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Effect of copper deposit morphology on the characteristics of a Pt(Cu)/C-catalyst obtained by galvanic displacement

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The mechanism of formation and the properties of the $Pt(Cu)_{st}$/C catalyst are largely determined by the dispersion degree of the initial copper deposit.

In the recent years, the galvanic displacement (GD) of a base metal (M_1) by a noble metal (M_2) has been increasingly used to reduce the content of platinum metals in electrocatalysts (catalysts).[1–5] The GD method decreases the content of scarce and expensive metals without a loss (and sometimes with an increase) in the catalytic activity.

It was found[2–4] that the core (Pt,Cu)–shell (Pt) structures are formed as a result of galvanic displacement under the open circuit conditions at a contact between electrolytic deposits (ed) of copper on glassy carbon (GC)[2,3] and on the Vulcan XC-72 carbon black[4] and the $PtCl_6^{2-}$ solutions. The catalysts obtained featured a high specific activity in the reaction of electrooxidation of methanol, but had a comparatively low specific surface area (5–15 m^2 g^{-1} of Pt). It was conjectured[4] that this is primarily due to the low dispersion degree of initial Cu_{ed}.

This work is dedicated to the effect of copper deposit morphology on the properties of a Pt(Cu)/C mixed catalyst obtained by galvanic displacement. The properties are compared for a number of $(Pt,Cu)_{st}$ catalysts (the subscript 'st' shows that the process of copper displacement by platinum reached a steady state) obtained by galvanic displacement. Changing the displacing agent ($PtCl_4^{2-}$ or $PtCl_6^{2-}$), carbon support morphology [Vulcan XC-72 carbon black + Nafion/GC[4] or carbon nanowalls (CNW)/GC[6]], the amounts of deposited copper, method of Cu deposition [electrodeposition (Cu_{ed}) or magnetron deposition (Cu_{spr})] were used for variation of the parameters of the initial Cu deposit. Further, the composite carbon black + Nafion/GC support[4] is denoted as C_{com}. A number of methods were used for the characterization of the samples (SEM, TEM, XPS, XRF analysis, voltammetry, *etc.*). The true surface area of the $Pt(Cu)_{st}$/C catalysts was determined on the basis of the adsorption of copper atoms (Cu_{ad}).[7,8] The values of the working electrode potential are presented *vs.* a reversible hydrogen electrode in the same solution.

The large copper crystallites of ~0.5–2 μm are formed on the C_{com} support under sufficiently high Cu 'loads' (~300 μg cm^{-2} of the geometric surface area) [Figure 1(*a*)]. Rather large particles of 0.5–1.0 μm are also predominant on CNW under application of Cu deposits with a similar mass [Figure 1(*b*)]. Herewith, the specific feature of CNW, the presence of laminar-type carbon crystallites, is eliminated.

The crystallite sizes on CNW under low Cu_{ed} 'loads' [Figure 1(*c*)] feature a wide scatter (from ~20 to ~200 nm), but they are generally lower than in the case of deposits *a* and *b*. Magnetron sputtering provides a very smooth dense layer of copper that is virtually non-porous [Figure 1(*d*)].

Figure 1(*a'*)–(*d'*) indicate that the sizes of metallic particles and their surface distribution change considerably after the displacement of copper by platinum. Deposit *a* is transformed into deposit $Pt(Cu)_{st}$(*a'*) including both very small particles (TEM

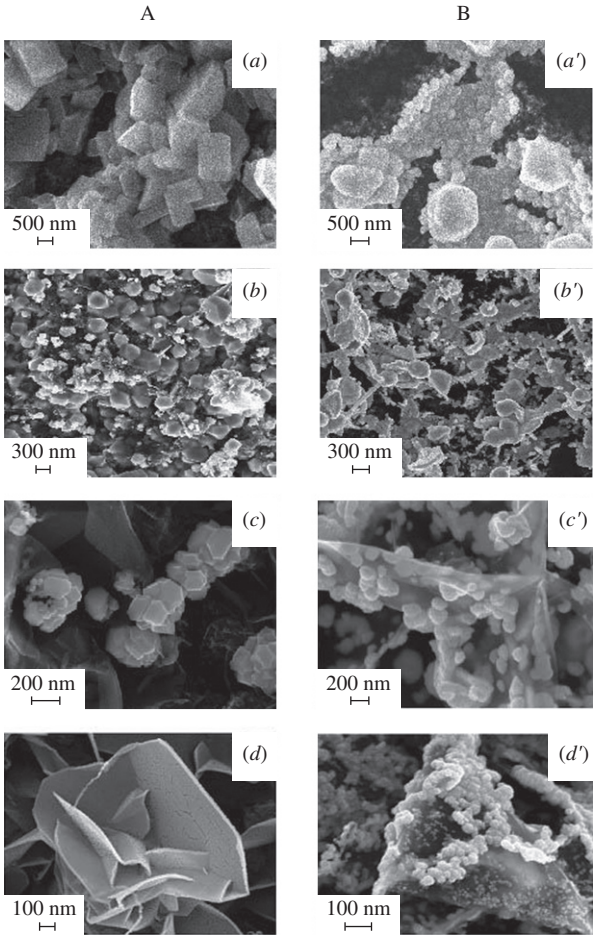


Figure 1 SEM images. (A) copper deposits: (*a*) Cu_{ed}/C_{com} (m_{Cu} = 300 μg cm^{-2} of the geometric surface); (*b*) Cu_{ed}/CNW (320 μg cm^{-2}); (*c*) Cu_{ed}/CNW (48 μg cm^{-2}); (*d*) Cu_{spr}/CNW (42 μg cm^{-2}); (B) $Pt(Cu)_{st}$/C or CNW after galvanic displacement of Cu from the (*a*)–(*d*) samples; the displacing agent: (*a'*) $PtCl_6^{2-}$, (*b'*)–(*d'*) $PtCl_4^{2-}$; the background solution, 0.5 M H_2SO_4.

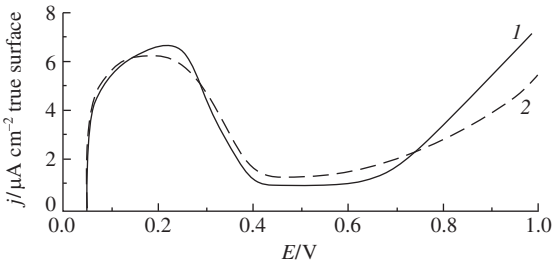


Figure 2 Anodic potentiodynamic curves for (*1*) Pt_{ed}/CNW (80 μg cm^{-2}) and (*2*) $Pt(Cu)_{st}$/CNW (from Cu_{spr}).

showed the presence of particles of several nanometers) and rather large conglomerates (>2 μm) formed as a result of the coalescence of small particles.[4] Note that the image presented corresponds to $Pt(Cu)_{st}/C_{com}$ [1(*a′*)], when the displacement agent was $PtCl_6^{2-}$ anions; however, a similar pattern was obtained in the corresponding experiment with $PtCl_4^{2-}$. After a large copper deposit on CNW is displaced, the amount of large particles decreases significantly, but a high amount of relatively small particles of 50–200 nm (*b′*) appears herewith. As follows from a comparison of Figures 1(*c*) and 1(*c′*), the predominant accumulation of metallic particles on CNW edges after the replacement of Cu by platinum is preserved, but the amount of particles on the wall planes herewith increases and the particle sizes decrease on the whole. In the case of Cu_{spr}, the displacement results in the accumulation of $Pt(Cu)_{st}$ particles on the wall edges and only a small amount of small particles is formed on the planes [Figure 1(*d′*)].

All the obtained samples had the core (Pt,Cu)–shell(Pt) structure.[2–4] This is evidenced by the similarity of potentiodynamic curves of these and an individual Pt deposit. Figure 2 compares, as an example, the *I*,*E*-curve for the $Pt(Cu)_{st}$ sample obtained from Cu_{spr} on CNW with a similar curve for Pt_{ed}. No ionization currents of Cu or Cu_{ad} are observed at the double layer region potentials. The formation of a compact Pt layer on the surface is also confirmed by XPS data. According to the latter, no more than 1 at% Cu is present in the surface layer of ~2 nm (the analytic peak of Cu is practically absent in the survey spectrum in Figure 3).

Table 1 shows that the initial surface morphology produces a strong effect on the characteristics of a $Pt(Cu)_{st}$ catalyst. Electrolytic catalysts with a relatively large mass, where copper is present in the form of large crystallites and their conglomerates (samples I–III) yield $Pt(Cu)_{st}$ structures with the average specific surface area of 10–15 m^2 g^{-1} of Pt and copper content of 25–35 at%. A great difference in the specific densities of Cu and Pt and in their crystal lattice parameters cause the destruction of initial metallic particles in the course of Cu displacement by platinum

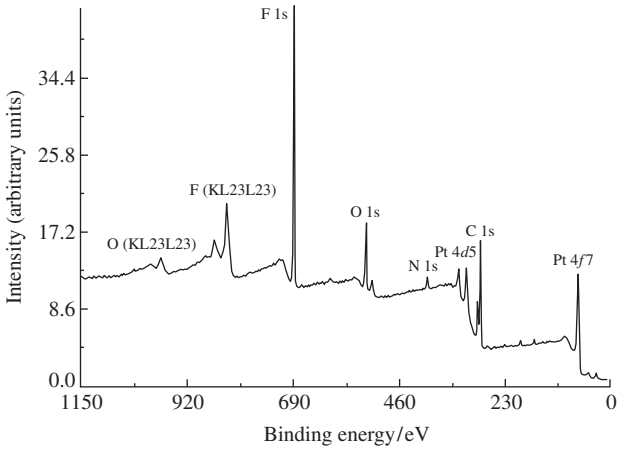


Figure 3 Survey XPS spectrum for $Pt(Cu)_{st}$/C (carbon black support).

Table 1 Data on the bulk composition and specific surface areas for the test $(Pt,Cu)_{st}$ catalyst samples.

Sample no.	Support	m_{Cu}/μg cm^{-2} of the geometric surface area (deposition method)	Pt : Cu (at%)	S/m^2 g_{Pt}^{-1}	d_{Cu}/nm
I	C_{com}^{a}	~300 (ed)	70 : 30	14–17	500–2000
II	C_{com}	~300 (ed)	75 : 25	12–14	500–2000
III	CNW	320 (ed)	65 : 35	8–11	500–1000
IV	CNW	44–52 (ed)	57 : 43	46±15	20–200
V	CNW	40–48 (spr)	80 : 20	11–17	∞

[a] This sample was obtained when the displacement agent was $PtCl_6^{2-}$; other samples were obtained using $PtCl_4^{2-}$.

(Figure 1). The formation of $Pt(Cu)_{st}$ particles of several nanometers was detected.[4] However, such particles form only a small fraction and most of the $Pt(Cu)_{st}$ deposit consists of large conglomerates with relatively small specific surface areas.

It appears unexpected that large $Pt(Cu)_{st}$ conglomerates, small specific surface area, and the lowest Cu content in the deposit (Table 1, sample V) are characteristic of the uniform initial copper distribution over the (Cu_{spr}) surface. On the one hand, this confirms the destructive character of the displacement process and, on the other hand, it allows assuming that copper displacement by platinum occurs according to several mechanisms.

$Pt(Cu)_{st}$ particles with the highest copper content and the highest specific surface area were obtained from a Cu deposit with the lowest initial particle size [Figures 1(*c*), 1(*c′*), Table 1, sample IV]. However, Table 1 contains only the integral values of parameters of the most promising $Pt(Cu)_{st}$/CNW catalyst. TEM shows the presence of both sufficiently large conglomerates (see Figure 4) and individual small particles (1–3 nm) in sample IV. As follows from the XPS data, nanometer particles contain practically no copper; that is, copper remains in large conglomerates (most probably, in their bulk part). The blocking of M_1 dissolution from the PtM_1 alloys as a result of the Pt surface layer (shell) formation was reported.[9]

Neither published data nor the results of this work allow one to describe in sufficient detail a complex multistage process of galvanic displacement. However, two major displacement routes can be pointed out (Scheme 1). Route I: displacement occurs within the initial Cu particle or Pt(Cu) particles formed as a result of destruction of the initial particle. Route II: the reactions of $Cu \rightarrow Cu^{2+} + 2e$ and $PtCl_4^{2-} + 2e \rightarrow Pt^0 + 4\,Cl^-$ are spatially separated and the electrons are transmitted through the conducting support.

In the case of large Cu deposits (Table 1, samples I–III), route I is obviously the main one, although the formation of small particles in sample III can largely occur *via* route II. The unexpectedly small presence of $Pt(Cu)_{st}$ particles on the CNW faces (planes) when copper magnetron deposition is used (sample V) can be

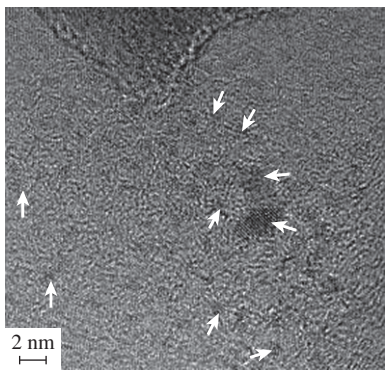
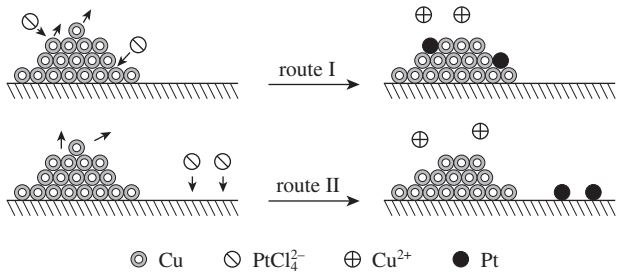


Figure 4 TEM image of $Pt(Cu)_{st}$/CNW (from Cu_{spr}).



Scheme 1 Copper displacement by platinum.

explained by the following mechanism. Cu displacement by platinum probably occurs at the highest rate on the edges of CNW and then Pt is predominantly deposited on Pt (on the edges) due to fast copper ionization on the faces (owing to the large surface area of the Cu/solution interface). Small particles on the faces of CNW [Figure 1(*d′*)] can be formed by route II. This agrees with the lowest copper content of sample V and the fact that the specific $Pt(Cu)_{st}$ surfaces are close to those observed for Pt/Pt.[10] The formation of nanometer Pt particles on the CNW faces in the course of $Pt(Cu)_{st}$/CNW formation from a small Cu electrodeposit (sample IV) points to the fact that the displacement process occurs *via* both route I and route II.

The presented results confirm the assumption that M_1 deposits with the highest dispersion degree must be used for the synthesis of bimetallic catalysts with the highest dispersion degree using the galvanic displacement technique. In this connection, the formation of a bimetallic catalyst with a highly developed surface is most probable when small initial deposits of displaced metal M_1 are used. However, owing to the complexity and multistage character of the displacement process, the effect of the dispersion degree of M_1 on the characteristics of the $M_2(M_1)$ catalyst can also largely depend on other factors, such as the structure of deposit M_1, the displacement rate and the nature of the support. In particular, the high conductivity of the support and the presence of a large number of sites for M_2 nucleation in it should assist obtaining structures with a higher dispersion degree.

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