

# PORE STRUCTURE, ADSORPTION PARAMETERS AND CATALYTIC PROPERTIES OF SOME TRANSITION METAL-DOPED CARBON FIBROUS MATERIALS

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## Introduction

It has been shown previously [1,2] that thermal decomposition of cellulose materials in the presence of various inorganic additives resulted in the increase in carbon residue yield during carbonization. Changes in pore structure and adsorption parameters can also be expected for carbon materials modified with inorganic dopants. In the present work the N<sub>2</sub> and H<sub>2</sub>O steam adsorption isotherms for some cellulose-based transition metal-containing activated carbon fibers (ACFs) have been measured.

## Experimental

The transition metal-doped ACFs were prepared by impregnation of a cellulose fibrous material (viscose felt) with aqueous solutions of (NH<sub>4</sub>)<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, NH<sub>4</sub>VO<sub>3</sub>, (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5 H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (an impregnation level was ~ 3.64 · 10<sup>-2</sup> M Me / 100 g cellulose), followed by thermal treatment of the impregnants according to the procedure described in Table 1. These samples are denoted hereinafter as ACF, Mo-ACF, V-ACF, W-ACF and Cr-ACF, respectively. The N<sub>2</sub> vapor isotherms at 77 K were obtained with a "Gravimat 4303" instrument (Germany); the H<sub>2</sub>O vapor adsorption isotherms at 293 K were measured using an adsorption gravimetric setup equipped with quartz microbalances (some experiments on H<sub>2</sub>O vapor adsorption were carried out with the samples preliminarily evacuated at 673 K). Catalytic activities of the transition metal-containing ACFs for cyclohexane dehydrogenation were determined using a conventional pulse chromatographic technique. For comparison, dehydrogenation activities of similar ACF-supported catalysts prepared by impregnation of a commercial cellulose-based activated carbon fiber (ANM; S<sub>BET</sub>=1104 m<sup>2</sup>/g) with the same corresponding ammonium salts, have also been measured.

## Results and Discussion

The N<sub>2</sub> vapor adsorption isotherms obtained are depicted in Fig. 1. To calculate the micropore structure parameters of transition metal-containing activated carbon fibers, the experimental nitrogen adsorption isotherms have been analyzed using Dubinin-Radushkevich and Dubinin-

Kadlec t/F-plot method equations. The values calculated (micropore volume,  $W_0$ , characteristic adsorption energy,  $E_0$ , average size of micropores,  $X_0$ , specific surface area of

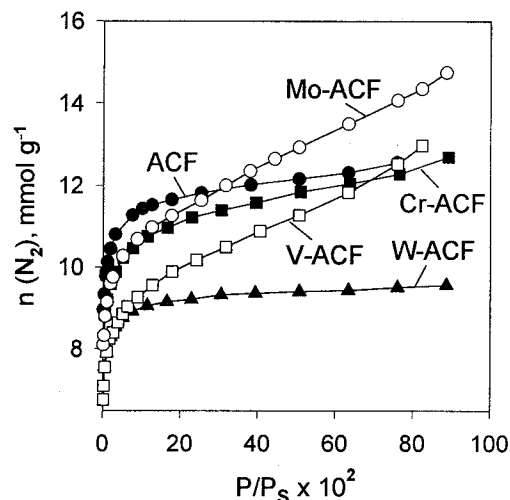


Figure 1. Nitrogen adsorption isotherms of the transition metal-doped activated carbon fibers at 77 K.

mesopores,  $S_{me}$  and BET specific surface area,  $S_{BET}$ ) are listed in Table 2. Analysis of water vapor adsorption isotherms (they are not presented here) was performed using a comparative method [3] providing the determination of the number of primary adsorption centers (PAC) (i.e. surface oxygen groups capable to form hydrogen bonds with H<sub>2</sub>O molecules) and estimation of the average size and volume ( $V_{0.95}$ ) of micropores (from H<sub>2</sub>O adsorption values at  $P/P_s=0.95$ ). Water adsorption data are also listed in Table 2.

Table 2 shows that micropore volumes for ACF, W-ACF, Cr-ACF and Mo-ACF samples, as determined from both N<sub>2</sub> and H<sub>2</sub>O adsorption isotherms, are very close; but for the V-ACF sample, these values are somewhat different. Such a result may be due to the presence of some amounts of ultramicropores in the V-ACF sample (these pores are not available for N<sub>2</sub> molecules but accessible for H<sub>2</sub>O molecules). The ACF, W-ACF and Cr-ACF specimens may be considered as essentially microporous materials while the Mo- and V-ACFs contain also substantial

amounts of supermicro- or/and mesopores ( $S_{me}=140 \text{ m}^2/\text{g}$ ). The latter fact may be attributed to the catalytic effects of molybdenum and vanadium ions on carbon oxidation during the activation process.

The amount of PAC ( $a_m$ ) on the surface of the W-modified ACF evacuated at 293 K is almost the same as that on the surface of the transition metal-free ACF. However, the PAC concentration tends to increase slightly for the Cr-ACF sample and to enhance markedly for the Mo- and V-doped ACFs (Table 2). These results are in consistency with total amounts of acidic groups in these materials, as determined by titration of the ACFs with 0.1 N NaOH, mg-eq/g: 2.2, 1.5, 0.53 and 0.42 for Mo-ACF, V-ACF, W-ACF and Cr-ACF, respectively.

A comparison of  $\text{H}_2\text{O}$  adsorption isotherms for the samples evacuated at 293 and 673 K (Table 2) suggests

that the increase in PAC for Mo- and V-ACFs is related to formation of mainly thermally unstable groups.

Catalytic activities of the above samples for cyclohexane dehydrogenation decrease in the order of: Mo-ACF>V-ACF>>Cr-ACF>W-ACF>ACF (Table 1). This is in contrast with the order observed for corresponding ANM-supported transition metal-containing catalysts: Cr/ANM>>V/ANM~Mo/ANM>ANM>W/ANM. The possible reason for such discrepancies in activities of Cr-containing catalysts is insufficiently developed mesoporous structure for the Cr-ACF sample as compared to that for Mo- and V-ACFs. Therefore, considerably less active sites are available for cyclohexane molecules to be dehydrogenated in the Cr-ACF catalyst compared with the Mo- and V-ACFs or corresponding Cr/ANM sample.

**Table 1.** Thermal treatment conditions, phase composition and catalytic properties of the transition metal-doped ACFs

Sample	Thermal treatment conditions	Additive content (as metal), at. %	Burn-off, %	Phase composition	Catalytic properties*	
					Benzene yield, mol. %	Selectivity, %
ACF	<i>Drying:</i> T=393 K, 4 h, air; <i>carbonization:</i> T=1273 K, Ar flow (25 ml/min), 1 h; <i>activation:</i> T=1173 K, Ar/ H <sub>2</sub> O flow (25 ml Ar/min, H <sub>2</sub> O/carbonized material mass ratio=0.5:1), 30 min.	-	30,1	röntgenamorphous	4.66	55.18
W-ACF		2,73	24,3	W; WC	5.81	58.37
Cr-ACF		2,88	30,1	traces of $\alpha\text{-Cr}_2\text{O}_3$	6.22	62.22
V-ACF		2,97	27,7	röntgenamorphous	20.06	93.22
Mo-ACF		2,70	30,8	$\alpha\text{-Mo}_2\text{C}$	21.81	90.01

\* Cyclohexane dehydrogenation at 873 K and  $\tau_c=1 \text{ s}$ .

**Table 2.** Pore structure and adsorption parameters of the transition metal-doped ACFs

Sample	Nitrogen vapor adsorption at 77 K					Water vapor adsorption at 293 K		
	$S_{\text{BET}}$ , $\text{m}^2/\text{g}$	$S_{\text{me}}$ , $\text{m}^2/\text{g}$	$W_{\text{O}}$ , $\text{cm}^3/\text{g}$	$E_{\text{O}}$ , kJ/mol	$X_{\text{O}}$ , nm	$V_{0,95}$ , $\text{cm}^3/\text{g}$	$a_m$ (293 K), mmol/g	$a_m$ (673 K), mmol/g
ACF	1210	40	0.39	22.5	0.53	0.40	0.41	0.35
Cr-ACF	1120	40	0.37	20.5	0.58	0.40	0.52	0.22
Mo-ACF	1140	140	0.33	22.3	0.54	0.37	0.92	0.15
V-ACF	940	140	0.28	22.3	0.54	0.42	0.94	0.35
W-ACF	925	10	0.32	21.9	0.55	0.30	0.42	0.17

## Conclusions

It has been shown that unlike to Cr (VI) and W (VI) additives, Mo (VI) and V (V) dopants had rather pronounced influence on the development of ultramicro-, supermicro- and mesopores and formation of superficial oxygen-containing groups (primary adsorption centers) in the cellulose-based ACFs. This increase in concentration of oxygen-containing primary adsorption centers is due to formation of mainly thermally unstable groups. Catalytic activities of the transition metal-doped ACFs for cyclohexane dehydrogenation have been found to correlate with their mesoporous structure development.

## References

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