

The Influence of Addition of Silver and Copper on the Reducibility of CrAl_3O_6 System¹

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Abstract—The influence of addition of silver and copper on the reduction behavior of binary oxide CrAl_3O_6 was investigated. The formation of copper chromite CuCr_2O_4 and silver chromate Ag_2CrO_4 during calcination process was observed. The intermediate phase CrO was detected when copper and silver-copper systems were reduced at temperatures above 500°C . This intermediate is formed from Cr_2O_3 , which is yielded by the initial reduction of $\text{Cr}_2\text{O}_4^{2-}$ species.

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Chromium oxide catalysts play an important role in many industrial processes and they are extensively used in many reactions such as oxidative dehydrogenation of isobutane [1–3], selective catalytic reduction of NO_x with ammonia [4, 5] and polymerization [6, 7]. The formation of chromia, chromates and/or chromites is possible because chromium ions occur in a varying state of oxidation. It is well known that copper [8] and zinc [9] chromites are widely used in many industrial processes such as production of methanol, fatty ester and higher alcohols.

Many chromium compounds like CrO_3 , $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{OH})_3$, Cr_2O_3 are used as catalyst precursors. Chromia-supported catalysts are usually prepared from chromium trioxide. The surface of CrO_3 catalysts treated in oxidative atmosphere contains chromate-like species $\text{Cr}_2\text{O}_4^{2-}$. Specific active sites on chromia based catalysts are needed for certain catalytic reactions, e.g. water gas shift reaction. According to predictions and direct observations, chromium occurs on the surface of chromia-supported catalysts in different oxidation states ranging from $\text{Cr}(\text{II})$ to $\text{Cr}(\text{VI})$ with specific species depending upon Cr loading, preparation procedure and treatment conditions [10–14].

In this work, the silver-chromium, copper-chromium, chromium-aluminum dioxides and copper and/or silver-copper supported catalysts were prepared. The XRD in situ analysis in a stream of 5% H_2 + 95% Ar and the temperature-programmed reduction were used to inquire into the mechanism of reduction of CrAl_3O_6 , copper and silver-copper supported catalysts. This work is aimed at the elucidation of the role

played by silver and copper additives in the reduction of CrAl_3O_6 binary oxide.

EXPERIMENTAL

Preparation of Catalysts

Catalysts were prepared according to the wet impregnation procedure. Chromium and aluminum nitrates were used to prepare the CrAl_3O_6 binary oxide. The mixture of chromium and aluminum hydroxides with an Al/Cr molar ratio of 3 was obtained by co-precipitation with ammonia, it was then filtered, washed out, dried and finally calcined at 400°C in air for 3 h. The chemical composition of the binary oxide can be given as CrAl_3O_6 ($S_{\text{BET}} = 157 \text{ m}^2/\text{g}$, predominant pore size is around 2 nm). Copper and silver phase was introduced on support according to the wet impregnation procedure making use of an aqueous solution of the corresponding nitrate. The supported catalysts were then dried and finally calcined in air at 400 and 700°C . The metal loaded catalysts had compositions like 5, 10 or 20% Cu on a Al_3CrO_6 support, and 5% Ag, 1% Ag + 20% Cu or 5% Ag + 20% Cu on a CrAl_3O_6 support. Silver-chromium and copper-chromium materials with the molar ratios $\text{Ag/Cr} = 2$ and $\text{Cu/Cr} = 1$ were prepared from the mixture of silver or copper nitrate and chromium(VI) oxide solutions by drying and calcining the mixture in air at 400°C for 3 h.

Characterization of Catalysts

Temperature Programmed Reduction (TPR- H_2).

The TPR- H_2 measurements were conducted using the automatic TPR system AMI–1 over the 25 to 900°C temperature range with the linear heating rate of $10^\circ\text{C}/\text{min}$. Samples (ca 0.1 g) were reduced in a

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stream of 40 cm³/min hydrogen (5% H₂ + 95% Ar). Hydrogen consumption was monitored by a thermal conductivity detector.

XRD measurements. Approximately 150 mg of the sample crushed in agate mortar was loaded in the sample holder made of glass ceramics (Macor). The gas mixture 5% H₂ + 95% Ar was used as a reducing reagent for the binary oxide support CrAl₃O₆. The sample was heated at a rate of 2°C/min. The high temperature wide-angle X-ray diffraction data were collected using a PANalytical X'Pert Pro diffractometer equipped with an Anton Paar XRK900 reactor chamber with 50°C steps from 50 to 850°C.

A PANalytical X'Celerator detector based on Real Time Multiple Strip technology capable of simultaneously measuring the intensities in the 2θ range of 10–90° was used.

Powder X-ray diffraction patterns were obtained at room temperature using a PANalytical X'Pert Pro MPD diffractometer in Bragg–Brentano reflecting geometry. Nickel filtered CuK_α radiation from a sealed tube was used. The samples were scanned at a rate of 0.0167° per step over the 5° ≤ 2θ ≤ 90° range with a scan time of 27 s step⁻¹. Because raw diffraction data contain some noise, the background was subtracted during the analysis using Sonneveld and Visser algorithm [15] and the data were smoothed using cubic polynomial [16]. All calculations were done with X'Pert HighScore Plus computer program [17].

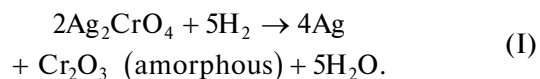
RESULTS AND DISCUSSION

Phase Composition

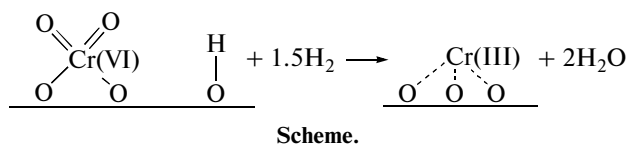
XRD patterns for the reference samples (silver-chromium and copper-chromium binary oxides) along with the samples of supported catalysts (20% Cu/CrAl₃O₆, 5% Ag/CrAl₃O₆ and 5% + 20% Cu/CrAl₃O₆) are given in Figs. 1–4. The patterns were acquired by in situ measurements of the samples subjected to the temperature—programmed reduction. The in situ XRD technique was used to study the composition of the samples as a function of the reduction temperature.

XRD in situ analysis indicated that only the peaks corresponding to the Ag₂CrO₄ phase [18, 19] are observed for the reference silver-chromium binary oxide reduced at 25 and 140°C. The results demonstrate that this phase is stable and cannot be reduced in these conditions. In the X-ray pattern recorded at 170°C the silver chromate as the main phase and metallic silver as a minor phase can be detected. For the samples treated at 200°C the main peaks consistent with the metallic silver phase develop and a diffraction peak at 2θ ≈ 31° attributable to the silver chromate phase is also observed. Disappearance of the silver chromate phase at a reduction temperature of 230°C can be explained by reduction of Ag₂CrO₄ and formation of the Cr₂O₃ phase that is amorphous to

X-rays. In the range from 230 to 500°C the reduction can occur by reactions like

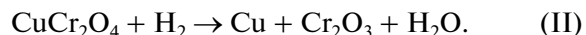


A possible mechanism governing the reduction is suggested by the scheme given below [20, 21]. At the initial step of the reduction process, surface Cr₂O₄²⁻ species are formed on the support. At the next step, two terminal oxygen atoms are removed, resulting in an intermediate structure with chromium bonded to the support via two oxygen atoms that gives Cr(II)O₂²⁻ species. During the reduction water is formed as a product of the interaction with hydrogen implying the oxidation of Cr(II) to Cr(III). To explain the apparent discrepancy, we suggest that a hydroxyl group may be involved in the reduction of the isolated tetrahedral CrO₄²⁻ species by hydrogen (see the scheme).



The presence of reflections due to metallic silver and crystalline α-chromia on the XRD pattern recorded at 500°C confirms our suggestion providing evidence in favour of the conclusion that the amorphous to X-rays phase of Cr₂O₃ which is not observed in the temperature range 230–500°C, transforms to crystalline α-Cr₂O₃ phase during the sintering process.

Based on the XRD in situ study of copper-chromium dioxide (the Cu/Cr molar ratio of 1) that served as a reference material, reflections from the copper chromite [22, 23, 24] phase are observed at the onset of the reduction process at temperatures ranging from 25 to 170°C. Therefore, the reference material at this temperature contains an irreducible copper chromite phase. An increase in the reduction temperature results in formation of α-Cr₂O₃ phase as indicated by corresponding XRD peaks discernable above 500°C. The source of this phase is believed to be a previously reduced copper chromite species:



The reduction of copper chromite also occurs by a mechanism that is similar to this for silver chromate phase outlined above. However a further increase in the reduction temperature leads only to the growth of the crystallites in the sample.

The results of the detailed XRD in situ study of CrAl₃O₆ were reported in our earlier work [18]. X-ray data showed the presence of chromium-alumina dioxide and chromium(III) oxide phases in the sample which when reduced at temperatures ≥400°C yields the crystalline α-Cr₂O₃ phase.

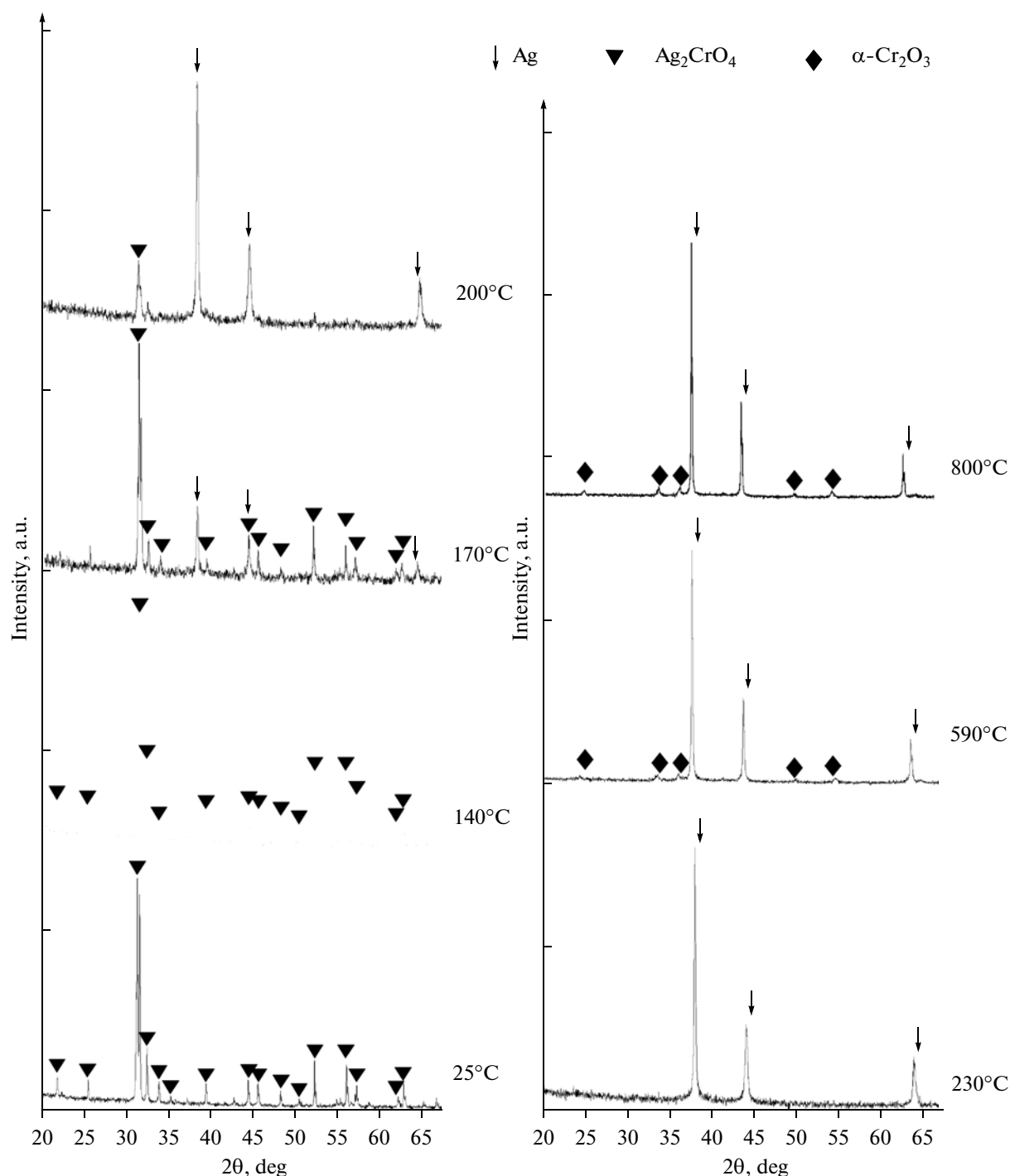


Fig. 1. X-ray powder patterns recorded during reduction of Ag_2CrO_4 at temperatures from 25 to 800°C.

The 20% $\text{Cu}/\text{CrAl}_3\text{O}_6$ supported catalysts showed reflections corresponding to the copper chromite, binary oxide, copper oxide, metal copper and $\alpha\text{-Cr}_2\text{O}_3$. The phase composition of the catalysts depends on the reduction temperature. The CuCr_2O_4 , CrAl_3O_6 and CuO phases detected up to 300°C confirm the results obtained for the reference materials. Increase in the reduction temperature changes the

phase composition. Treatment with hydrogen at 300°C and higher temperatures leads to formation of the metallic copper from copper chromite [22–24] and copper oxide. Reflections of the crystalline $\alpha\text{-Cr}_2\text{O}_3$ are visible in the X-ray diffraction patterns registered for the samples treated at $\geq 500^\circ\text{C}$ but this phase cannot be observed at a lower reduction temperature. The last observation suggests that as in the case

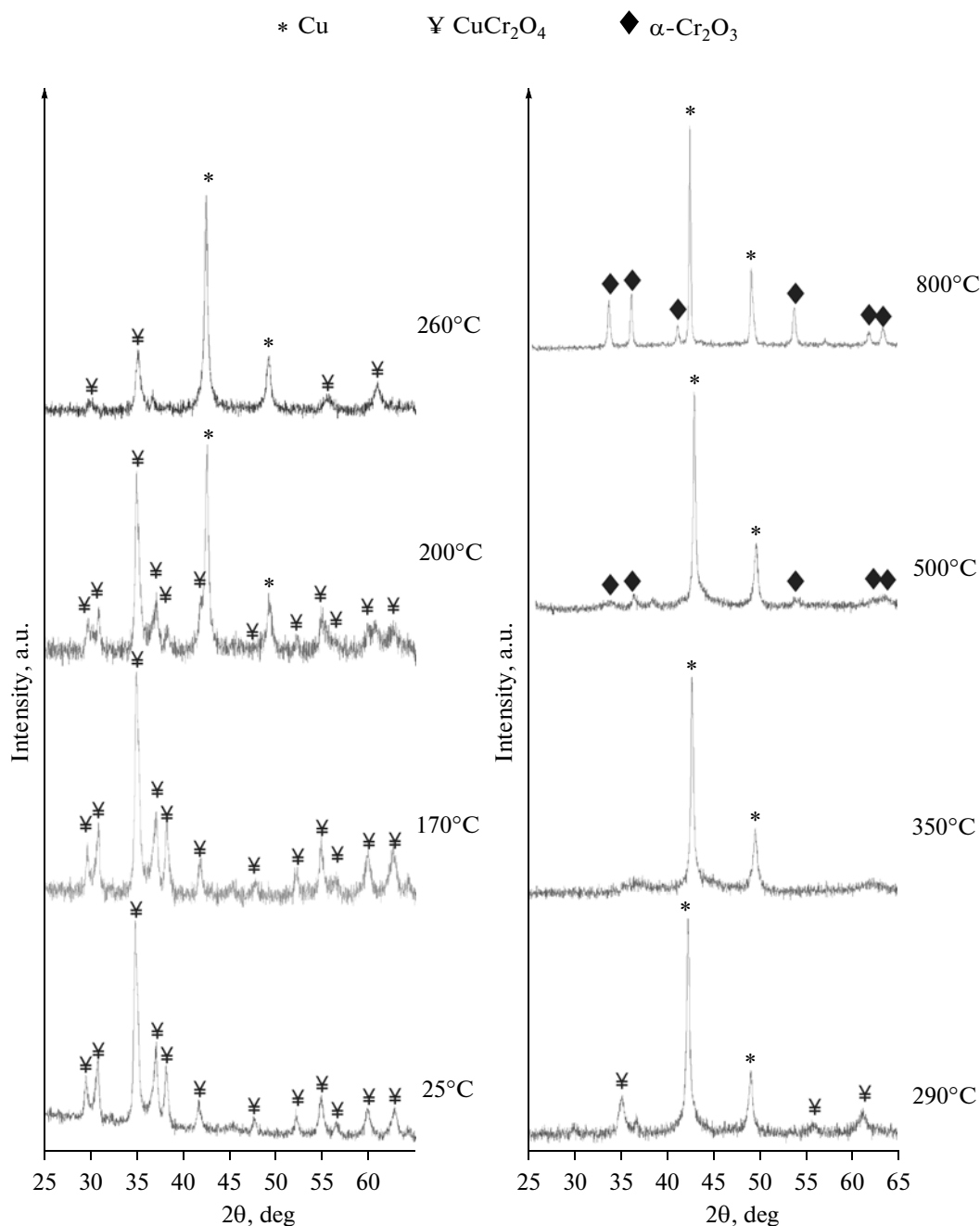


Fig. 2. X-ray powder patterns recorded during reduction of CuCr₂O₄ at temperatures from 25 to 800°C.

of the reference samples this oxide exists as an amorphous to X-rays phase in the range from 300 to 500°C.

It is instructive to note the appearance of an unstable CrO phase at 600°C as a result of reduction of particularly small Cr₂O₃ species, amorphous to X-rays. We suggest that occurrence of this phase can be explained by the dissociative adsorption of hydrogen on the surfaces of copper or silver crystallites which are probably highly dispersed on the support. At the next step hydrogen atoms thus formed can reduce the α-Cr₂O₃ phase to produce CrO. We could observe this

sequence of events neither for the silver-chromium and copper-chromium used as the reference materials nor for the chromium-alumina binary oxide. The dissociative adsorption of hydrogen on surfaces of copper or silver crystallites has however been repeatedly reported in literature.

In addition to peaks corresponding to CrAl₃O₆, CrO₃, Ag₂O and α-Cr₂O₃, two additional reflections from spinel structures (CuCr₂O₄, Ag₂CrO₄) [18, 19, 24] can be seen on the X-ray diffraction pattern of the 5% Ag + 20% Cu supported catalyst reduced at

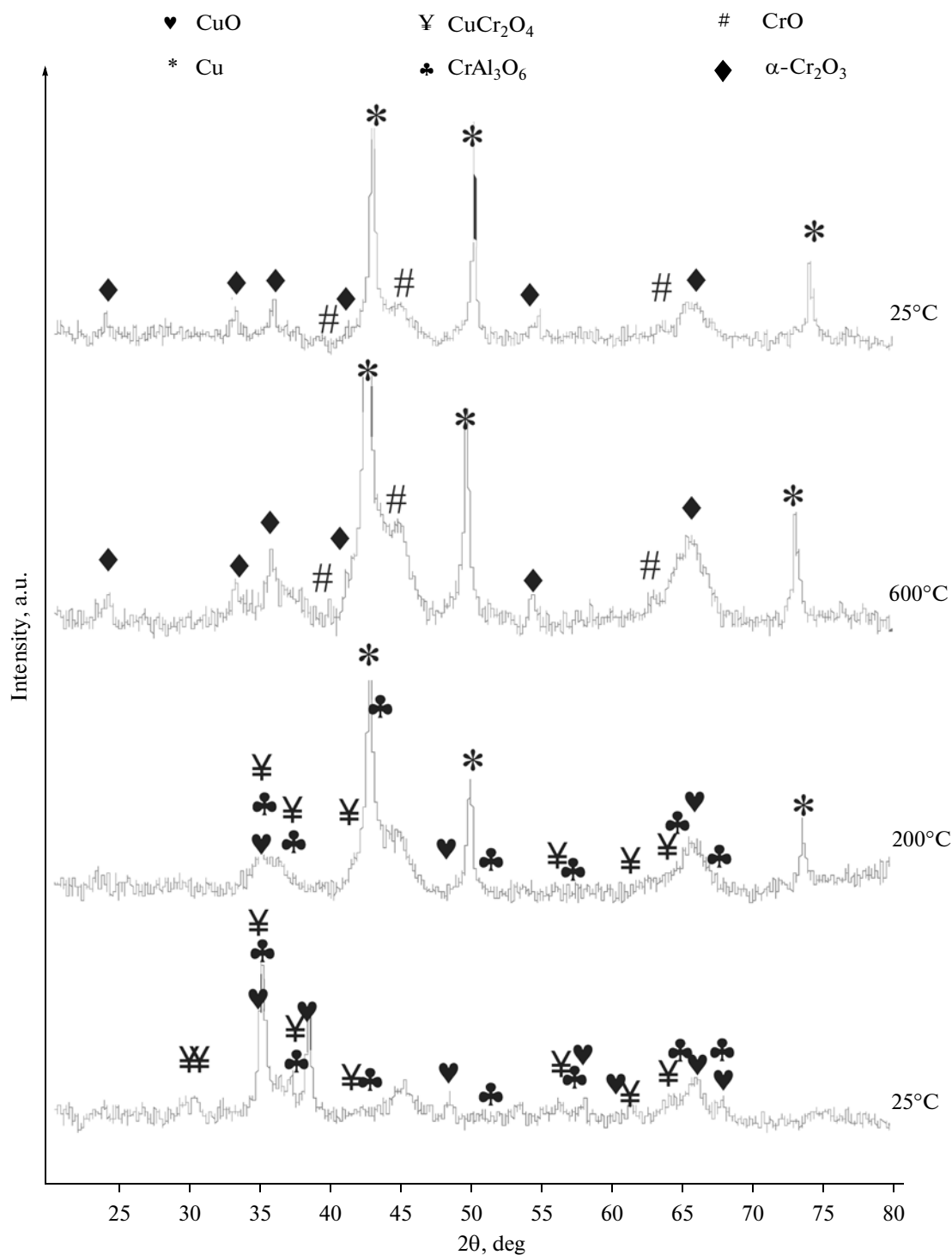


Fig. 3. X-ray powder patterns recorded during reduction of 20% Cu/CrAl₃O₆ catalyst at temperatures from 25 to 600°C.

≤300°C. These phases are present in the copper supported catalyst reduced at the same temperatures. As evidenced by XRD in situ measurements, a metastable CrO phase can be detected in the copper or/and silver–copper supported catalysts reduced at temperatures above 550°C. This phase disappears after cooling

and re-exposition on the air and it cannot be found in binary oxides.

Conventional XRD measurements carried out for binary oxide (CrAl₃O₆), copper, silver and silver–copper supported catalysts calcined at various temperatures were described in our earlier work [18]. Binary

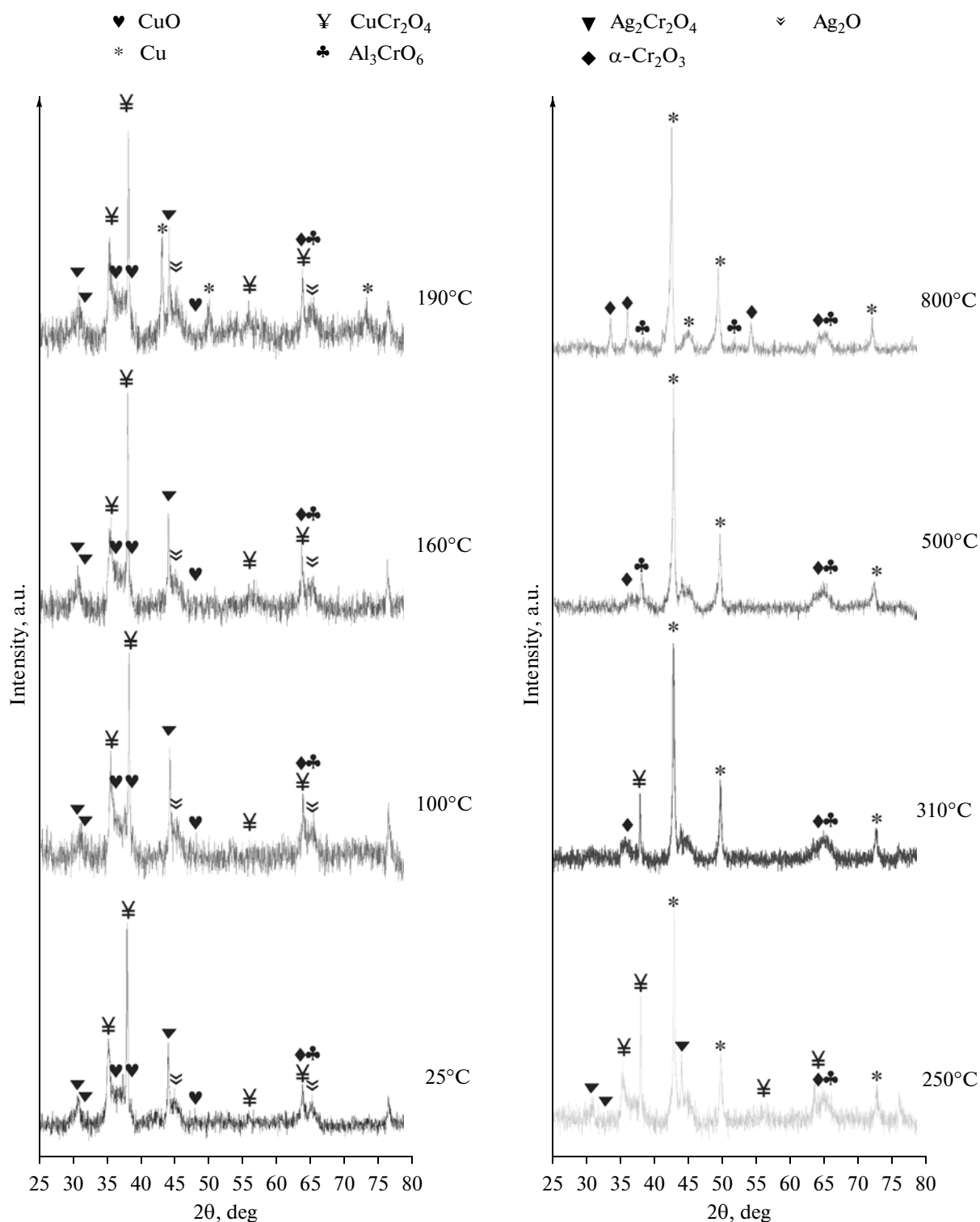


Fig. 4. X-ray powder patterns recorded during reduction of (5% Ag + 20% Cu)/CrAl₃O₆ catalyst at temperatures from 25 to 800°C.

oxide Al₃CrO₆ calcined at 400, 700 and 900°C was reported to contain no crystalline phases apart from α-Cr₂O₃ and spinel. Those results are in good agreement with TPR data obtained for the chromium-alu-

minum system. Introduction of copper or/and silver into the binary oxide results in formation of spinels CuCr₂O₄, Ag₂CrO₄ along with copper or/and silver oxides. The occurrence of these phases was confirmed

by the reduction effects which can be distinguished by the relevant TPR profiles.

Abu-Zied [19] investigated silver/chromia catalysts calcined at various temperatures and confirmed that samples heated from 300 to 500°C are composed of silver chromate as a major phase with a minor amount of chromic oxide. For the catalysts calcined at 600°C the author observed silver chromite phase which becomes the predominant phase when the samples were treated at 700°C. We found the presence of the same phases in the catalytic system calcined at 400°C, but we failed to observe transformations of the spinel structure at higher temperatures. On heating to higher temperature (700 and 900°C) only the growth of crystallites was detected in all samples. In addition, the catalyst with low silver loading does not show peaks characteristic of the Ag_2O phase. This indicates that silver is highly dispersed in these catalysts as small crystallites undetectable by X-rays.

Reduction Studies

The results of TPR measurements for chromic oxide, reference materials (silver-chromium, copper-chromium), binary oxide CrAl_3O_6 , mono and bimetallic supported catalysts calcined in air at 400°C are presented in Fig. 5. To better understand the reduction process in the systems of interest these results are supplemented by the reduction profile of Cr_2O_3 . The TPR profiles recorded for different samples at temperatures ranging from 200 to 400°C reveal chemical interactions between Cr(VI) atoms and vicinal oxygen ligands such as terminal or bridging atoms bonded to alumina surface [20, 21]. The TPR curve for Cr_2O_3 shows only one reduction effect which is attributed to reduction of the Cr(VI) oxidized phase formed from the previously reoxidized phase of Cr_2O_3 . The TPR profile of binary oxide CrAl_3O_6 shows only one reduction effect similar to that found in the case of Cr_2O_3 . In accordance with XRD in situ measurements this observation suggests that the effect is associated with reduction of the same species as those reduced by treating Cr_2O_3 . The reduction of copper-chromium and silver-chromium samples was carried out in a hope to define more accurately the reduction process of copper and bimetallic silver-copper supported catalysts. The reduction profiles of reference materials as well as those of copper and silver copper catalysts show two reduction steps which can be assigned to two modes of reduction experienced by Cr(VI) oxidized phases. The first effect can be ascribed to readily reducible and highly crowded islands like chromates whereas the second one can be attributed to reduction of atomically dispersed chromates. Moreover, the role of water produced in the reduction process cannot be ignored because the oxidation numbers of Cr entities depend on whether H_2O molecules are desorbed or re-adsorbed on the support surface.

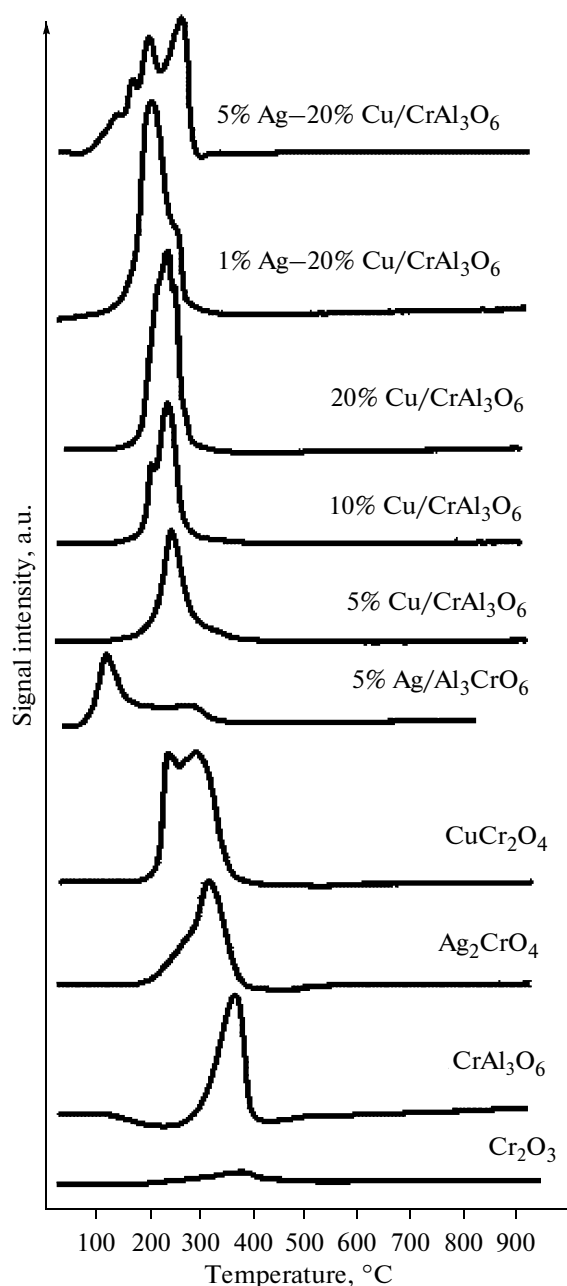


Fig. 5. TPR profiles for mono and bimetallic supported catalysts calcined in air for 4 h at 400°C.

Based on TPR curves for mono- and bimetallic catalysts (Fig. 5) introduction of silver and/or copper into binary oxide shifts the reduction profile to lower temperatures and improves reducibility of the binary oxide. The estimated consumption of hydrogen confirms that introducing metal improves reducibility of binary oxide. Analysis of the reduction behavior of supported copper catalyst shows that reducibility of that system depends on the extent of copper loading. For the 5 wt % Cu catalyst only one reduction step is observed in which copper oxide and two different Cr(VI) oxidized species are reduced. The increasing

copper loading brings about an additional effect attributed to reduction of copper chromites and copper oxide. In the case of the 5% Ag/CrAl₃O₆ system two reduction steps can be discriminated similar to those found with copper catalysts. The first step is related to reduction of silver oxide and an initially oxidized Cr(VI) species while the second step includes the reduction of the species detected on copper supported catalysts. In the reduction of the binary oxide the rate of reduction can be accelerated with reduction effects shifted to lower temperatures by adding silver into the Cu/CrAl₃O₆ catalyst.

On the TPR profile recorded for the (1% Ag + 20% Cu)/CrAl₃O₆ system one can distinguish two steps of reduction representing conversion of the same phases which were registered on the monometallic catalyst. The only difference is that the first reduction effect involves reduction of silver chromate and silver oxide. With increasing silver loading in the silver-copper supported catalyst four partially resolved reduction effects became discernible. The first effect is attributed to reduction of silver oxide; the second one is probably explained by reduction of copper oxide. The reduction step near 200°C associated with the highest consumption of hydrogen can be assigned to reduction of copper chromite and silver chromate [18]. These assignments are confirmed by XRD in situ powder patterns acquired for the sample (5% Ag + 20% Cu)/CrAl₃O₅ at 160°C which suggest formation of copper chromite, silver chromate along with trace amounts of copper and silver oxides (Fig. 4). However at 190°C additional peaks from metallic copper appear. At 250°C the sample contains metallic copper, copper chromite and silver chromate. Occurrence of these phases implies that copper chromite and silver chromate are reduced at higher temperature. The last reduction peak with maximum at 270°C (Fig. 5) illustrates the reduction of Cr⁶⁺ oxo-species that at this temperature give relevant XRD reflections.

Our main conclusions can be summarized as follows:

(1) XRD in situ measurements carried out for copper, silver-copper and binary oxide CrAl₃O₆ systems subjected to reductive treatment indicate that mono and bimetallic catalysts behave differently from other catalysts in that they show the presence of an unstable CrO phase above 550°C which disappears after cooling and re-exposition on the air.

(2) The binary oxide CrAl₃O₆ is reduced *via* one step and this step involves reduction of Cr(VI) species.

(3) Introduction of copper or/and silver into CrAl₃O₆ system improves reducibility of the binary oxide and causes the appearance of an additional low temperature effect when the samples are reduced. Depending upon the catalyst composition, these effects are connected with reduction of copper chromite, silver chromate, or copper and silver oxides.

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