

POSTER

Effect of NH_3 treatment on the catalytic oxidation of carbon catalysed by Cu and Mo

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INTRODUCTION

It is known that the dispersion of catalysts on the carbon surface can be improved by chemical treatment of the carbon (1-4). Functional groups can affect the carbon/metal interaction leading to changes on the catalytic behaviour.

The aim of this work is to study to what extent chemical surface treatments influence carbon reactivity as well as molybdenum and copper dispersion on charcoal under air gasification conditions.

Several catalyst preparation techniques were used. The modified carbons were analysed by XPS and FTIR.

EXPERIMENTAL

Support treatment with NH_3 . The process was conducted in a tube furnace in a continuous flow mode ($100 \text{ cm}^3/\text{min}$ of NH_3) at various temperatures: 200, 400 and 600°C (raised at $5^\circ/\text{min}$) and held at the reaction temperature for 3 h. Sample N600-6 only was held for 6 h. The samples were washed with DD water until the pH of the eluent was neutral and dried in vacuum. N200, N400, N600 and N600-6 denote the carbon thus prepared. The samples were characterised by N_2 adsorption at 77 K on a Micromeritics ASAP 2010 V1.01 B (Table 1). The PZC was determined placing 0.5 g of each carbon in plastics bottles with 5 ml of DD water, the bottles were sealed and shaken during 48 hours. The pH of the slurry was then measured.

Catalyst preparation. Three methods of catalyst addition were investigated. The precursors were ammonium heptamolybdate and copper nitrate. Catalyst were prepared by physical mixture, by incipient wetness impregnation and by equilibrium adsorption at different pH preadjusted with HCl and NaOH. The samples were filtered after reaching the equilibrium (24 hours) and dried in vacuum at 100°C overnight. The amount of Cu and Mo remaining in solution was analysed by atomic absorption spectroscopy and ICP respectively.

Thermogravimetry. The kinetic experiments were conducted isothermally in a C. I. Electronics MK II microbalance with continuous recording of change in weight. A charcoal BDH33033 was used. All the system was purged with a stream of N_2 . The measurements were made by introducing flowing air at a constant rate of $4 \text{ cm}^3/\text{s}$.

In situ XRD studies. The experiments were conducted in a Rigaku D/max III C diffractometer with a Cu(α) radiation source (40 mV, 30 mA), equipped with a high temperature special chamber. Air and N_2 were flowed at a rate of $2.5 \text{ cm}^3/\text{s}$.

FTIR analysis. Spectra were recorded on a Nicolet 740 single channel Fourier Transform Spectrophotometer with N_2 purge. These were obtained by co-addition of 50 scans at a resolution of 4 cm^{-1} in the range $600\text{--}4000 \text{ cm}^{-1}$. The original spectra were corrected with a curved baseline. The pellets were prepared by mixing 2.3 mg carbon with 0.3 g KBr. Samples were dried overnight at 110°C in vacuum and pressed just before recording.

XPS analysis. XPS spectra were collected by an Escalab 200A spectrometer using unmonochromatized Mg K α radiation. The pressure in the analysis chamber was 1×10^{-9} mbar. The energy scale of the spectrometer was calibrated using the Ag signal at 368.26 eV. Detailed spectra were collected with a pass energy of 10 eV.

RESULTS AND DISCUSSION

Table 1 shows the chemical and textural characteristics of the samples used. No significant surface area change was observed, as referred previously (1). A significant mesoporosity increase was observed in samples nitrated at temperatures above 400°C . Treatment with NH_3 lead to an increase in the surface basicity, as can be seen from the PZC values (Table 1).

Table 1. Characteristics of the samples

Sample	PZC	S (m^2/g)	V (cm^3/g)
BDH	2.54	1288	0.27
N200	6.65	1212	0.26
N400	7.51	1106	0.23
N600	8.07	1104	0.23
N600-6	7.40	1136	0.23

S-Surface Area obtained by the BET equation, V-Micropore Volume

Figure 1 shows the effect of surface treatment and initial pH of the solution on the Cu and Mo uptake. The adsorption of ammonium heptamolybdate is higher at $\text{pH} < \text{PZC}$. Electrostatic interaction between the support and molybdenum anions occurs when the carbon surface exhibits positive charge (1-3). The adsorption of copper nitrate seems to be independent of surface treatment and pH conditions. Maximum uptake of molybdenum was observed with carbon sample N400 at $\text{pH}=2$.

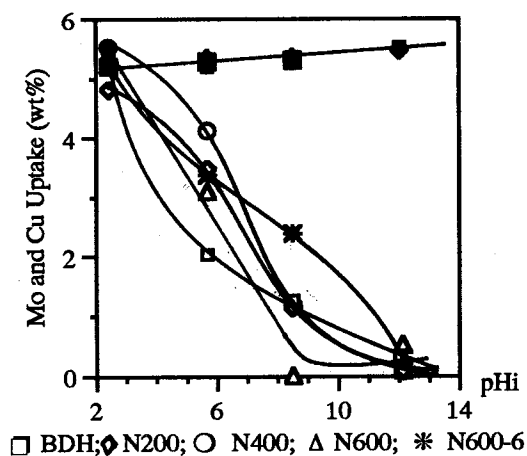


Figure 1. Influence of initial pH (pH_i) on catalysts uptake for carbon treated with NH_3 . (black symbols for Cu and white for Mo).

XPS- The surface compositions evaluated by XPS analysis are shown on Table 2. Treatment with NH₃ leads to an increase of nitrogen groups.

The binding energy (BE) of 284.6 eV of the graphitic peak was used as a standard for the others peaks. The position and assignment of C1s peaks are given in Table 3. The O1s spectra were fitted to four peaks with BEs 531.0-532.1, 532.3-533.3, 533.5-534.0 and 535.5-536.1 eV. The O1 was assigned to C=O type oxygen (C=O, COOR) and the O2 and O3 peaks were both assigned to C-O type oxygen (C-OH and COQR) respectively. The samples N600 and N600-6 have a O2 peak with BE 532.9 eV. Some authors assigned this peak to quinone type oxygen. The O4 peak may be due to adsorbed water. The N1s spectra were fitted to four peaks with BEs 398-399, 399-400 and 400-401 eV. The N1 peak was assigned to pyridine-like N, the N2 and N3 peaks were assigned to amides (CONH2) and aliphatic amines respectively. The N4 peaks at 402.8-405.3 eV were assigned to N-oxides. The areas of these peaks are presented on Table 4.

Table 2. Surface compositions (atomic %)

Sample	C	O	N
BDH	85.8	14.2	-
N200	84.7	11.4	3.9
N400	84.1	9.7	6.2
N600	88.1	6.9	5.1
N600-6	88.4	5.2	6.4

Table 3. Position and assignments of C_{1s} peaks

Peak no.	Binding energy (eV)	Assignment
0	284.6	Graphitic,aromatic
1	285.6	Aliphatic
2	286.4	C-OH, C-O-C
3	287.7	C=O
4	288.8	COOH, COOR
5	290.1	CO ₂
6	291.2	Plasmon

Table 4. Area (%) of C1s, O1s and N1s for the treated samples

	O1	O2	O3	O4	N1	N2	N3	N4
BDH	20	24	40	10	-	-	-	-
N200	23	23	33	11	52	-	44	4
N400	38	26	27	5	51	24	18	7
N600	15	14a	43	27	58	-	32	-
N600-6	21	22a	39	18	57	29	9	-

a Quinone

FTIR- The original carbon shows an absorption at 1700 cm⁻¹ indicating the presence of carboxylic acid groups, as observed by XPS also. In the reaction with NH₃ the absorption at 1600 cm⁻¹ increases by induction of several groups such as imide, amide, lactam and pyridine or pyrrole, as referred by Jansen et. al.(4). Some quinones may be present, which absorb at 1550-1680 cm⁻¹. Absorption at 1250 cm⁻¹ increases, indicating the presence of ether, alcohol or phenolic groups. The absorption band at 1700 cm⁻¹ decreases sharply with increasing treatment temperature. In samples N600 and N600-6 this band falls off suggesting the disappearance of carboxylic acid groups, as observed by XPS.

In conclusion, in nitrated samples the effect of temperature and time introduces different surface groups. Treatment at 200°C (3 hours) introduces pyridines and the highest amount of amines observed. At 400°C (3 hours) some amines seemed to be converted to amides. The sample treated at 600°C exhibits the same functional groups as sample N200. When the initial oxygen carbon content is high, treatment with NH₃ (600°C) also introduces changes on oxygen surface groups. The carboxylic groups seem to be in part converted to quinones.

In order to check the effect of surface treatment on catalyst dispersion, samples with maximum uptake of Cu and Mo were

gasified in air. The rates using different catalyst addition methods were compared (Table 5). Above 500°C, mass transfer limitations were detected in some systems. Addition of Mo precursor by IW and by EA is roughly equivalent. The catalyst dispersion achieved is almost the same. Nitrated samples are less reactive than untreated ones. Reactivity is not only related to catalyst dispersion but depends also on the thermostability of the functional surface groups, crystallites size, ability of the catalyst species to undergo reduction/oxidation and changes on the electronic density of the carbon surface as well.

Table 5. Rates of gasification (rx10⁵ (s⁻¹)) of the systems BDH and N400 with catalysts addition by different methods.

	T (°C)	COPPER			MOLYBDENUM			NONE
		PM	IW	EA*	PM	IW	EA**	
BDH	300	38.2	21.0	5.4	0.8	0.5	0.4	0.003
	400	630	560	477	6.2	61.5	61.3	0.3
	500	m.t.l.	m.t.l.	m.t.l.	49.5	762	868	7.8
N400	300	261	16.3	29.4	0.4	0.1	1.2	0.02
	400	318	447	591	21.8	12	16.3	1.3
	500	454	m.t.l.	m.t.l.	596	686	797	25.5

(*pH=12; **pH=2) PM-Physical Mixture; IW-incipient Wetness Impregnation; EA-Equilibrium Adsorption

So far in situ XRD experiments were performed in nitrogen and air with the untreated sample only. With ammonium heptamolybdate no peaks were detected in N₂ up to 650°C. The results suggest that either crystallites sizes are very small or a lack of crystallinity due to polymeric species occurs. Previous work (5, 6) has shown that molybdenum salts decompose to MoO₃ and later converted to MoO₂ (N₂, 25-700°C). In air, MoO₃ and Mo₄O₁₁ appeared above 450°C and the reduction to MoO₂ was observed. Decrease of reactivity may be due to precursor polymerization preventing catalyst reduction, as referred by other authors (1-3). TPD and future in situ XRD experiments for all samples may clarify these results.

In the case of copper nitrate the results are not clear. With samples prepared by EA the dispersion seems to be lower than that obtained by PM or IW. A high heating rate of drying, may lead to larger crystallites. Also precipitation of Cu(OH)₂ might occur at high pH thus preventing uniform dispersion of the catalyst (1). As temperature increases dispersion seems to be improved. In the case of nitrated samples a significant increase in mesoporosity was detected, and catalyst seems to be better dispersed by PM. Using copper nitrate, in situ XRD experiments showed that the phases present under reaction conditions (25-550°C) were CuO, Cu₂O and Cu. Under N₂ (25-650°C) only Cu₂O and Cu were observed.

REFERENCES

1. C.A. Leon y Leon, Ph. D. Thesis, Dep. of Materials Science and Engineering, The Pennsylvania State University, University Park, PA (1992).
2. J.M. Solar, F.J. Derbyshire, V.H.J. de Beer and L.R. Radovic, "J. Catal.", **129**, 330 (1991).
3. Godfried M.K. Abotsi and Alan W. Scaroni, "Carbon", **28**, 79 (1990).
4. R.J.J. Jansen and H. Van Bekkum, "Carbon", **32**, 1507 (1994).
5. I.F. Silva, Ph. D. Thesis, Universidade Nova de Lisboa, Monte de Caparica (1993).
6. C. Moreno-Castilla, F. Carrasco-Marín and Rivera-Utrilla, "Fuel", **69**, 354 (1990).

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