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# Study of the deactivation and regeneration of copper chromite on γ-alumina and magnesium chromite on γ-alumina catalysts for fuel combustion

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The causes of the deactivation of catalysts for fuel combustion $MeCr_2O_4/\gamma\text{-}Al_2O_3$ (Me = Cu or Mg) have been investigated using a variety of complex physical-chemical methods: IRS, ESDR, XPS, TPD and a pulse microcatalytic method. It has been concluded that the observed deactivation of catalysts during fuel combustion is due to the combined effect of high temperatures and reduction media.

**Keywords:** Catalyst characterization; IRS; TPD; XPS; ESDR; oxide catalysts; deactivation; fuel combustion

## 1. Introduction

A novel and efficient fuel combustion technique has been developed at the Institute of Catalysis which uses catalytic heat generators (CHG) in a fluidized bed [1]. The CHG apparatus, which is designed for various technological processes, uses two types of catalysts. These are: copper chromite on γ-alumina ($CuCr_2O_4/\gamma\text{-}Al_2O_3$) and magnesium chromite on γ-alumina ($MgCr_2O_4/\gamma\text{-}Al_2O_3$). The catalysts for fuel combustion are complex supported systems of oxides. During CHG operation they are subjected to stoichiometric air/fuel mixtures at high temperatures. This leads to deactivation of the catalysts due to changes in the phase composition of the active components. Thus, the preparation of active and stable catalysts for fuel combustion requires detailed information of the nature of the active components. In the present work the causes of the deactivation of copper chromite on γ-alumina and magnesium chromite on γ-alumina catalysts for fuel combustion have been investigated by a variety of instrumental methods: IR spectroscopy, electron spectroscopy of diffused re-

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flectance (ESDR), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and a pulse microcatalytic method.

## 2. Experimental

*Samples.* Samples of the copper chromite on γ-alumina catalysts were obtained by impregnation of $Al_2O_3$ spherical granules with a solution of copper dichromate, followed by drying and thermal treatment at 970 K. Samples of the magnesium chromite on γ-alumina catalysts were prepared by impregnation of $Al_2O_3$ spherical granules with a solution of magnesium dichromate, followed by drying and calcination at 1010 K. The samples containing 20 wt% of the active component per weight of chromite were investigated.

*Infrared spectroscopy.* IR-spectra of adsorbed CO were recorded on a Specord IR-75 spectrometer. To investigate CO adsorption we used a special low-temperature cell capable to cool samples down to 170 K and a special vacuum dosing stopcock to feed small amounts of CO into the cell [2,3].

*X-ray photoelectron spectroscopy.* To study the electronic state of catalysts XPS experiments were carried out on an ESCA-3 VG electron spectrometer. The vacuum levels in the analyzer and preparation chambers were $1–2 \times 10^{-7}$ and $5 \times 10^{-6}$ Pa, respectively. XPS spectra were calibrated according to the C 1s line whose binding energy was taken to be $E_b = 285.0$ eV [4].

*Electron spectroscopy of diffused reflectance.* ESDR spectra of powdered catalyst were recorded on a Specord M40 spectrometer at 45000–11000 $cm^{-1}$.

*Pulse microcatalytic method.* These experiments were carried out in a plant reactor and in a laboratory unit similar to those described in refs. [5,6]. The He flow rate was 40 $cm^3$/min; pulse continuation was 20 s. The reaction products were analyzed chromatograficálly.

To investigate CO oxidation, a 5% CO + He mixture was employed. The reaction was carried out at 670 K. Freshly prepared catalyst samples were pretreated in oxygen at the reaction temperature for 1 h, then purged in He at the same temperature for 20 min. The catalyst samples in CHG were pretreated in He at 670 K for 1 h. To investigate $C_4H_{10}$ oxidation, a 0.5% $C_4H_{10}$ + He mixture was used. The reaction was performed at 670 K.

## 3. Results and discussion

The high initial activity of the fresh copper chromite on γ-alumina catalyst in the oxidation reaction of carbon monoxide is due to cations Cu(II) within the surface of copper chromite and in surface clusters CuO (fig. 1). Centres with chromium cations in the highest oxidation states are bound to the support surface and solid solutions of the aluminate type. These contain cations of

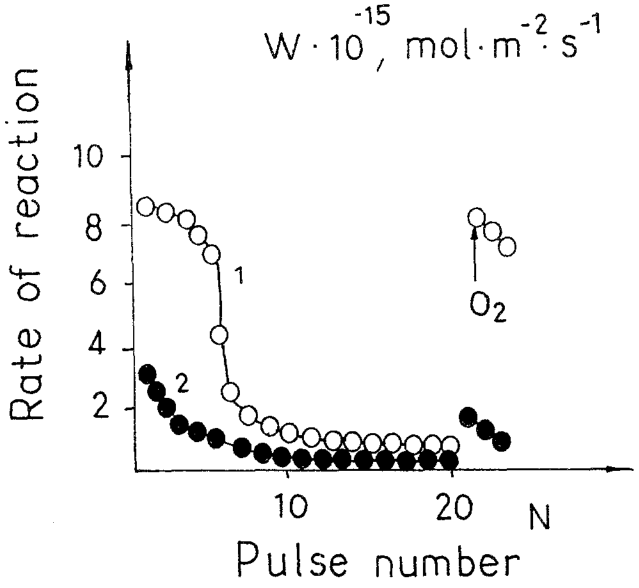

Fig. 1. Dependence of the CO oxidation rate on pulse numbers over catalysts: (1) $CuCr_2O_4/\gamma$-$Al_2O_3$ (initial); (2) $CuCr_2O_4/\gamma$-$Al_2O_3$ (after CHG).

bivalent copper and are less active in the CO oxidation reaction. It was shown by IRS and XPS that during the use of this catalyst in CHG, as well as during the unsteady-state oxidation reaction, a partial reduction of Cu(II) to Cu(I) occurs (fig. 2), which leads to an activity loss in the oxidation reaction. In the fresh magnesium chromite on γ-alumina catalyst, the activity for carbon monoxide oxidation is controlled by the centres containing chromium cations in the highest oxidation degrees stabilized on the active component surface. Reduction of these centres during the CHG process and under conditions of the unsteady-state oxidation reaction, leads to a slight decrease in activity for the CO oxidation reaction [2,4].

The cations of Cr(VI) within the composition of the copper chromite on γ-alumina catalyst contribute greatly to the rate of oxidation of carbon monoxide.

It has been shown previously [7] that fresh copper chromite on γ-alumina and magnesium chromite on γ-alumina catalysts possess high activity in the oxidation of methane and butane, while the samples of catalysts after use in CHG are much less active for complete oxidation of hydrocarbons. In the present work the pulse microcatalytic results, as well as those arising from TPD and ESDR, have shown that the high initial activity of all the chromium-containing catalysts in reactions of complete oxidation of hydrocarbons is determining by centres containing chromium cations in the highest oxidation states stabilized in a support structure as well as in the active component structure. A portion of the chromium cations, reduced in the CHG process or at unsteady-state oxidation

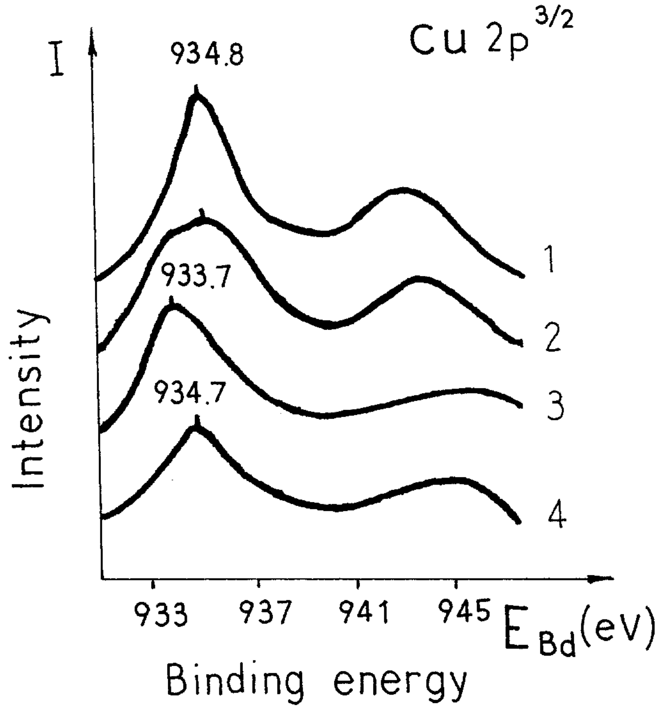

Fig. 2. XPS spectra of samples of the alumocopperchromium catalyst: (1) initial; (2,3) after exploitation in CHG; (4) after reoxidation with oxygen at 770 K. Spectral region is Cu $2p_{3/2}$.

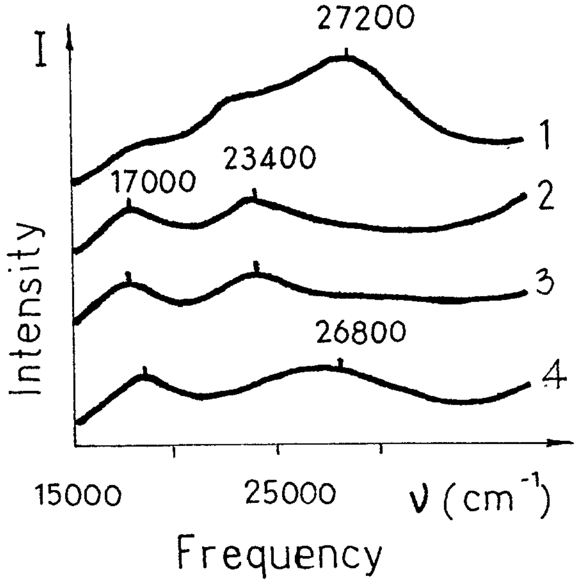

Fig. 3. ESDR spectra of samples of the alumomagnesium catalyst: (1) initial; (2) after exploitation in CHG; (3) after reduction under conditions of unsteady-state reaction; (4) after reoxidation with oxygen at 670 K.

reaction conditions, is easily reoxidized with oxygen (fig. 3), which in turn leads to a partial increase in activity for complete oxidation of hydrocarbons and fuels.

It has been shown that cations of Cu(II) within the composition of the copper chromite on $\gamma$-alumina catalyst contribute greatly to the rate of oxidation of methane and butane, and these centres also play a significant role in a complete oxidation of some intermediate products. Severe treatment of catalysts by stoichiometric air/fuel mixtures and high temperatures during fuel combustion leads to a change in volume and surface phase composition of the catalysts. Solid solutions of the composition of $MeCr_{2-x}Al_xO_4$ and $\alpha$-$Cr_{2-x}Al_xO_3$ are formed as a result of the interaction of an active component with a support [7].

The separate contributions of high temperature (800–1400 K) and reduction media to deactivation of catalysts have shown that each of these factors alone does not bring about substantial decrease of activity of the catalysts.

## 4. Conclusion

This work allows us to conclude that the observed deactivation of copper chromite on $\gamma$-alumina and magnesium chromite on $\gamma$-alumina catalysts during fuel combustion is due to the combined effect of high temperatures and reduction media.

We have shown that all initial chromium-containing catalysts have active centres including chromium cations in high oxidation states. After exploitation of catalysts in CHG the reduction of centres containing Cr(VI) occurs as well as the reduction of Cu(II) to Cu(I) for copper containing catalyst.

The reaction environment in the CHG unit causes the interaction of the active components with the support resulting in the formation of a solid solution of the type $MeCr_{2-x}Al_xO_4$, where Me = Mg, Cu.

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