Physical Chemistry

Surface solid-state interactions in copper—nickel—cement catalysts for hydrogenation of oxygen

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The surface phase composition of alumocalcium cement-supported CuO and CuO—NiO catalysts prepared by chemical mixing has been studied using the method of thermo-vacuum curves of electric conductivity. The deactivation of these catalysts due to overheating to 800 °C under conditions of hydrogenation of oxygen is rationalized by the partial extraction of CuO (and NiO) from the stabilizing structure of the support solid solutions and by sintering of the extracted oxides and the reduced metallic phase. Complete regeneration of the CuO—NiO—talum catalysts can be achieved if a considerable amount (20 %) of copper hydroxocarbonate is added.

Key words: copper—nickel—cement catalysts; surface phase analysis; electric conductivity; solid-state interactions.

Systems based on alumocalcium cements are efficient catalysts for purification of technological gases from oxygen.[1] However, long-term service or disturbances of regimes of preparation or hydrogenation (casual overheating) may substantially decrease their activity. The low-temperature deactivation of a NiO—CuO—cement (talum) catalyst for the hydrogenation of oxygen is explained[2] by the destruction of the specific structure of its active surface. High-temperature deactivation seems to also be caused by disturbances in the structure of the metastable surface solid solutions (that provide an active state of the surface) accompanied by partial liberation of copper and nickel oxides. On the one hand, this results in depletion of the surface solid solutions in the active components (CuO, NiO), and, on the other hand, in sintering of the liberated oxides with the metallic phase thus generated.

In order to regenerate this deactivated catalyst an attempt to re-enrich its near-surface layer with an active component seemed expedient. This could be achieved by calcination in air, which should result in the oxidation of the sintered metallic phase and in the topochemical interaction between the oxides formed and the carrier. In addition, before calcination the deactivated

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catalyst could be mixed with an additional portion of an active oxide (or its precursor). Preliminary experiments have shown the possibility of this type of dry regeneration in principle.[3] In the present work, the topochemical processes that accompany deactivation and regeneration of the catalysts by this method are discussed based on the results of surface phase analysis using the method of thermo-vacuum electroconductivity curves (TVE-curves) of the samples obtained.

Experimental

Two catalysts containing alumocalcium cement (talum) were chosen for study. The samples were prepared by chemically mixing copper and nickel hydroxocarbonates (CHC and NHC, respectively) with talum. The components were mixed in 25 % aqueous ammonium hydroxide at 75 °C (see Ref. 4). The composition of the first catalyst was CuO(20 %)—NiO(15 %)—talum, and that of the second one was CuO(35 %)—talum.

Samples were calcinated for 5 h at 400 °C in air and were reduced immediately before testing for 1 h in a flow of H_2 at 450 °C.

The activity of samples in the hydrogenation of oxygen was determined as the temperature at which conversion α = 50 % ($T_{0.5}$) was achieved.

Artificial deactivation of the catalyst was performed in the reaction medium by increasing the temperature to 800 °C. Deactivated samples were regenerated by the following methods: (1) calcination in air for 5 h at 400 °C; (2) addition of CuO (10 or 20 %) with subsequent heating in air for 5 h at 250 °C; (3) addition of CHC (10 or 20 %) with heating in air for 5 h at 300 °C.

The phase state of the catalyst surface was monitored by surface phase analysis based on TVE-curves.[5] TVE-curves were plotted from the electric conductivity values (σ/Ohm^{-1} cm^{-1}) of molded pellets of the catalyst. The conductivity was measured at direct current in the regime of a stepwise increase in the temperature of heating in a vacuum (T_{vac}) from 100 to 400 °C.

Here we present the TVE-curves plotted from the values of the activation energy of conductivity (E_σ), which were calculated from the reversible Arrhenius temperature dependences of σ after each temperature increase to a new value of T_{vac} and storage at this temperature to a constant value of $\sigma_{T_{\text{vac}}}$.

Results and Discussion

The changes in the catalyst activity depending on pretreatment are presented in Table 1. Overheating decreases the activity of both catalysts studied: the values of $T_{0.5}$ for the thus-deactivated catalysts are 30—40 °C higher than those for the original catalysts. In the case of the CuO(35 %)—talum catalysts, none of the regeneration methods tried was efficient. Moreover, heating in air and addition of 10 and 20 % CuO or NHC did not regenerate the catalyst and, on the contrary, resulted in an additional decrease in its activity (as compared with the deactivated sample). In the case of the CuO(20 %)—NiO(15 %)—talum catalyst, this decrease in activity was observed only after the addition of 10 % CuO or CHC, whereas heating in air and, especially, the introduction of 20 % of additives resulted in the desired increase in activity. Complete regeneration was attained using 20 % CHC as the additive.

The changes in the phase composition of the catalyst surface can be monitored by following the TVE-curves (Fig. 1). In the initial state, the surface of the CuO(35 %)—talum catalyst (see Fig. 1, *a*, curve *1*) contains not the CuO free phase, but a solid solution[6] (Al_2O_3 from the carrier dissolved in CuO). The surface of the carrier becomes exposed in the deactivated sample due to sintering of the reduced copper: curve *2* characterizes the solid solution of CuO in Al_2O_3. Curve *2* in Fig. 1, *a* is close to the band of talum, which attests to the fact that the solid solution is depleted in the copper-containing component (the phase of the sintered copper metal does not appear in the TVE-curves, because its enlarged crystals do not form chains of continuous contacts, however, these crystallites are well determined by X-ray analysis). In all of the cases, the TVE-curves after regeneration treatments are immediately adjacent to the band of CuO (at T_{vac} = 100—250 °C), *i.e.*, the surface of the samples is covered to a great extent with the CuO phase. However, this newly formed phase is not completely free. It begins to interact with the carrier, as can be seen from the devia-

Table 1. Effect of regeneration conditions on the temperature of half-conversion in the hydrogenation of oxygen on talum-containing catalysts

Catalytic system	$T_{0.5}$/°C						
	Original catalyst	Deactivated catalyst	Regenerated samples				
			by thermal treatment at 400 °C	by addition of CuO (%)		by addition of CHC (%)	
				10	20	10	20
CuO(35 %)—talum	115	140	145	170	150	175	160
NiO(15 %)—CuO(20 %) —talum	135	175	155	210	155	220	130

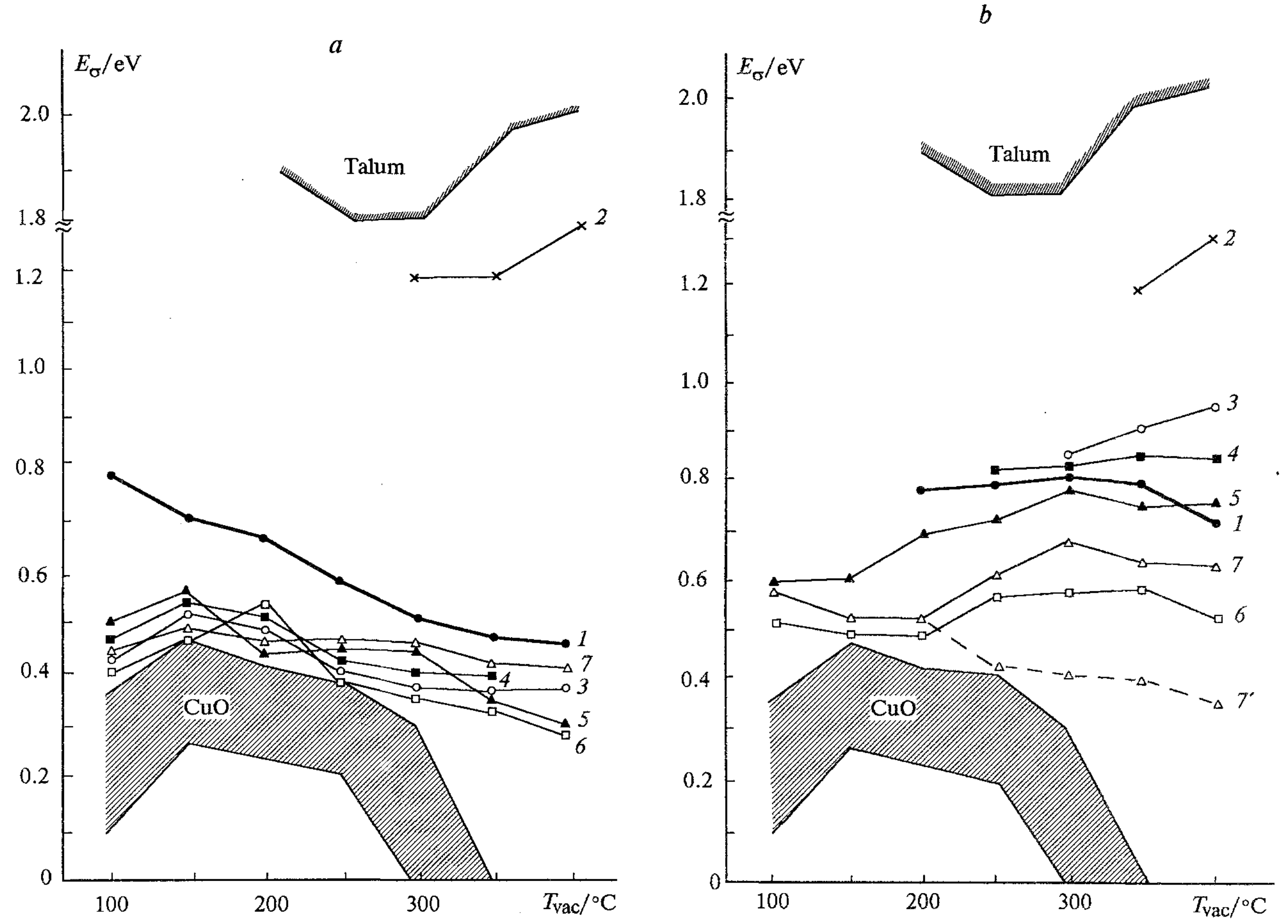

Fig. 1. TVE-curves for CuO(35 %)—talum (*a*) and CuO(20 %)—NiO(15 %)—talum (*b*) catalysts after different treatments: original catalyst (*1*); deactivated catalyst (*2*); regenerated (*3—7*) (*3*, 400 °C; *4*, 10 % CuO; *5*, 10 % CHC; *6*, 20 % CuO; *7* and *7′*, 20 % CHC).

tion of curves *3—7* (see Fig. 1, *a*) from the band of CuO at T_{vac} > 300—400 °C, which indicates the elevated stability of these CuO layers with respect to reduction at high T_{vac} typical of standard samples of copper oxide.

It follows from the results considered that in the case of the CuO(35 %)—talum catalyst the conditions of regeneration are sufficient for "spreading" CuO over the carrier surface stimulated by the surface interaction that has begun, but they do not make possible an intense topochemical reaction between CuO and the carrier to form solid CuO—Al_2O_3 solutions. After regeneration treatments, all of the samples of the catalyst have low activity despite the fact that a considerable part of their surface in the operating state contains metallic copper.[7] This confirms the previous conclusion about the relatively low activity of Cu^0 and Ni^0 in the hydrogenation of oxygen on catalysts based on cements, because when there is a small excess of hydrogen the high activity of these catalysts is determined by the metal—oxide interface.[4]

A solid solution based on oxides of active metals is present on the surface of the initial CuO(20 %)—NiO(15 %)—talum catalyst[6] (see Fig. 1, *b*). The carrier surface, *i.e.*, the solid solution of active oxides in Al_2O_3, becomes exposed (curve *2* is similar to the band of talum) after deactivation accompanied by sintering of the metallic phase, like in the case of the CuO(35 %)—talum catalyst. The regeneration treatments result in recovery of the surface solid solution based on CuO and NiO, which is enriched with copper oxide to a different extent (see Fig. 1, *b*, curves *4—7*). However, the addition of 20 % CuO or CHC (curves *6* and *7*) does not result in a quasi-free surface phase of CuO, as has been observed after regeneration of the CuO(35 %)—talum catalyst (see Fig. 1, *a*). Perhaps this phase is formed when 20 % CHC is introduced (see Fig. 1, *b*, curve *7′*; this curve results from the appearance of a kink on the Arrhenius plot[5]). It is suggested that this is a consequence of a more intense interaction between CuO and the support than occurs with the CuO(35 %)—talum catalyst. The topochemical interaction that appears in this case to form a solid CuO solution in Al_2O_3 is apparently promoted by the presence of NiO (with which CuO easily forms solid solutions), but it is still hindered, and higher content of the additive (20 %) is needed to achieve the concentration of the solid solution needed to regenerate the activity to the initial level.

Taking into account the previous conclusions about the structural features of the active surface of the catalysts based on cements and about the reasons for low-temperature deactivation of these catalysts during hydrogenation of oxygen,[2,4] one can interpret the experimental results as follows.

In the method of chemical mixing used for the preparation of cement-containing catalysts the original components interact at 400 °C to form a highly nonuniform, but rather stable (metastable) structure, which ensures the formation of a catalytically active surface. In the initial state, active MO oxides (M = Cu, Ni) exist on the surface of these catalysts as solid solutions of Al_2O_3 in MO. The MO + Al_2O_3 islets are stabilized at certain regions of the surface of the cement framework due to the interaction of Al_2O_3 of the framework with MO and, in addition, due to residual CO_3^{2-} anions in the area of the boundary between the active solid solution and the framework (low-temperature solid solutions are formed and, hence, anionic stabilization[4] takes place during anionic modification).

A reduced form of the catalyst participates in hydrogenation of oxygen, however, only a part of the active phase is in the oxidized state under the conditions of the catalysis, and a metal—oxide boundary exists on the surface of the operating catalyst (more exactly, it is a M^n/M^{2+} boundary, where $n = 0$ for M = Ni and $n = 0$ or 1+ for M = Cu, since three valent states of copper, *viz.*, 0, 1+, and 2+ coexist on the surface under the reaction conditions, according to the data of XPS[7]).

Overheating the sample results in its deactivation and in weakening of the connection between the surface islets and the framework. This occurs, on the one hand, due to the removal of modifying anions and, on the other hand, due to the beginning of structuring of the solid solution, which laminates to form a MAl_2O_4 phase and to liberate free oxide. This oxide is not any longer stabilized by the framework, therefore, the reduction of the sample with this partly destroyed structure of the surface before the beginning of catalytic hydrogenation results in the complete reduction of the liberated MO to the metal; the possibility of the existence of the active M—MO interface considerably decreases, and the catalyst is deactivated.

The suggested regeneration of the active structure of the deactivated catalyst due to the direct topochemical reaction of the cement framework with the active oxide, CuO (or CHC), is strongly hindered, because solid-phase reactions between the oxide components begin at elevated temperatures (800—1000 °C).[2] Therefore, it is not surprising that the regeneration of the activity is not achieved when the deactivated catalyst is heated without the addition of an active oxide, as in the case when there is an unsufficient content of the additive: the copper oxide that appears is only sufficient for "spreading" over the framework surface without interaction. The additional deactivation, which is possible in these cases instead of the expected regeneration, can be explained by the fact that the "spread" oxide may cover the remaining active regions on the surface.

Complete regeneration of the activity by the topochemical method occurs only through a combination of three conditions: the use of a more reactive additive (CHC), its increased concentration (20 %), and enhanced reactivity of the framework due to the existence of NiO in its structure.

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