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ALKALI DOPED (Na, K) Cu/Cr_2O_3:Al_2O_3 CATALYSTS FOR WATER GAS SHIFT REACTION

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The effect of precipitating agent (alkali ions Na, K) on copper-chromium-aluminum systems has been examined. Catalysts precipitated by alkali ions present lower CO conversion in comparison with ammonia catalysts because of their higher crystallinity degree and harder susceptibility to reduction. Catalysts obtained with NaOH are characterized by higher alkali metal concentration and by its uniform distribution on their surface as compared with KOH-derived ones.

INTRODUCTION

Water gas shift reaction (WGS) is one of the most common known widely applied reaction in industry. It is used to obtain hydrogen-rich gas for applications of fuel cell power generation [1]. Examples of commercially used catalysts in WGS are copper-zinc and copper-cerium, which are still under wide research. Widely discussed were already copper–zinc–alumina (CZA) catalysts, because of their industrial implementation in 1960's for instance to WGS reaction. That gave the suggestion to improve the selectivity of CZA catalysts, one of the ideas was alkali impregnation of CZA systems.

Currently the most interesting aspect of catalysts used in WGS and methanol synthesis are systems promoted by alkali ions. It was reported by many scientists that alkali ions improve both activity and selectivity of CZA catalysts. Such a result was observed for catalytic reduction of NO by CO or hydrocarbons with presence or without oxygen [2–3] also in oxidation reactions of: NO [4], ethanol [5], hydrocarbons [6] and carbon monoxide [7, 8]. It confirms the promising effect of alkali ions to numerous reactions like methanol synthesis and WGS, what become our current investigation.

Moreover the modification of ternary oxide catalysts became an interesting aspect, in our case we investigated the influence of precipitating agent (alkali ions Na, K) on copper-chromium-aluminum systems because of their promising effect based on avoiding sintering [9, 10].

EXPERIMENTAL

Catalysts preparation. Nitrates of copper, chromium, and aluminum were used as a support material precursor. Bi-oxides were prepared by coprecipitation method of appropriate hydroxides using sodium and potassium hydroxide. The homogeneous mixtures were dried (T = 100 °C for 24 h) and calcined in air atmosphere at various temperatures (400, 700, and 900 °C) for 3.5 h.

The specific surface area (S_{BET}). The specific surface area and porosity for catalysts and their supports were determined with an automatic sorptometer Sorptomatic 1900. Samples were prepared at 250 °C during 12 h evacuation and after that low temperature nitrogen adsorption-desorption measurements were carried out.

Temperature programmed reduction (TPR-H_2). The TPR-H_2 measurements were carried out in an automatic TPR system AMI-1 in the temperature range 25–900 °C with the linear heating rate 10°/min. Samples (weight around 0.1 g) were reduced in hydrogen stream (5 % H_2 – 95 % Ar) with the gas volume velocity 40 cm^3/min. Hydrogen consumption was monitored by a thermal conductivity detector.

Phase composition – XRD measurements. Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano reflecting geometry. Copper CuK_α radiation from a sealed tube was utilized. Data were collected in the range 5–90° 2θ with step 0.0167° and exposition per one step of 27 s. Due to the fact that raw diffraction data contain some

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noise, the background during the analysis was subtracted using Sonneveld and Visser algorithm and next the data were smoothed using cubic polynomial. All calculations were done with X'Pert HighScore Plus computer program.

Surface morphology and composition (SEM-EDS, TOF-SIMS). The catalysts studied were characterized by scanning electron microscopy with field emission S-4700 (Hitachi, Japan) equipped with energy dispersive spectrometer (Thermo-Noran, USA) and time-of-flight secondary ion mass spectrometry ToF-SIMS IV (IONTOF GmbH, Germany). Before SEM-EDS investigations the samples analyzed were placed on carbon plasters and coated with carbon or Pd/Pt targets using a Cressington 208 HR system (Cressington Scientific Instruments Ltd., UK). EDS spectrum and maps showing elemental composition and surface distribution were collected from SEM pictures using different magnification and, additionally, from single points. In order to perform an analysis using the ToFSIMS method (positive and negative spectra and images) the samples were placed on a steel plate. The accelerating voltage for X-ray intensity measurement and for SEMimage observation was 25 kV, using a probe current of 0.3 nA. ToFSIMS measurements of the chosen material were performed with a 5 kV Ga^+ primary ion source (2.5 pA pulse current). A flood gun was used to compensate the surface charging.

Catalytic activity tests. Activity tests in WGS reaction were carried out using the atmospheric pressure flow reactor using a gas mixture of pure CO and H_2O with molar ratio 1:2.5. The catalysts were stabilized in reaction stream for 1.5 h at 250 °C. The mass of the catalyst used in these experiments was typically 0.2 g and total rate was 15 cm^3/min. WGS reaction was investigated in the temperature range 250–400 °C.

RESULTS AND DISCUSSION

Specific surface area and alkali content. The measurements of specific surface area (SSA) were carried out on a series of copper-chromium-aluminum catalysts precipita-ted by ammonia, sodium or potassium hydroxides. From the initial measurements, an increase in SSA was observed for catalysts precipitated by hydroxides. Moreover, along the increase of alkali molecular mass, an increase in SSA was observed. Another trend is observed from data collected in Table, the decrease in copper loading follows the increase in SSA.

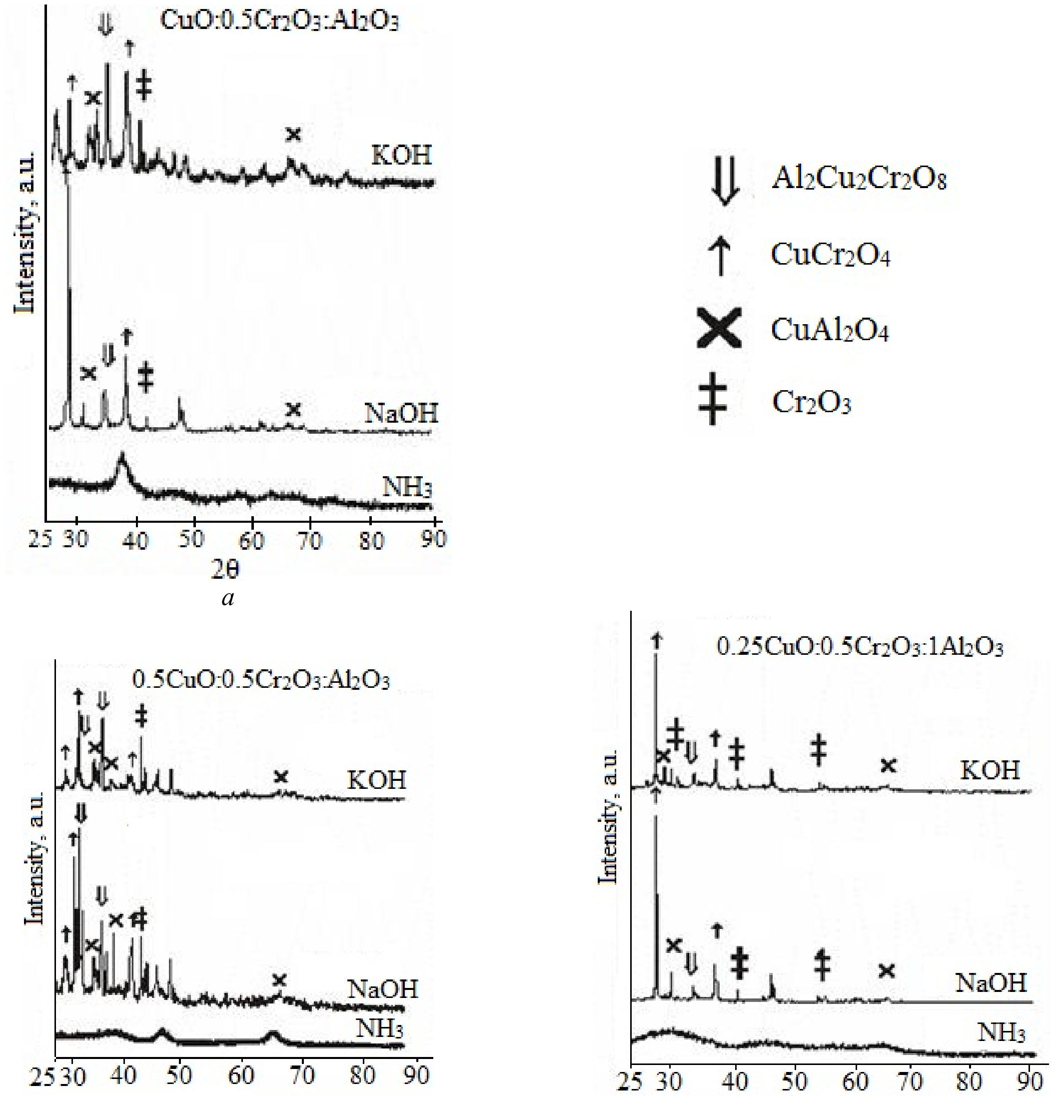
Table. Specific surface areas of $CuO:Cr_2O_3:Al_2O_3$ catalysts precipitated by NH_3, NaOH, KOH

	Specific surface area, m^2/g		
Type of catalyst **Precipitating agent**	**1Cu/ $0.5Cr_2O_3$ $:1Al_2O_3$**	**0.5Cu/ $0.5Cr_2O_3$ $:1Al_2O_3$**	**0.25Cu/ $0.5Cr_2O_3$ $:1Al_2O_3$**
NH_3	14	15	17
NaOH	17	19	21
KOH	25	27	27

Phase compositions studies. The effect of ternary catalysts ($xCuO:yCr_2O_3:zAl_2O_3$) constitution on phase composition studies is presented in Fig. 1. The XRD patterns recorded for samples calcined at 400 °C confirmed presence of spinell forms like $CuCr_2O_4$, $CuAl_2O_4$, $Al_2Cu_2Cr_2O_8$. The presence of a compound like $Al_2Cu_2Cr_2O_8$ could be also explained by a copper-oxygen-chromium linkages what is detailed in paragraph concerning surface morphology. For $2\theta = 30°$, 39° $CuAl_2O_4$ was visible, while spinel $CuCr_2O_4$ was related to the reflexes situated for the angles of $2\theta = 35°$, 37.1° [10]. Formation of spinel compounds was caused by solid-solid interactions of CuO with Al_2O_3, and CuO with Cr_2O_3 [8–11]. In our previous works for catalytic systems like 1 % Ag–20 % Cu/$CrAl_3O_4$ the presence of copper chromite was confirmed already at 400 and 700 °C [12].

Catalysts precipitated from NaOH are characterized by the highest crystallinity degree while the samples obtained from KOH are less crystalline and those from NH_3 present amorphous character. Such a result is surprising taking into account the results of SSA. The catalysts precipitated by ammonia are characterized by lower SSA than those for alkali systems.

Change in phase composition was observed (Fig. 1). With the decrease in copper oxide loading, the decrease in copper chromite but the increase of chromium oxide was detected. For catalyst $0.25CuO:0.5Cr_2O_3:1Al_2O_3$ the presence of Cr_2O_3 was confirmed in higher scale than for other investigated samples.



a

b

c

Fig. 1. XRD Patterns for CuO:Cr_2O_3:Al_2O_3 catalysts precipitated by NH_3, NaOH and KOH

Reduction studies. The reduction was carried out for all the catalysts investigated with different molar ratios and expanding them by precipitation agents. As reference materials, TPR profiles of Cr_2O_3, CuO/Cr_2O_3, PdO/Al_2O_3, CuO/Al_2O_3 were studied. The profiles of temperature programmed reduction for mentioned above compounds are presented in Fig. 2, *a*. The TPR result recorded for PdO/Al_2O_3 system shows that palladium oxide is reduced in the low temperature range (60–110 °C).

Surface morphology and composition. The SEM-EDS analysis showed that catalysts precipitated by alkali ions are characterized by less uniform surface morphology than corresponding material (ammonia – Fig. 3). Alkali catalysts are characterized by more crystalline surface in comparison to ammonia samples, what is easy to observe in the Figs. 4 and 5. Moreover, alkali precipitated catalysts present similar morphology to each other and similar elements distribution over the catalyst surfaces. The element analysis of the copper-chromium-aluminum systems surface confirms in case of alkali catalysts the presence of potassium and sodium what is presented in the Figs. 4 and 5. Generally, investigated catalysts are characterized by uniform element distribution over the Cu:Cr:Al catalyst surfaces.

The analysis by TOF-SIMS confirmed the presence of copper-oxygen-chromium linkages (Fig. 6).

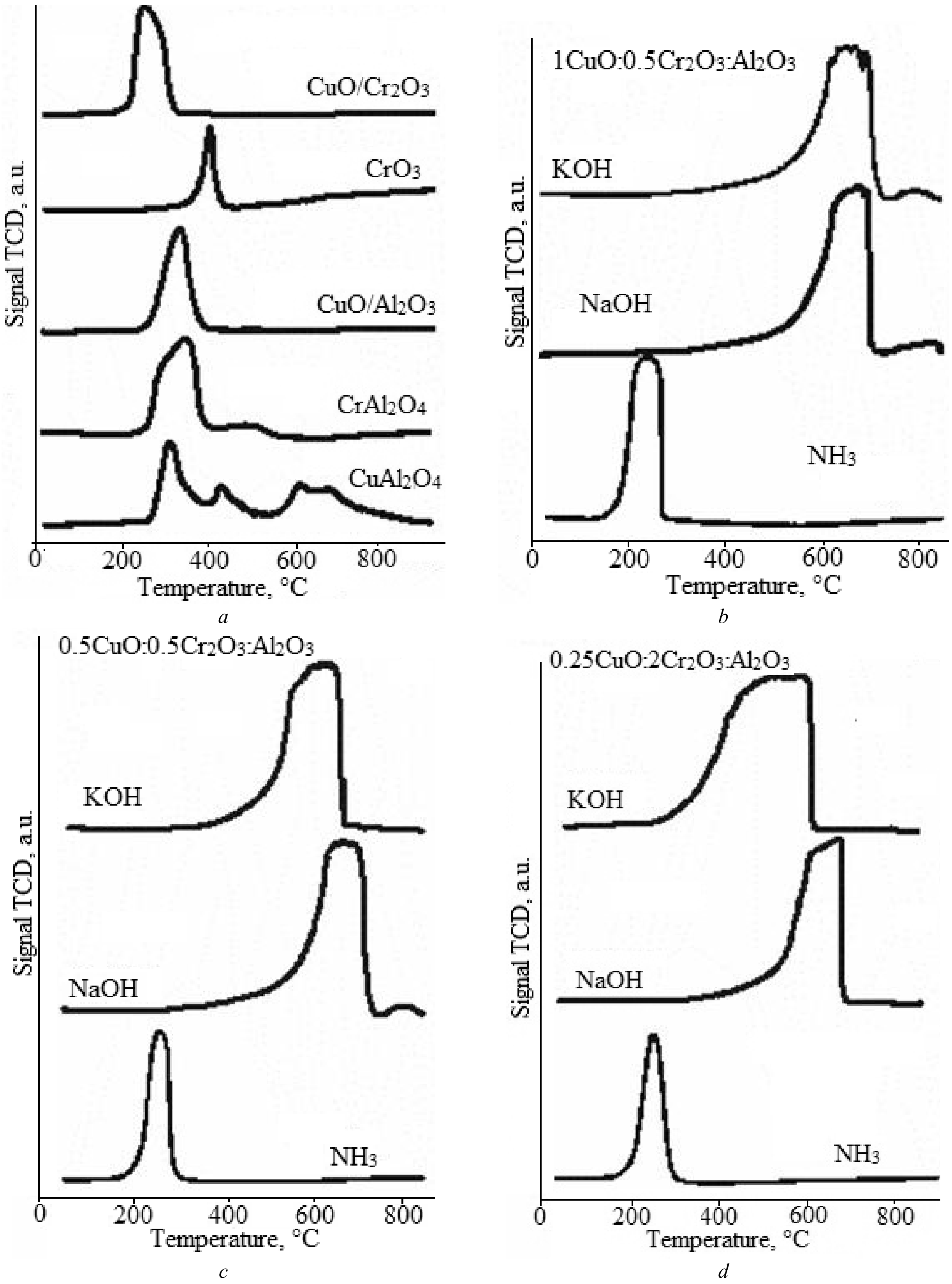
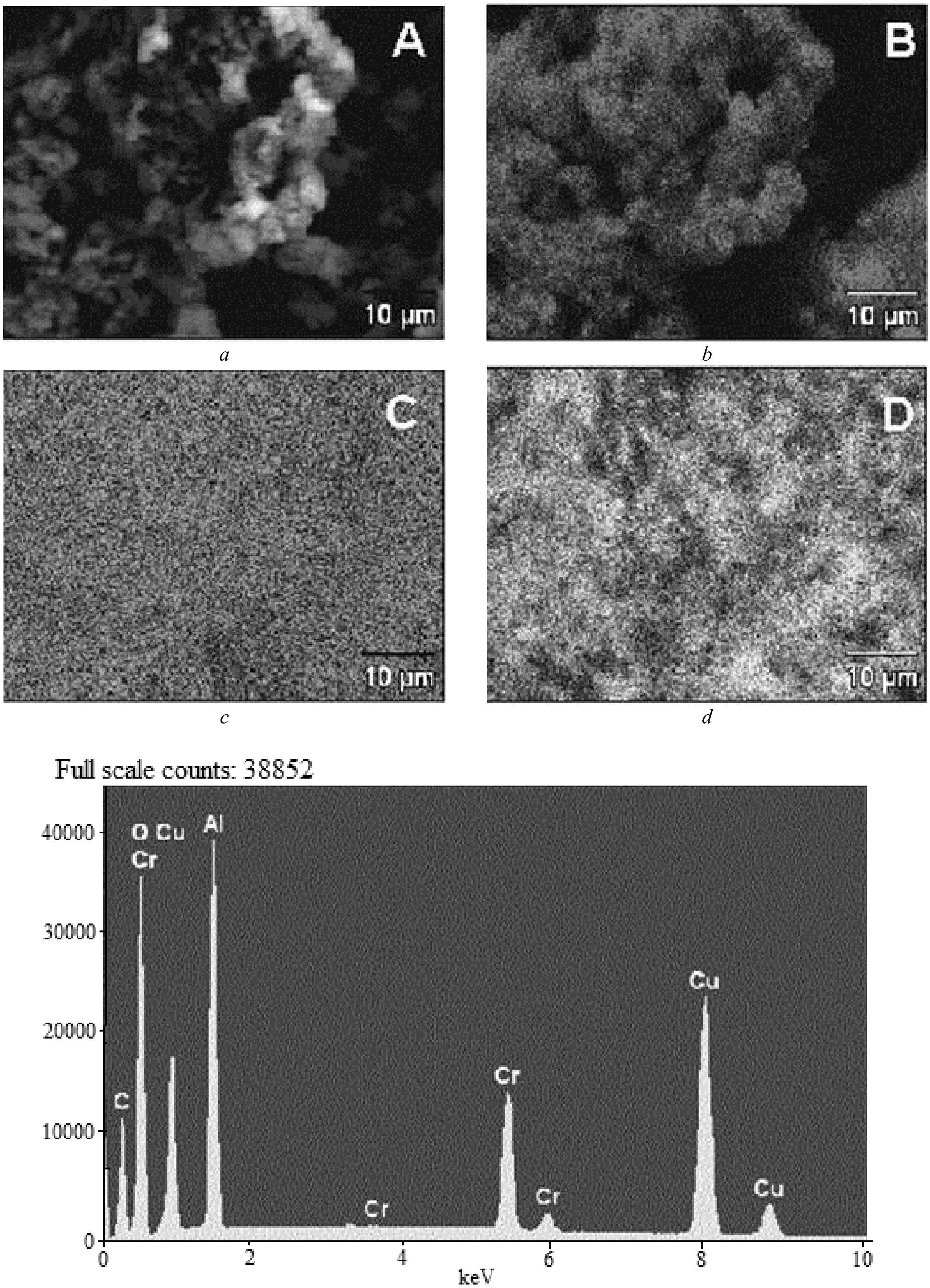
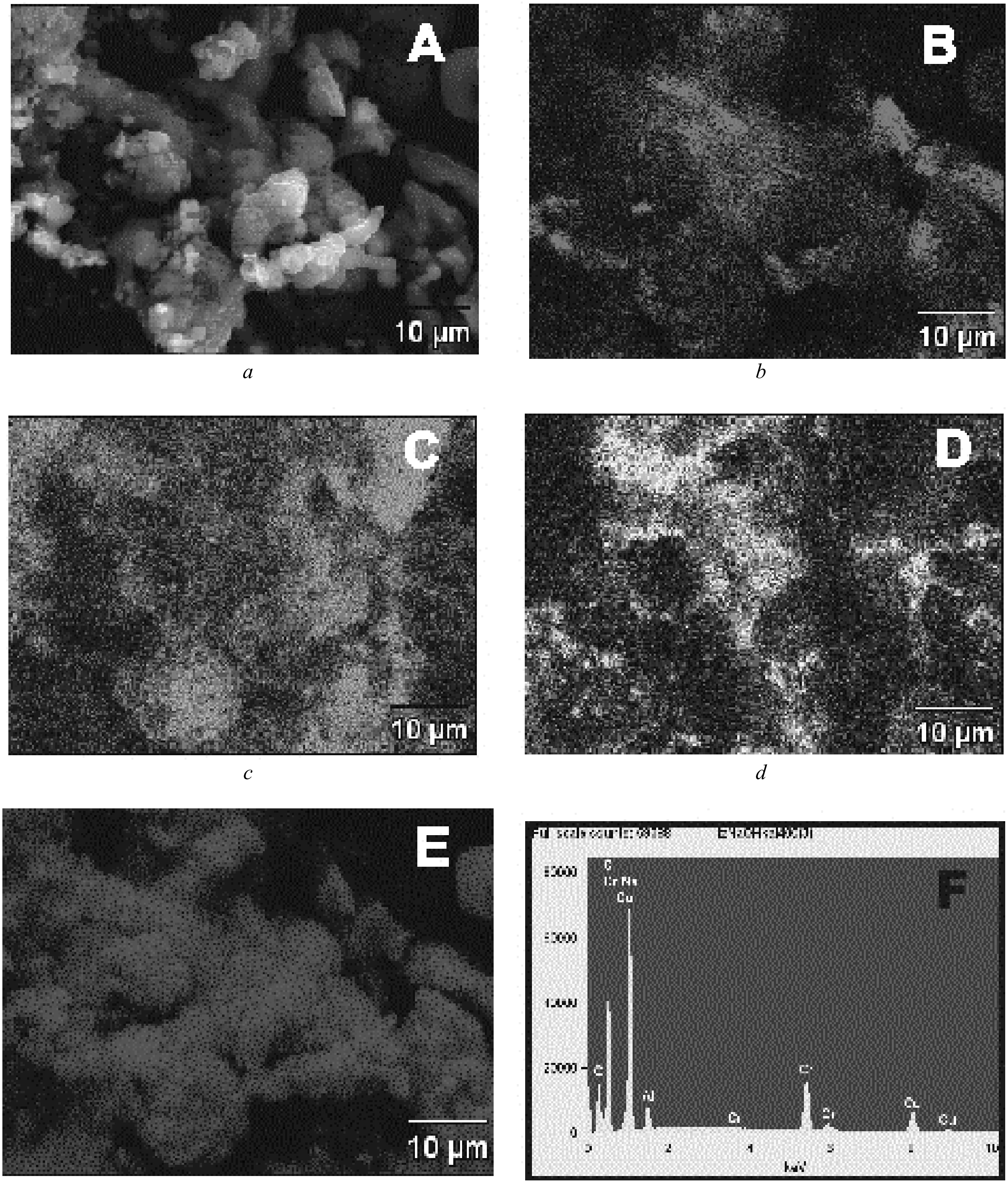


Fig. 2. Temperature programmed reduction profiles of reference compounds *(a)* and of $CuO:Cr_2O_3:Al_2O_3$ catalysts precipitated by NH_3 *(b)*, NaOH *(c)*, KOH *(d)*



a *b* *c* *d* *e*

Fig. 3. Surface image *(a)*, element distribution over copper-chromium-aluminum catalysts precipitated by NH_3, aluminum *(b)*, chromium *(c)*, copper *(d)*, surface element spectrum *(e)*

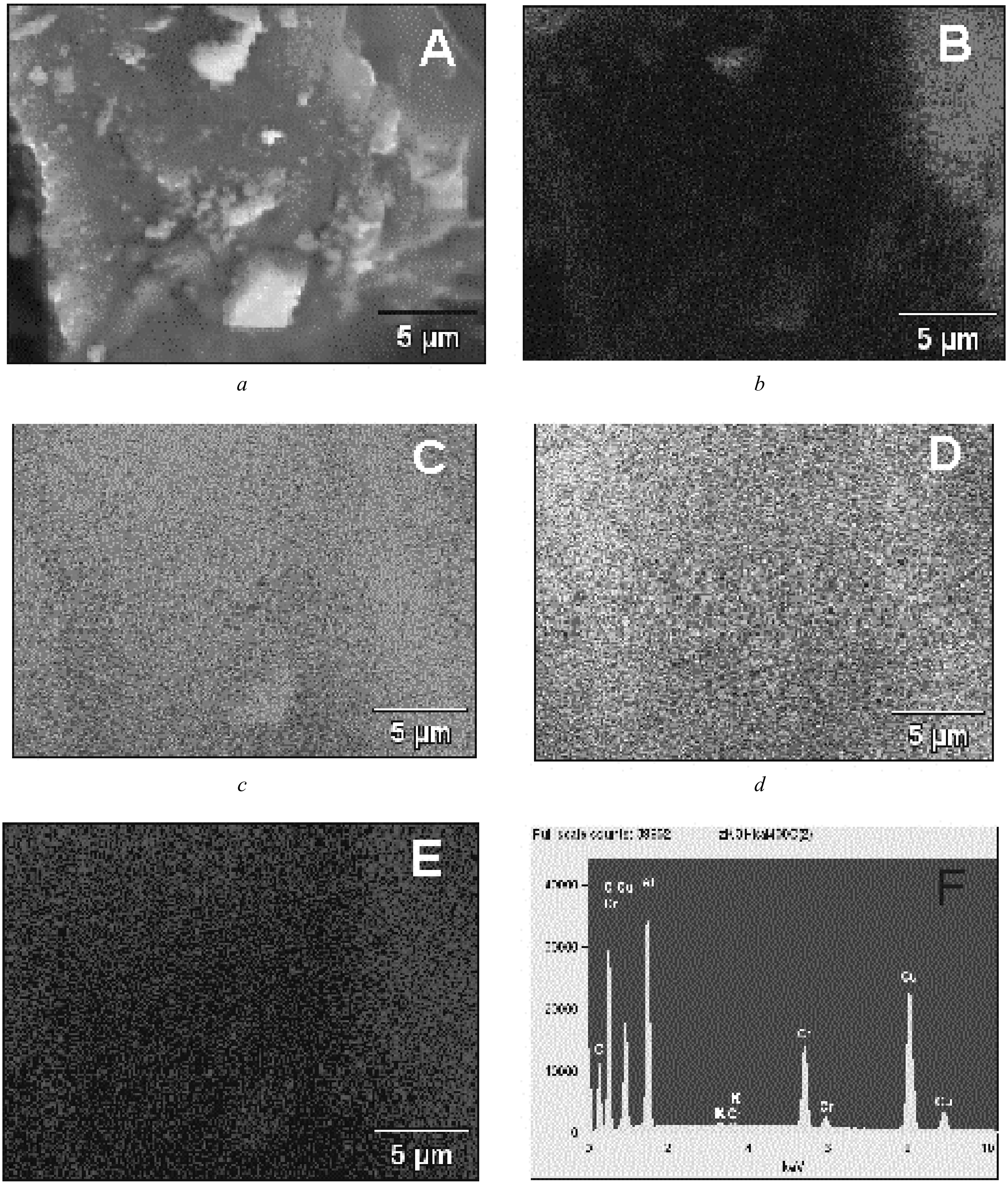


a *b*

c *d*

e *f*

Fig. 4. Surface image *(a)*, element distribution over copper-chromium-aluminum catalysts precipitated by NaOH, aluminum *(b)*, chromium *(c)*, copper *(d)*, sodium *(e)*, surface element spectrum *(f)*



a b c d e f

Fig. 5. Surface image *(a)*, element distribution over copper-chromium-aluminum catalysts precipitated by KOH, aluminum *(b)*, chromium *(c)*, copper *(d)*, potassium *(e)*, surface element spectrum *(f)*

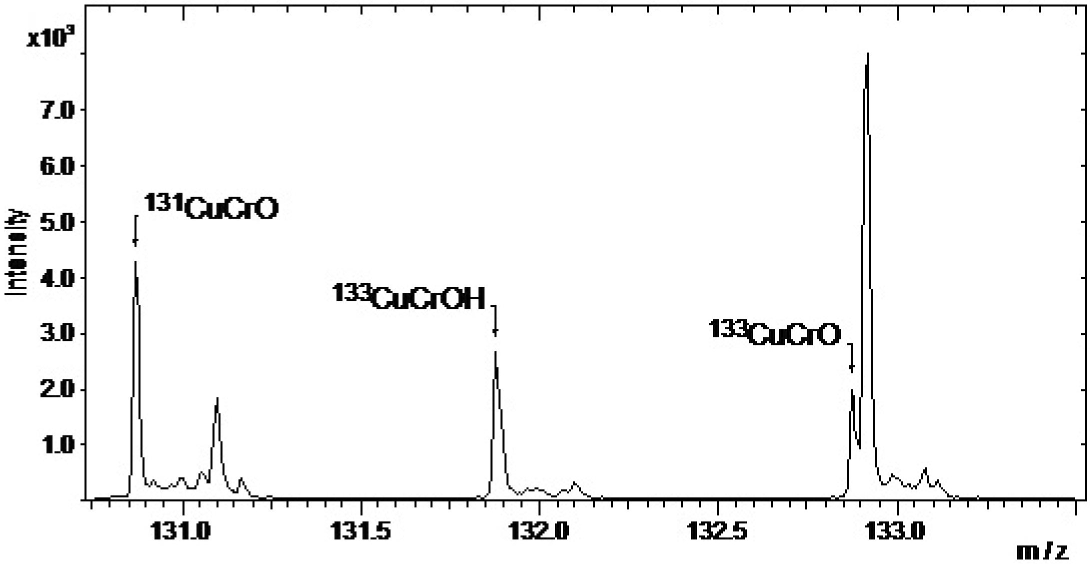


Fig. 6. TOF-SIMS results for copper-chromium-aluminum catalysts

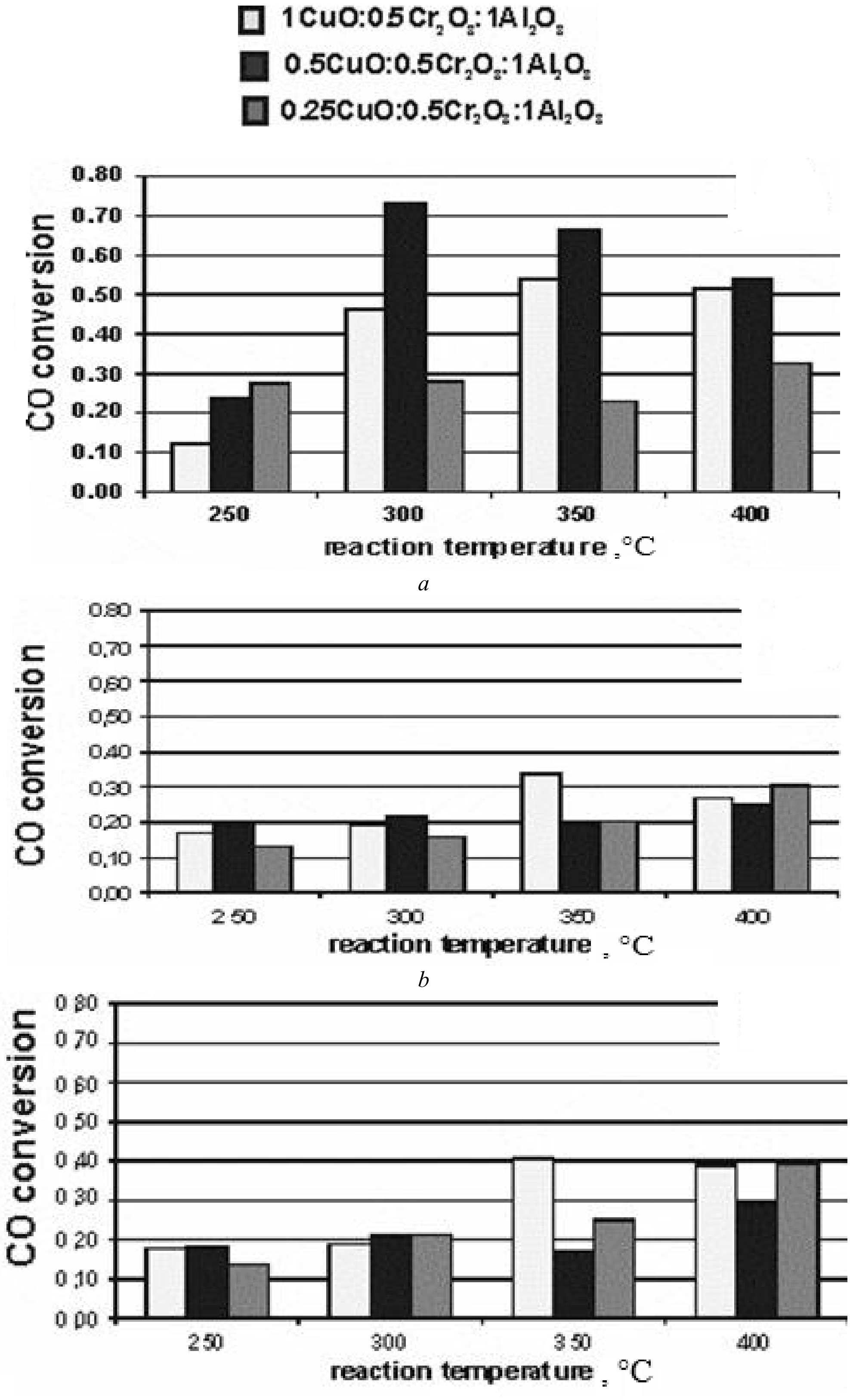
Catalytic activity tests. The results of CO conversion over Cu-Cr-Al catalysts precipitated by NH_3, NaOH, KOH are presented in Fig. 7. In all presented cases 100 % selectivity towards CO_2 was observed. Reference catalysts precipitated by ammonia show the highest activity 0.73 for $0.5Cu/0.5Cr_2O_3{:}1Al_2O_3$ at 300 °C while for the rest catalysts $1Cu/0.5Cr_2O_3{:}1Al_2O_3$ and $0.25Cu/0.5Cr_2O_3{:}1Al_2O_3$ the highest CO conversion was detected at 0.54 for 350 °C and 0.34 for 400 °C respectively. The catalyst with middle amount of copper is the most effective at low temperature while two other systems at 350–400 °C.

The fundamental observation for alkali doped systems is that with the increase in reaction temperature causes an increase in CO conversion. For catalysts precipitated by KOH with molar ratios Cu:Cr 1:1 and 0.25:1 the highest catalytic activity (0.45 conversion of CO) was observed while for catalysts obtained by using NaOH (Fig. 7, *b*) the highest CO conversion was detected at 350 °C at the level of 0.35. Similar tendency was observed by Kowalik et al. [13]. The first one is correlated with the reaction temperature. In their case the temperature range was 200–240 °C, but the CO conversion was more significant than in our case. They observed 3 times higher conversion at 240 °C than at 200 °C. In this paper the results indicate at least 2 times higher conversion at 400 °C that at 250 °C. The influence of alkali addition in Kowalik's paper was also analogical to our results [13]. Unfortunately, there is no direct correlation between catalysts molar ratio and CO conversion in the field of investigated catalysts.

Catalysts precipitated by sodium and potassium are characterized by lower activity according to reference catalysts obtained by ammonium. Similar observation was determined by Kowalik et al. [13]. Moreover, Panagiotopoulou and coworkers investigated also the influence of alkali ions on CO conversion in WGS reaction but on the TiO_2 catalysts promoted by Pd and Pt. Their results claim opposite result to ours and Kowalik's. They reported that impregnation by alkali improves activity of TiO_2, the 100 % conversion was obtained already at 340 °C while thar over unpromoted one – at 390 °C [14]. In present paper the most effective catalyst occurred samples precipitated by ammonia.

CONCLUSIONS

Catalysts precipitated by alkali hydroxides present lower CO conversion in comparison with ammonia catalysts because of catalysts higher crystallinity degree and harder susceptibility to reduction. Alkali (Na, K) hydroxides precipitated catalysts present crystalline character already at 400 °C, while ammonia Cu:Cr:Al catalysts are amorphous. Catalysts obtained by NaOH are characterized by higher sodium concentration and its uniform distribution on their surface as compared with KOH precipitated catalysts.



a

b

c

Fig. 7. CO conversion results for Cu:Cr:Al catalysts precipitated by NH_3 *(a)*, NaOH *(b)*, KOH *(c)*

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Доповані лужними (Na, K) гідроксидами каталізатори Cu/Cr_2O_3:Al_2O_3 конверсії водяного газу

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Досліджено ефект осаджуючого агента (гідроксиди лужних металів Na, K) на мідно-хромо-алюмінієві системи. Каталізатори, осаджені гідроксидами лужних металів, виявляють нижчу конверсію CO порівняно з тими, що осаджені амоніаком, через більший ступінь кристалічності та більшу стійкість до відновлення. Каталізатори, одержані за допомогою NaOH, характеризуються більшим вмістом лужного металу та його однорідним розподілом на поверхні порівняно з тими, що одержані за допомогою KOH.

Допированные щелочными (Na, K) гидроксидами катализаторы Cu/Cr_2O_3:Al_2O_3 конверсии водяного газа

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Изучен эффект осаждающего агента (гидроксиды щелочных металлов Na, K) на медно-хромо-алюминиевые системы. Катализаторы, осажденные гидроксидами щелочных металлов, проявляют более низкую конверсию CO по сравнению с осажденными аммиаком благодаря большей степени кристалличности и стойкости к восстановлению. Катализаторы, полученные с помощью NaOH, характеризуются большим содержанием щелочного металла и его однородным распределением на поверхности по сравнению с полученными с помощью KOH.