The effect of calcination temperature on properties and activity of Cu/ZnO/Al$_2$O$_3$ catalysts ♣

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The paper presents the results of the investigation on the influence of calcination temperature of Cu-Zn-Al catalyst precursor, on physicochemical properties and catalytic activity for water gas shift reaction. A model precursor of chemical composition corresponding with a typical commercial catalyst and prepared by coprecipitation method was studied. It has been shown that the temperature of calcination step determines the surface properties of the final catalyst, the active phase dispersion, and thus significantly affects the catalytic activity.

1. INTRODUCTION

Many types of catalysts used in industry are produced by synthesis of a precursor (which is usually a complex system of salt with low solubility in common solvents) in the first step and its thermal and mechanical treatment, leading to the final form of the catalyst. This method is also used for the production of Cu/ZnO/Al$_2$O$_3$ catalysts, which are applied in many important industrial processes such as water gas shift or the synthesis and steam reforming of methanol.

Data available in the literature show that catalytic properties of such systems significantly depend on the structure of a precursor and its preparation method. The precursor is a mixture of complex hydroxycarbonates of copper-zinc-aluminum with a hydrotalcite-type structure. Other crystalographic structures can also be present [1,2]. At special conditions of precursor materials thermal

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♣This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65th birthday

decomposition (calcination) high-dispersion components systems can be obtained. For this reason calcination of precursor is an important step in a process of catalyst activation.

It seems that $Cu/ZnO/Al_2O_3$ catalysts obtained from hydrotalcite-like precursors posses the best catalytic properties such as high and constant activity [3]. There is an extensive literature study on this type of systems such as Cu-Ni-Al [4], Cu-Mg-Al [5], Cu-Zn-Cr [6]. Numerous works on preparation and properties of Cu-Zn-Al precursors are mainly focused on the structure [7-9], kinetic studies and physicochemical properties [10, 11]. There are few works about mechanisms of processes running during the thermal decomposition of these systems. The paper by Frost [12] presents the results of calcinations in the range 30-500ºC limited to precursors of stoichiometric composition of hydrotalcite $Cu_xZn_{(6-x)}Al_2(OH)_{16}CO_3*4H_2O$, $(Cu^{2+}+Zn^{2+})/Al^{3+}=3$, different content of copper and zinc $(0 \leq x \leq 6)$. The results indicate a multi-course of this process, which consists of the stages of evolution of adsorbed water, dehydroxylation and decomposition of carbonate groups. The study of thermal and spectroscopic methods shows that during the calcination process changes in the relative positions of hydroxyl and carbonate groups in the crystallographic structure occur [13]. The paper by Millar contains a proposal for a mechanism including intermediate products of decomposition of Cu and Zn hydroxycarbonates [14].

The following paper presents the study of thermal decomposition conditions of the model precursor (up to 700°C), whose composition is in the range for typical copper catalysts applied in water gas shift and methanol synthesis processes. An effect of calcination temperature on the properties of catalysts has been studied for several values of this parameter corresponding to several characteristic bands.

2. MATERIALS AND METHODS

Preparation. A model $Cu/ZnO/Al_2O_3$ catalyst with a metal mole ratio: (Cu+Zn)/Al=3 and Cu/Zn=1 was prepared by coprecipication of a precursor from a solution of Cu, Zn, Al nitrates (analytically pure). Sodium carbonate solution was a precipitating agent. An acidic nitrate solution and an alkaline carbonate solution were added simultaneously to a small amount of redistilled water at 65–70°C, with the pH value of the precursor suspension being maintained in the range 7–7.4. The formed suspension was agitated vigorously during precipitation and aging. The material obtained was washed and filtered until Na^+ ions were removed completely and in the next step it was dried. The dry precursor material was formed into tablets and then crushed to 0.1–0.2mm grain fraction.

Phase composition. Precursor phase composition was analyzed with an XRD method using a CuKα radiation (the length of radiation wave was 1.542Å) and manganese filter as a monochromator. A scintillation counter was used for impulse counting and data were analyzed by an XRAYAN application for phase analysis with full spectra processing.

Calcination. The calcination process of the precursor was examined by a tempe-rature-programmed method. A Zielinski-type glass reactor [15] was used in a flow apparatus (Figure 1). Measurements were taken on a sample weight at 100mg in a stream of helium (flow rate 40ml/min) with a linear temperature increase rate 5°C/min, in temperature range 20–700°C. Produced steam was freezed out in a dry ice bath, and concentration of CO_2 produced was monitored using TCD. Calcination profile – a dependence of CO_2 concentration as a fun-ction of temperature – was obtained.
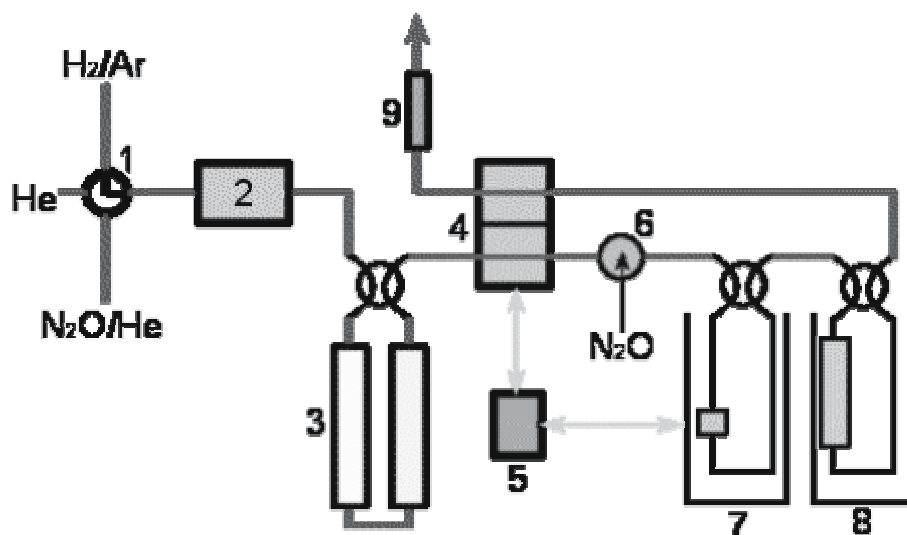

Fig. 1. Diagram of apparatus for temperature-programmed and chemisorption investigations. 1 – three-way valve, 2 – mass flow controller, 3 – oxygen trap and drying section, 4 – TCD detector, 5 – computer, 6 – sample loop, 7 – gradientless Zielinski reactor, 8 – dry ice cold trap, 9 – flowmeter.

Reducibility. Reducibility of catalyst samples obtained by calcination of precursors at temperatures: 250, 380, 495, 550 and 670°C for 30 min., was studied in the same apparatus using temperature-programmed reduction (TPR). A gradientless Zielinski-type reactor was used, samples at 30mg were treated with 5% H_2/Ar mixture at temperature increase rate 5°C/min. Steam produced

was freezed our in dry ice bath, and changes of the concentration of hydrogen were monitored by TCD detector. The TPR profiles of the samples – dependence of H_2 concentration on temperature were obtained.

Dispersion. The dispersion of copper was determined with a chemisorption method which consists in impulse N_2O titration of reduced catalyst sample [16-18]. Measurements were carried out in a gradientless Zielinski reactor, in the same glass flow apparatus like calcination and reducibility tests.

**Activity.** Catalytic activity measurements were carried out in the process of water gas shift (WGS):

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \Delta H° = - 41 kJ/mol \qquad\qquad (1)$$

in a 4-channel Tiomkin reactor [19] at the following conditions:

- reactive gas flow rate .... 55 l/h,
- grain size 0.1–0.2mm,
- pressure .... 2.5 MPa,
- temperature............................. 240°C,
- gas load................................... 60 Ndm^3/h,
- steam/gas ratio......................... 2

3. RESULTS AND DISCUSSION

The XRD spectrum of the precursor material is presented in Figure 2. The data indicate the mono phase composition. A system of hydrated basic copper-zinc-alumina carbonates crystal phases with a various number of copper, zinc, alumina atoms in the hydrotalcite-like phase $Cu_xZn_{(6-x)}Al_2(OH)_{16}CO_3 \cdot 4H_2O$ was identified. The phase $Cu_3Zn_3Al_2(OH)_{16}CO_3 \cdot 4H_2O$ (the average crystallite size is 23nm) is predominant. Other phases are present in trace amounts.

Figure 3 shows the precursor's temperature-programmed calcination profile with the CO_2 emission due to the following reaction following:

$$Cu_3Zn_3Al_2(OH)_{16}CO_3 \rightarrow 3CuO + 3ZnO + Al_2O_3 + CO_2 + 8H_2O$$
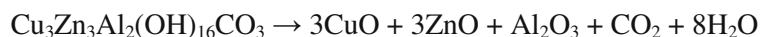
These bands indicate that the process of thermal decomposition (calcination) runs in the temperature range 100–670°C through several stages, which can highlight the following temperature ranges:

- dominant wide low temperature band: 100–380°C
- medium temperature band: 380–550°C
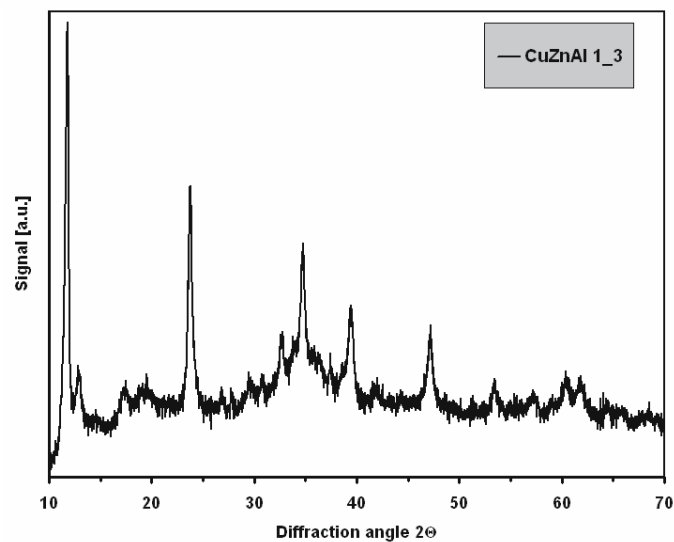- narrow and intense high temperature band: 550–670°C
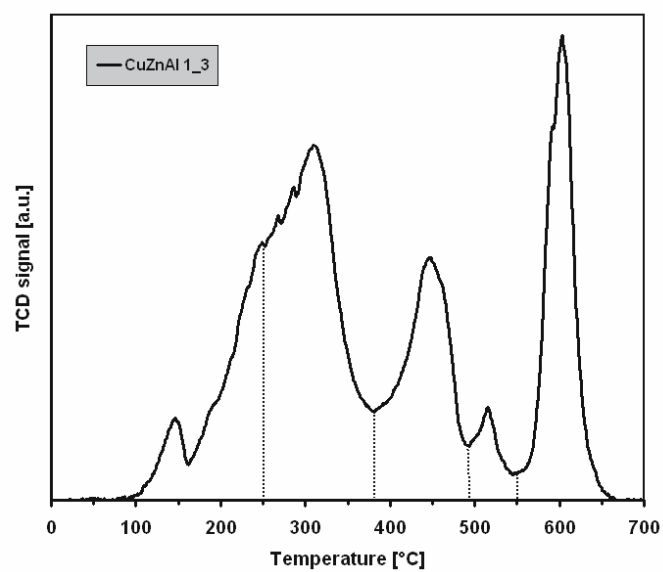
Fig. 2. Diffraction pattern of CuZnAl precursor.

Fig. 3. Temperature-programmed calcination profile of a CuZnAl precursor.

Based on the above profile, several characteristic temperatures were selected: 250 (standard precursor's reduction temperature) 380, 495, 550 and 670°C. At these values of temperature the precursor material was calcined for further research.

Figure 4 shows the effect of calcination temperature on reducibility of the catalysts. In general the reduction process proceeds in two stages. It indicates the presence of at least two forms of reducible copper. The total reduction of copper oxide forms is obtained in the temperature range up to 300°C. Due to calcination temperature growth the shift of temperature bands towards lower values is observed. The increase in calcination temperature, therefore, facilitates the reduction of the catalyst.
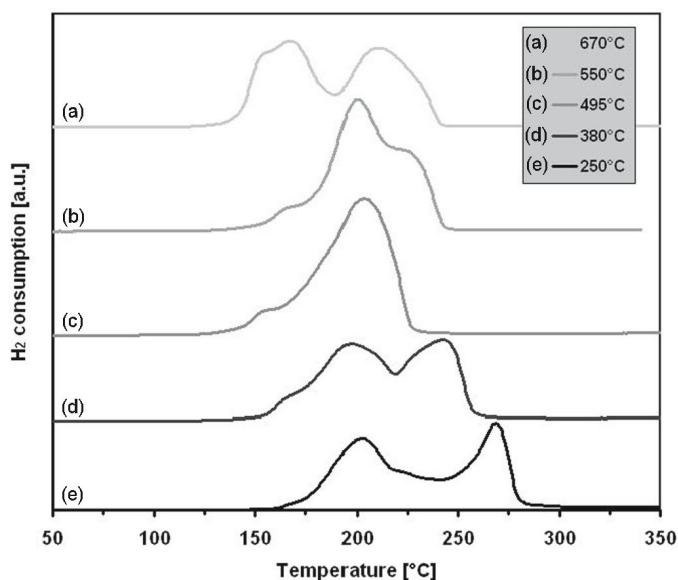

Fig. 4. TPR profiles of Cu/ZnO/Al$_2$O$_3$ catalysts after calcinations at characteristic temperature values.

The results of a reaction rate of water gas shift measurements are shown on Figure 5. They reveal that the catalyst obtained by calcination at 250°C exhibits the highest activity.

With the increase of calcination temperature, the activity decreases clearly. Two-fold decrease was observed for the catalyst obtained by calcining the precursor at the highest temperature (670°C). A similar relationship was found for the dispersion of copper, although the TPK graph (Figure 3) showed bands

corresponding to further decomposition of the precursor that should as a result give the increased amount of easily reducible copper oxide.

It can be assumed, that a side effect of high temperature calcination is a more intensive sintering and recrystallization of copper, which gives in consequence decreasing of dispersion and catalyst activity, respectively. This finding may be confirmed by the results of measurements summarized in the table below. They show that the amount of reduced copper is constant at calcination temperature above 380°C. However, the amount of surface copper, which is a measure of dispersion, decreases with increasing calcination temperature.
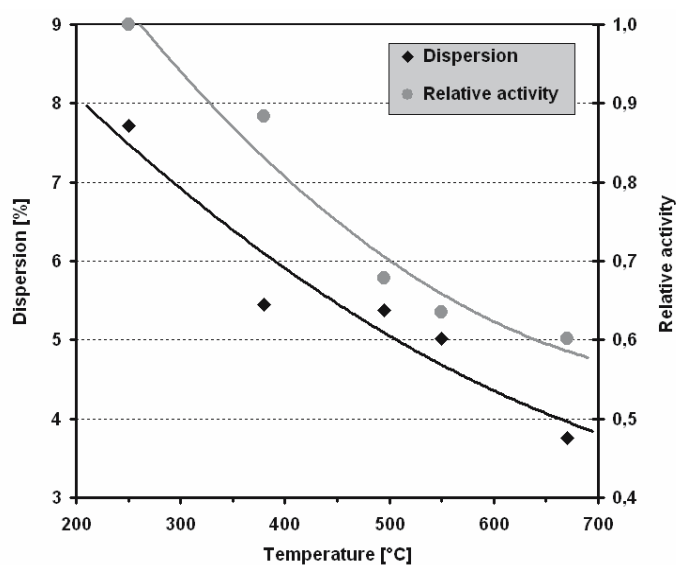

Fig. 5. Dependence of $Cu/ZnO/Al_2O_3$ catalyst dispersion and the relative activity on calcination temperature.

Tab. 1. $Cu/ZnO/Al_2O_3$ catalysts characteristics.

$t_{calcination}$ [^{o}C]	Total ammount of copper [µmol Cu/$g_{kat.}$]	The ammount of copper surface [µmol Cu/$g_{kat.}$]	Dispersion [%]
250	3451	266	7.7
380	4012	219	5.5
495	4000	215	5.3
550	4053	203	5.0
670	4044	152	3.7

4. CONCLUSIONS

- The calcinations of hydrotalcite type Cu-Zn-Al precursors is a complex process running in a wide temperature range (100–670°C),
- increase of precursor calcination temperature reduces the dispersion of copper and catalytic activity,
- specific activity of copper does not depend on the precursor calcination temperature.

5. REFERENCES

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CURRICULA VITAE

Paweł Kowalik graduated and received his Ph.D. from Maria Curie-Sklodowska University (1998 and 2007, respectively). Since 2008 he is the head of Catalyst Research Department of INS Puławy. The main field of his scientific interest is applied catalysis.

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