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Ethanol dehydrogenation over copper supported on carbon macrofibers

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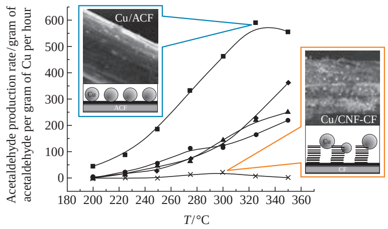
Activated carbon fibers were found promising as a catalyst support in terms of better copper dispersion, providing high catalytic activity in ethanol dehydrogenation.



The conversion of ethanol into acetaldehyde is of considerable current interest due to a growing demand for petroleum-independent chemicals technologies.[1] For this purpose, catalysts with an improved activity and efficiency are needed. Copper-containing catalysts are well-known promising systems for alcohol dehydrogenation reactions.[2–5] It is generally accepted that a support plays a crucial role in the efficiency of such systems.

Carbon materials characterized by unique properties (thermal conductivity, mechanical stability, high resistance towards acidic and basic media, relative simplicity to manage the surface properties, *etc*.) are widely applied as supports for metal-containing catalysts.[6–8] Within a variety of carbon materials, filamentous woven cloths made of carbon macrofibers (few microns in diameter) are of great interest. When compared with conventionally used granules, these materials have a number of advantages such as a better reaction flow distribution, geometric flexibility and possibility to fit reactors of any design.[9–12] For instance, catalysts based on fibrous carbon were efficiently implemented for the selective hydrogenation of but-2-yne-1,4-diol performed in a loop[13] or batch reactor,[14] as well as for highly exothermic gas reactions performed in micro-structured reactors, where the application of powders or granules is restricted.[15]

Recently, we described copper supported on carbon as a promising catalytic system for ethanol dehydrogenation.[16] In the case of activated carbon fibers (ACFs), the catalytic activity was two times higher than that of granulated carbon support. This difference is due to a fine distribution of copper on the ACF surface. At the same time, a wide range of carbon-based fibers and cloths, which differ in the manufacture technologies, starting raw materials and surface properties, is commercially available. A new trend consists in the development of carbon-carbon composites with a hierarchical structure.[17–22] In this approach, the surface of carbon macrofibers is modified with carbon nanotubes (CNTs) or nanofibers (CNFs). The composites were successfully applied as adsorbents[18,19] or catalyst supports.[20–22]

The aim of this study was to compare different fibrous carbon materials to be used as the supports of copper-containing catalysts for ethanol dehydrogenation.

The following carbon materials were studied: SW1001 commercial carbon fibers (CCF); AW1103 activated carbon fibers produced from polyacrylonitrile [ACF (PAN)] by CoTHmex, Taiwan; UVIS AK-T-0,4 activated carbon fibers produced from hydrated cellulose [ACF (HC)] by Uvicom Co Ltd., Russia; and CNF-CF carbon–carbon composite obtained by the catalytic chemical vapor deposition (CCVD) of ethylene on the surface of carbon fibers (UKN-M, Argon Co Ltd., Russia) with deposited nickel particles. In the latter case, nickel particles were removed by acidic treatment followed by washing with deionized water in order to avoid the undesirable effect of nickel on catalytic performance. The surface area of the composite (33 m^2 g^{-1}) significantly exceeds that reported for the initial carbon macrofibers (2 m^2 g^{-1}).[23]

Table 1 summarizes the surface characteristics[†] of the test supports determined by low temperature adsorption of N_2.

Table 1 Textural parameters of fibrous carbon supports.

Support	S_{BET}/m^2 g^{-1}	$V_{\Sigma pore}$/cm^3 g^{-1}	V_{micro}/cm^3 g^{-1}
CNF-CF	33	0.134	0.015
CCF	170	0.075	0.070
ACF (PAN)	1042	0.513	0.418
ACF (HC)	1049	0.483	0.430

[†] Low temperature N_2 adsorption tests were performed on an ASAP 2020 instrument (Micromeritics, USA). The samples were heated in a vacuum at 250 °C for 3 h before the measurements. The specific surface area was calculated using the BET method.

The sample morphology was studied on a MIRA3 SEM instrument (TESCAN, Czech Republic). Images were acquired in the secondary electron imaging mode at an accelerating voltage of 5 kV.

Activated carbon fibers with a well-developed microporous structure show the highest surface area (> 1000 m^2 g^{-1}) regardless of the precursor. According to the adsorption–desorption isotherms for ACF (HC) provided by Uvicom, these fibers contain mesopores with an estimated size of 4 nm. Meanwhile, the scanning electron microscopic (SEM) analysis showed the presence of macropores of 200–300 nm in the ACF (HC) sample. The surface of ACF (PAN) and CCF is more or less smooth, as evidenced by SEM measurements; nevertheless, it shows narrow flaws along the fiber axis. The carbon-carbon composite (CNF-CF) is characterized by the lowest surface area in the studied set of samples. The covering of the macrofiber surface with nanofibers results in an uneven porous structure with an averaged pore size of 4 nm.

In addition to the textural properties of carbon supports, acidity and adsorption ability related to the presence and amount of surface oxygen-containing groups (carboxyl, lactone, carbonyl and phenol groups) have an effect on the dispersion of active component particles and on metal-support interactions.[24] Generally, the higher the surface area and oxygen content, the better the dispersion of an active component. It is believed that oxygen-containing groups on the surface of carbon fiber enhance its interaction with a catalyst precursor dissolved in water and with the metal particles formed and, hence, decrease the rate of sintering.[25,26] Note that the CNF-CF sample was hydrophobic, while all others were hydrophilic. This fact encouraged us to use two different approaches for the catalyst preparation. In both cases, incipient wetness impregnation was used for the deposition of the active component. The loading of copper was 5 wt%, and copper nitrate was used as a precursor. The solvent was either water or methanol for hydrophilic or hydrophobic fibers, respectively. It is known that the electrolytic dissociation of salts in aqueous and non-aqueous solutions proceeds *via* different mechanisms. As a result, the role of surface oxygen-containing groups is diminished significantly. Thus, by applying methanol to the preparation of a catalyst based on hydrophilic carbon fibers [Cu_m/ACF (PAN)], an attempt was made to clarify whether such groups have an impact on the final catalytic performance.

The test samples were preliminary activated and then examined in ethanol dehydrogenation‡ using the conditions under which the catalysts showed high selectivity for acetaldehyde formation.[16]

$$\text{EtOH} \leftrightarrow \text{MeCHO} + \text{H}_2 \qquad (1)$$

Figure 1 shows the rate of acetaldehyde production. The highest catalytic activity was observed for Cu/ACF (PAN) prepared by impregnation with water solution of the salt precursor. In this case, the yields of acetaldehyde approached an equilibrium value. Cu_m/ACF (PAN) synthesized in methanol as a solvent exhibited twofold lower activity, hence indicating the impact of the support surface chemistry on the formation of active sites. Despite the huge difference in surface areas between Cu/CCF and Cu/ACF (HC), 170 and 1049 m^2 g^{-1}, respectively, their catalytic behaviors were very similar. Both low surface areas and unfavorable surface properties of the carbon-carbon composite were the reasons for the lowest activity of the Cu/CNF-CF catalyst, providing ethanol conversion of less than 5%.

According to the experimental data (Figure 2), the sizes of copper particles and their distribution correlate with the catalytic activity of the samples. The narrowest particle-size distribution

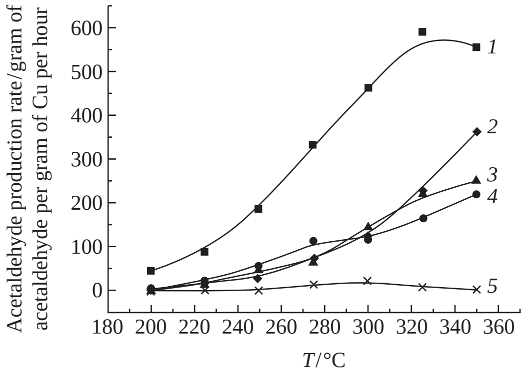


Figure 1 Temperature dependence of acetaldehyde production rate over the test catalysts: (*1*) Cu/ACF (PAN), (*2*) Cu_m/ACF (PAN), (*3*) Cu/ACF (HC), (*4*) Cu/CCF, and (*5*) Cu/CNF-CF.

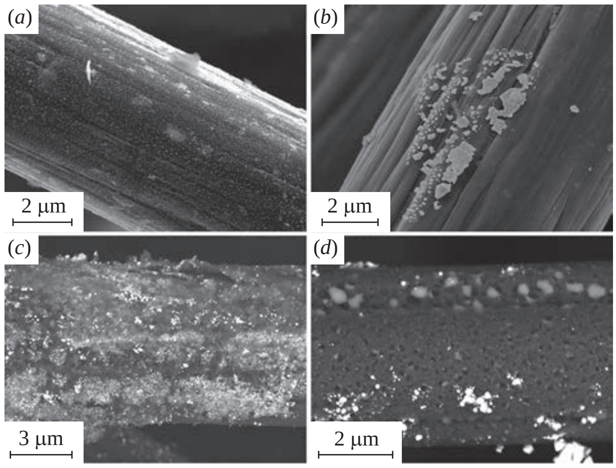


Figure 2 SEM images of the test catalysts: (*a*) Cu/ACF (PAN), (*b*) Cu/CCF, (*c*) Cu/CNF-CF, and (*d*) Cu/ACF (HC).

was observed for the Cu/ACF (PAN) sample. The average size of copper particles was 15 nm. Similar images were obtained for Cu/CCF and Cu/ACF (HC). The size of copper particles in these samples was in a range from 15 to 80 nm [Figure 2(*b*),(*d*)]. At the same time, large agglomerates (~200 nm and more) were also present. In spite of a uniform distribution of copper in Cu/CNF-CF sample [Figure 2(*c*)], the average particle size as high as 100 nm could cause the decreased activity. It can be thus inferred that the metal–support interaction is a key parameter affecting the copper dispersion and distribution and hence determining the catalytic properties.

In summary, the ethanol dehydrogenation over copper-containing catalysts based on a fibrous carbon support strongly depends on the average size and distribution of the copper particles. These factors are related to the surface properties of the support, including the surface area and oxygen-containing groups.

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‡ The catalytic experiments were carried out in a fixed-bed flow reactor under atmospheric pressure at 200–350 °C. Before the reaction, the samples (0.47 ml) were heated stepwise in Ar and reduced in a hydrogen flow at 350 °C for 2 h. Ethanol (93 wt%) was fed at LHSV of 32 h^{-1}. The liquid and gaseous products were analyzed by gas chromatography on Tsvet-800 and LKhM-8MD (Russia) instruments, respectively.

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