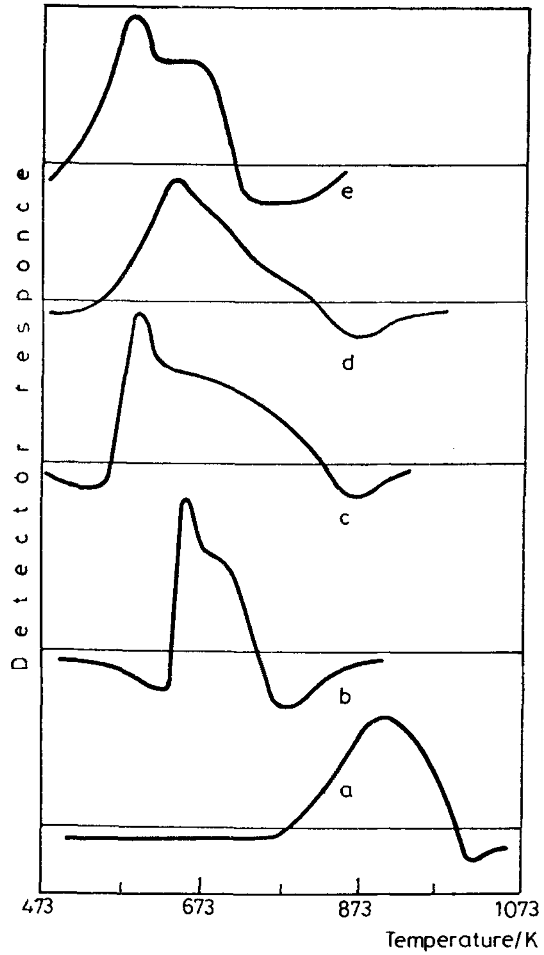

Fig. 6 TPR profile for (a) active carbon, (b) Cu–C, (c) Cd–C, (d) Zn–C, (e) Ni–C

has recently been studied in detail by Brynmoore [17]. He observed that low-temperature peaks are associated with small pores, and high-temperature peaks with large pores. This explanation fits very well for active carbon-supported copper and nickel. Similar TPR profiles have been reported by others, but not discussed [18–20].

In each case, the reduction peaks immediately followed a small but clear hydrogen desorption trough, indicating that there is evidently an overlap between the processes of reduction (including hydrogen chemisorption) and hydrogen desorption. To obtain the correct ratio of M/H for the reduction, the quantity desorbed was also determined, as approached by Bond *et al.* [21].

Table 2 TPR measurements on active carbon and active carbon supported metals

Adsorbent	Hydrogen uptake			Hydrogen desorption			
	T_{max} /°C	v_H	M/H	T_{max}/°C	v_H	M/H	net M/H
Carbon	649	89	–	734	39	–	–
Cu–C	395	651	1.67	435	72	0.092	1.59
Ni–C	348	736	1.73	450	82	0.096	1.63
Zn–C	391	683	1.79	635	171	0.192	1.61
Cd–C	319	402	1.81	453	49	0.108	1.70

v_H = μmol·g^{-1}

The values of M/H (Table 2) are less than 2, showing that the supported metals are present in monovalent and divalent forms, as discussed earlier. Furthermore, XRD analysis demonstrates that these metal(II) chlorides are partially reduced to metal(I) chloride, and there appears to be no indication of the formation of a stoichiometric compound particularly at low concentration [22]. This means that active carbon acts as a reducing agent, resulting in the forma-

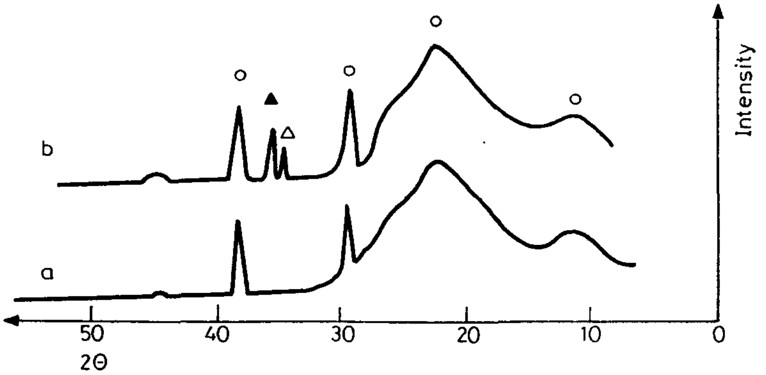

Fig. 7 X-ray patterns of (a) active carbon, (b) active carbon containing copper 0.0296 per 100 g. (o) Carbon (Δ) Cu(I)–Cl (▲) Cu(II)–Cl

tion of metal(I) chloride. These results display some similarities to those of Komiyama [23], who concluded that copper(II) chloride and active carbon react during preparation, resulting in the formation of copper(I) chloride and hydrochloric acid.

Conclusion

This TPR study shows that cadmium and zinc supported on the surface of active carbon are dispersed as a disordered phase, but do not interact chemically with the carbon under the conditions used. In the cases of supported nickel and copper, two distinct types of Ni(II) and Cu(II) species are present on the surface of the active carbon, and are distinguished by temperature differences in their maxima during TPR. The existence of the two reduction peaks for nickel and copper is related to more reducible species which are mainly situated in micropores with a mean pore radius of 11 Å and less reducible species (in large pores with a mean radius of 20 –35 Å).

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Zusammenfassung — Mit Hilfe einer temperaturprogrammierten Reduktion (TPR) wurde der Einfluß von Aktivkohlenstoff als Trägermaterial auf die Reduzierbarkeit der getragenen Metalle (Ni, Cu, Cd, Zn) untersucht. Die TRP-Profile zeigen, daß sich der Aktivkohlenstoff als Dispersionsmittel verhält und daß das getragene Metall eher als unregelmäßigen Phase dispergiert ist als in Form einer stöchiometrischen Verbindung. Der bei der Reduktion verbrauchte Wasserstoff zeigt, daß die Metallreste als mono- und bivalente Formen vorhanden sind. Es wurden auch Hochtemperatur-Reduktionspeaks beobachtet, die auf der Grundlage von Metall-Oberfläche-Wechselwirkungen und der Porösität des Aktivkohlenstoffes erklärt wurden. Die Stickstoffadsorption läßt erkennen, daß die Porösität des Aktivkohlenstoffes wegen des zunehmenden Verschließens der Poren abnimmt, wenn Metalle auf der Oberfläche von Aktivkohlenstoff aufgetragen werden.