

TRANSITION METAL-DOPED CARBON FIBROUS MATERIALS: PREPARATION, CHARACTERIZATION, AND DEHYDROGENATION ACTIVITY

Yu.G. Kryazhev, I.Ya. Petrov, G.P. Khokhlova, and Yu.F. Patrakov
Institute of Carbon Materials Chemistry, SB RAS, Kemerovo 650099, Russia

Introduction

Carbon fibrous materials (CFM) are extensively studied as catalyst supports for various reactions [1,2]. Usually, carbon fiber-supported catalysts are prepared by impregnation of CFM with active component precursors, followed by thermal treatment of impregnated substrates to decompose supported substances. Yermolenko *et al.* [3] have proposed a novel method for preparation of carbon fibrous catalysts, including carbonization of transition metal-impregnated cellulose fibers in an inert atmosphere, followed by their activation with appropriate oxidizing agents (air, CO₂, H₂O, etc.); Pt-containing CFM, obtained in such a way, exhibited considerable activities both in cyclohexane dehydrogenation and in *cis-trans*-isomerization of 1,2-dimethylcyclopentane. In the present work we attempted to combine the simplicity of the Yermolenko's method with abilities of some transition metal additives to enhance carbon residue yield during cellulose pyrolytic degradation.

Experimental

Preparation. The cellulose fibers (CF) modified with catalytic additives were prepared by impregnation of the initial cellulose material (viscose fiber) with (NH₄)Mo₂O₇, NH₄VO₃, and (NH₄)₁₀W₁₂O₄₁ · 5 H₂O (an impregnation level was $3.64 \cdot 10^{-2}$ M Me/100 g CF for each of the salts), followed by drying at 110° C for 4 h. Carbonization of the samples was performed in a quartz tube (i.d. - 40 mm, length - 500 mm) placed into a tube furnace, upon heating up to 1000° C in a flow of Ar (20-30 ml/min) and storing at the ending temperature for 1 h. Activation of the CFM was carried out with water steam (H₂O/CFM mass ratio of 0.5:1) at 900° C for 30 min in an Ar/H₂O steam atmosphere (rate of Ar flow - 20-30 ml/min). Alumina- and carbon-supported Mo (VI), V (V), and W (VI) oxides were prepared by impregnation of a commercial γ -Al₂O₃ (A-64, S=200 m²/g) or an activated carbon ('Sibunit', S=365 m²/g) with corresponding transition metal salts, followed by drying at 120° C for 4 h and calcining in air at 600° C for 6 h.

Characterization. Thermogravimetry (TG), step-wise pyrolysis gas chromatography (SPGC), and mass spectrometry (MS) were employed to study the influence of the additives chosen on the cellulose decomposition.

Dehydrogenation activity. Activities of Mo (VI)-, V (V)-, and W (VI)-doped CFM and corresponding alumina- or carbon-supported transition metal oxides for cyclohexane dehydrogenation were measured using a conventional pulse technique (600° C, $\tau_c = 1$ s).

Results and Discussion

According to the TG and SPGC data, thermolysis of the CF samples started at ~ 200° C and finished at ~ 600° C. The thermogravimetric experiments showed that when the metal additives doped to the initial cellulose material, the marked displacement of weight-loss maxima to lower temperatures has been observed in the DTG curves (from 300° C for the pure CF to 265, 255, and 245° C for the W-, V-, and Mo-modified CFs, respectively). Simultaneously, the SPGC measurements (Fig. 1) revealed a shift of water evolution maxima to lower temperatures and enhanced H₂O yields for transition metal-doped CFs (especially, for the Mo-doped sample).

The MS analyses suggested that among the main volatile products evolving during the CF decomposition there are H₂O (m/e=18), CO (m/e=28), CH₂O (m/e=29), propylic alcohols and CH₃COOH (m/e=57), dehydrated fragments of cellulose chains (m/e=74 and 126), and some others (Table 1). These data also confirm the SPGC result on water proportion increases in mixtures of volatile pyrolysis products when cellulose modified with transition metals, i.e. the metal additives studied catalyze effectively cellulose dehydration reactions. Moreover, the SPGC and MS data indicate (see Fig. 1 and Table 1) that transition metal additives suppress CO and CO₂ elimination reactions and retard cellulose depolymerization processes (decrease in cellulose chain fragments evolution in the MS spectra). This results in substantial diminution in carbon losses during the CF decomposition.

The efficiency of additives studied with respect to carbon formation from cellulose is the following: Mo (VI) > V (V) > W (VI). The yield of carbon residues increased from 16 wt. % for pure cellulose fiber to 23, 29, and 32 wt. % (after subtracting the metal content) for W-, V-, and Mo-doped CF, respectively.

Activities of the transition metal-doped CFM for cyclohexane dehydrogenation were rather high and comparable or superior to those of corresponding alumina- and carbon-based catalysts (Table 2).

Table 1. Mass spectrometric data on volatile products evolution during carbonization of transition metal-doped cellulose fibers^{*)}

m/e	Initial cellulose fiber		Mo-doped cellulose fiber		V-doped cellulose fiber		W-doped cellulose fiber	
	I	D	I	D	I	D	I	D
18	19.6	0.15	58.6	0.40	55.6	0.30	54.8	0.36
28	12.9	0.10	13.1	0.09	16.7	0.09	14.3	0.09
29	14.6	0.10	14.3	0.10	18.8	0.10	18.2	0.12
44	19.2	0.14	18.5	0.12	19.3	0.10	17.4	0.11
57	19.5	0.14	17.0	0.12	17.6	0.10	15.0	0.10
60	16.0	0.11	12.0	0.08	12.4	0.07	11.6	0.08
74	12.9	0.10	1.50	0.01	3.4	0.02	1.5	0.01
85	14.0	0.10	5.20	0.03	15.0	0.08	8.5	0.05
126	8.5	0.06	4.6	0.03	17.3	0.09	10.8	0.07
R	0.15 : 0.85		0.42 : 0.58		0.35 : 0.65		0.36 : 0.64	

I - peak intensity (in arbitrary units);

D - relative component fraction in mixture of volatile pyrolysis products;

R - H_2O/Σ Carbon-containing products peak intensity ratio.

^{*)} There are listed the most intensive peaks.

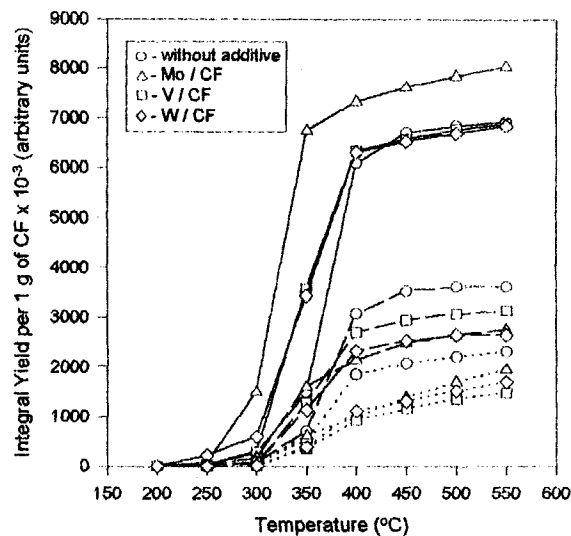


Fig. 1. Effects of Mo (VI), V (V), and W (VI) additives on the integral yields of H_2O (solid lines), CO_2 (dashed lines), and CO (dotted lines) during thermal destruction of cellulose fibers (the SPGC data).

Table 2. Dehydrogenation activities of some Mo-, V-, and W-containing catalysts

Catalyst	Transition metal content (as Me), wt. %	S_{BET} , m^2/g	Benzene yield, mol. %	Selectivity, %
CFM	-	276	55	84
Mo-CFM	10.7	420	77	84
V-CFM	7.2	465	68	70
W-CFM	18.6	380	48	65
$MoO_3/\gamma-Al_2O_3$	8.8	148	50	69
$V_2O_5/\gamma-Al_2O_3$	7.6	154	71	74
$WO_3/\gamma-Al_2O_3$	19.3	147	27	51
$MoO_3/Sibunit$	11.5	167	71	77
$V_2O_5/Sibunit$	7.8	179	78	85

Conclusions

Molybdenum (VI), vanadium (V), and tungsten (VI) additives catalyze effectively cellulose dehydration and suppress carbon-containing product formation reactions during carbonization of cellulose fibers. This results in the increase in carbon residue formation and enhances the CFM yields. Efficiency of the additives studied on the pyrolytic cellulose degradation is the following: Mo (VI) \gg V (V) $>$ W (VI). It has been found that catalytic activities of Mo-, V-, and W-containing CFM for cyclohexane dehydrogenation were comparable or superior to those of corresponding alumina- and carbon-supported transition metal oxides.

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References

1. Ross, R.A., Fairbridge, C., and MacCallum, J.R., *Carbon*, 1985, 23, 209.
2. Mochida, I., Kawano, S., Kisamori, S., Fujitsu, H., and Maeda, T., *Carbon*, 1994, 12, 175.
3. Olfierieva, T.G., Bragin, O.V., Yermolenko, I.N., and Safonova, A.M., *Kinet. Katal.*, 1977, 18, 933.