Physicochemical properties of gold catalysis used in oxidation of odor gases

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Gold modified hopcalite catalysts were prepared by impregnation method and characterized in thiophene oxidation. For studying the physiochemical properties of the systems XRD, TPR, ToF-SIMS, SEM-EDS methods were used. Commercial hopcalite shows low activity in oxidation of thiophene and the loss of its activity during the reaction is observed. Gold addition improves its activity in thiophene oxidation but does not prevent its deactivation probably due to non-homogenous distribution of Au on catalyst surface.

1. INTRODUCTION

Odor sulfur compounds coming from animal production present an increasingly difficult and pressing problem. They are known as: thiols, dimethyl sulphides, dimethyl disulphides or hydrogen sulphide. They generated intolerable odor even at extremely low concentrations. People living near odor sources are concerned about comfort of their life but moreover about potential health effects (they are exposure to increased eye irritation, nausea, weakness). Until now are not strict standards determining quantity of odor compounds in air in Poland. However significant increase in the number of complain from the public about odor oblige government to be concerned about preventing generation of unpleasant smell or reducing it. Catalytic oxidation is a one from well-established technologies for odor elimination [1].

Most uses catalysts for incineration of organic compounds are classified into two groups: supported noble metals and metal oxides such as: Mn, Cr, Co, Cu, V, Ni [2,3,4]. Some specific combinations of metal oxides may have several

characteristic features that improve their catalytic activity in oxidation reaction. For this reason from many years attention has been focused on using copper-manganese mixed oxides in the form of hopcalite due to its high activity as oxidation catalysts [5, 6, 7, 8, 9]. Mixtures of metal oxides and noble metals gain an increasing interest as catalyst for total oxidation as well [10, 11, 12]. More recently the investigation of the activity of gold catalyst was concentrated on the oxidation of organic compounds since Haruta and co-workers [13] demonstrated that supported gold catalysts show high activity towards oxidation reactions. Numerous studies indicate that copper and manganese oxides modified with Au show promising activity in incineration of organic molecules such as: acetone [14], n-hexane [15], ethane or propane [16]. However, mixed manganese and cooper oxides modified with gold have not been widely discussed.

The aim of our preliminary study is to obtain active Au-modified hopcalite catalyst for oxidation of sulfur compounds. The first step of the work was to prepare Au-hopcalite catalyst by using impregnation method and study its activity in oxidation of thiophene.

2. EXPERIMENTAL

The Au-Cu-Mn catalysts were prepared by the wet impregnation method of hopcalite (supplied by "Inowrocław Zakłady Chemiczne Soda") with aqueous solutions of $AuCl_3 \cdot HCl \cdot 4H_2O$ (POCh Gliwice) in order to obtain noble metals loading: 0.2, 0.5 or 1 wt.%. After impregnation the samples were dried at 130 °C for 0.5 h and then calcined in static air at 400 °C for 4 h.

Catalytic activity measurements were carried out in a quartz flow reactor using 200 mg of catalyst. The reactant mixture 1.5% C_4H_4S and 20% O_2 in He was passed through the reactor with the flow rate of 40 cm^3/min. The analyses of the reactor effluent were performed with on-line gas chromatography equipped with TDC detector and HayeSep Q column. The thiophene conversion and selectivity to CO_2 were calculated as follows:

$$\% \ C_4H_4S \text{ conversion} = \frac{(C_4H_4S)_{in} - (C_4H_4S)_{out}}{(C_4H_4S)_{in}} \times 100$$

$$\% \ C_4H_4S \text{ conversion to } CO_2 = \frac{f \times P_{CO2}}{4 \times P_{tot}} \times 100$$

$(C_4H_4S)_{in}$ – inlet C_4H_4S concentration
$(C_4H_4S)_{out}$ – outlet C_4H_4S concentration
f – corrective factor

4 – stochiometric factor

P_{CO_2} – quantity of C_4H_4S moles transformed to CO_2

P_{tot} – total quantity of C_4H_4S moles transformed during reaction.

Temperature programmed reduction (TPR) measurements were carried out in an Altamira AMI-1 instrument equipped with a TDC detector. Analysis was performed by using mixture of 5%H_2/95%Ar with a flow rate 50 cm^3/min 900 °C. The process was carried out up to 900°C with linear temperature increase 10 °C/min.

X-ray diffraction patterns were recorded by a Simens D 5000 diffractometer using the Cu Kα radiation. Data were collected in the range of 10–80° 2θ with the scanning step 0.02 °C.

The secondary ions mass spectra were recorded with a TOF-SIMS IV mass spectrometer manufactured by Ion-Tof GmbH, Muenster, Germany. The instrument is equipped with Bi liquid metal ion gun and high mass resolution time of flight mass analyzer. Secondary ion mass spectra were recorded from an approximately 100 µm × 100 µm area of the spot surface. During measurement analyzed area was irradiated with the pulses of 25 keV Bi^+ ions at 10 kHz repetition rate and an average ion current 1 pA. The analysis time was 50 s for both positive and negative secondary ions giving an ion dose below static limit of 1×10^{13} ions/cm^2. Secondary ions emitted from the bombarded surface were mass separated and counted in time of flight (ToF) analyzer. Ion images were recorded using a pulsed beam of 25 keV Bi_3^+ ions at the frequency of 10 kHz. Average primary ion current was 0.14 pA. Before ToF-SIMS analysis powder samples were tableted in order to obtain plain surface, which allows achieving higher lateral and mass resolution.

3. RESULTS AND DISCUSSION

Figures 1 and 2 present activity of hopcalite catalysts in thiophene oxidation. Commercial hopcalite shows low activity in oxidation of thiophene. The maximum of C_4H_4S total conversion reaches only about 20% at 340 °C. Above this temperature the decrease in commercial hopcalite activity is observed. The addition of gold greatly improves activity of the commercial system. The catalyst with the highest concentration of gold (1%) is the most active. The total conversion of thiophene over these systems reaches above 80% at 370 °C. However the loss of activity of Au-modified systems during the reaction is observed as in the case of commercial hopcalite.
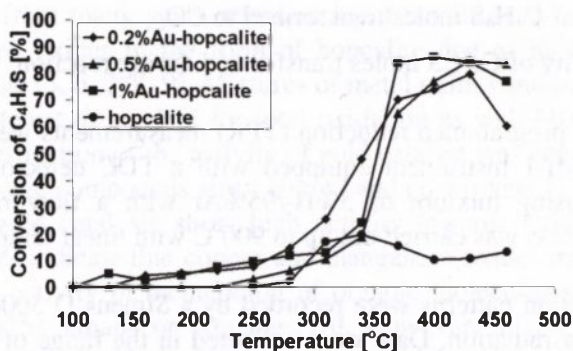
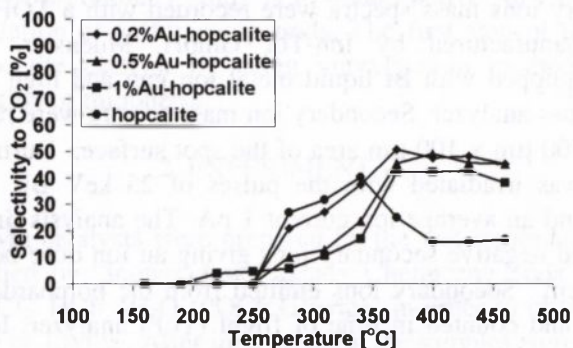Fig. 1. Activity of hopcalite catalysts to CO_2 in oxidation of thiophene.

Fig. 2. Selectivity of hopcalite catalysts to CO_2 in oxidation of thiophene.

CO_2 is not only the product of the reaction (Figure 2). Conversion of thiophene to carbon dioxide reaches about 50% in the case of the catalysts with gold addition. Commercial hopcalite is slightly less active towards oxidation to CO_2. The loss of his oxidative performance to CO_2 with the reaction temperature can be clearly seen.

The deactivation process of hopcalite was discussed in the literature in CO oxidation [17,18,19]. It was proposed that the active form of catalysts in CO oxidation can be an amorphous spinel whose general formula can be described as: $(Cu_\alpha^+ Mn_{1-\alpha}^{2+})_A (Cu_{1-\alpha}^{2+} Mn_\alpha^{3+} Mn^{4+})_B O_4^{2-}$ [20]. In such a spinel the differently charged Cu and Mn ions can be present in tetrahedral and octahedral sites. It is proposed that redox couples $Cu^{2+} + Mn^{3+} \rightarrow Cu^{1+} + Mn^{4+}$ can be responsible for high activity of the catalyst in oxidation reaction. The loss of activity is attributed to the change of surface concentration of copper and manganese ions or surface segregation of impurities of the catalysts, such as alkali metal ions, occurring during crystallisation of the spinel [17]. However some studies suggest

that $CuMn_2O_4$ spinel in crystalline form can also be an active phase in CO oxidation [21].

In order to characterise commercial and Au-modified hopcalite structure, XRD analysis was carried out. The results of XRD measurements are shown in Figure 3.
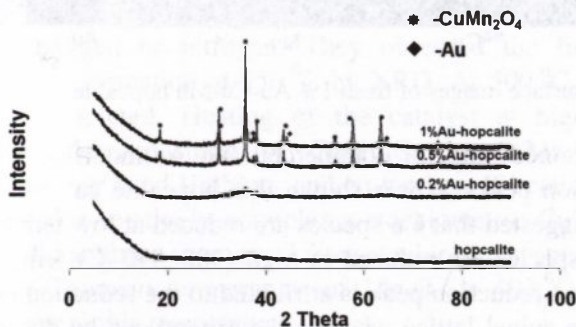

Fig. 3. XRD diffraction patterns of commercial and Au-modified hopcalite.

Commercial catalyst is in the amorphous form as well as the catalyst with the lowest gold content (0.2%). After the addition of higher Au quantity (0.5, 1%) crystallisation of the spinel occurs. The reflexes due to the presence of metallic gold on 0.5% $Au-CuMn_2O_4$ and 1% $Au-CuMn_2O_4$ catalysts surface are also observed (Figure 3), indicating a non-homogeneous distribution of Au particles.

SEM-EDS results also demonstrate low dispersion of Au. The spectrum presented in Figure 4 b) taken from the plain spot seen in Figure 4a) shows existence of Au crystallites on 1% $Au-CuMn_2O_4$ surface with the size of several micrometers.

To determine the distribution of all elements on the catalyst surface, ToF-SIMS images were collected for 1% $Au-CuMn_2O_4$ from catalyst surface area 35.2 µm×35.2 µm (Figure 5). The elements of the spinel, Mn and Cu ions are homogenously distributed, on the other hand areas of enhanced Au surface concentration can be observed in ToF-SIMS images.
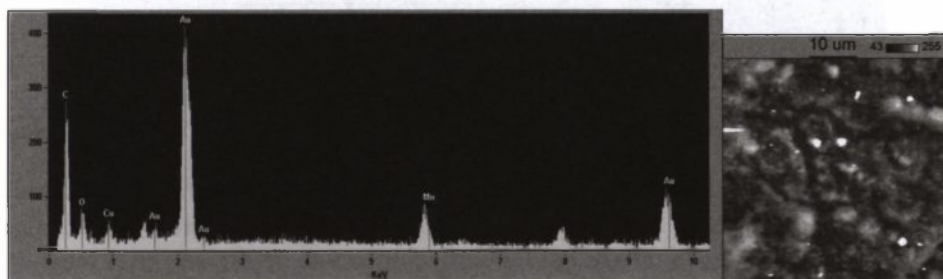

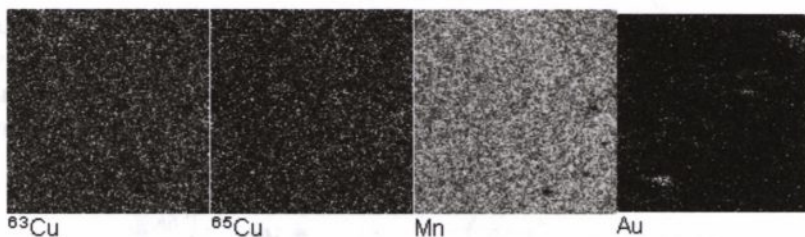Fig. 4. SEM-EDS spectrum of 1% Au-Cu-Mn hopcalite.

Fig. 5. ToF-SIMS surface images of fresh 1% Au-Cu-Mn hopcalite.

TPR patterns obtained both for commercial and Au-modified hopcalite clearly show two reduction peaks. It was shown that hopcalite can be reduced in two stages. Tanaka suggested that Cu species are reduced at low temperatures (150–350°C) and Mn species are reduced in high (300–550 ^{0}C) temperature regions [22]. Thus, the first reduction peak is attributed to the reduction of Cu^+ and Cu^{2+} ions to Cu^0 in the spinel lattice whereas the second can be due to reduction of differently charged manganese ions Mn^{3+} and Mn^{4+} to Mn^{2+}. The reduction of Mn^{2+} to Mn^0 has not been observed even at very high temperatures because of its larger negative value of reduction potential [23]. For commercial hopcalite two reduction maxima are located at about 200 and 250 ^{0}C. After Au addition the shift of both reduction peaks towards higher temperatures is observed. They are shifted to 210, 300; 240, 340; 260, 370 for 0.2% Au-CuMn$_2$O$_4$, 0.5% Au-CuMn$_2$O$_4$, 1% Au-CuMn$_2$O$_4$ respectively. It can be clearly seen that gold addition contributes to the worse reducibility of the catalysts.
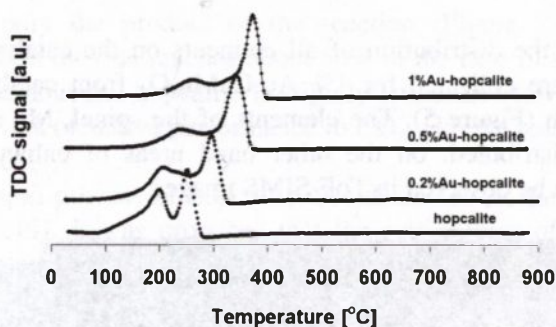

Fig. 6. TPR profiled of commercial and Au-modified hopcalite.

In order to study the loss of activity of commercial and Au-modified catalysts XRD and ToF-SIMS analysis of spend samples were carried out. The composition of commercial and gold modified hopcalite before and after reaction is presented in table 1. Composition of non-modified and modified catalysts after

the reaction is similar. Crystallisation of amorphous phase of commercial catalyst occurs during the reaction thus the crystalline phase of $CuMn_2O_4$ spinel in spend sample is observed. XRD analysis of catalysts after the reaction indicates also partial decomposition of the spinel structure to manganese and cooper oxides and probably to $CuMnO_4$. Veprek and all [17] have studied structural changes of commercial hopcalite during heating at different temperatures in oxygen or nitrogen. They observed the first indication of crystalline $CuMn_2O_4$ formation at $350\ ^0C$ by XRD. At $500\ ^0C$ crystallisation of the spinel was completed. Heating of the catalyst at higher temperatures $(1110\ ^0C)$ caused decomposition of $CuMn_2O_4$ to $CuMn_2O_4$, Mn_3O_4 and $CuMn_2O_4$. On the other hand Huthings and co-workers [9] claim that calcination at $500\ ^0C$ produced a relatively amorphous stochiometric $CuMn_2O_4$ phase. At $600\ ^0C$ Cu-Mn solid solution segregated from stochiometric spinel to $Cu_xMn_{3-x}O_4$ and Mn_2O_3. The Tamman temperature of Mn_2O_3 is $403\ ^0C$ thus solid state reactions may occur at this temperature.

ToF-SIMS results confirm partial decomposition of the spinel phase during the reaction. ToF-SIMS images indicate the presence of areas of enhanced surface concentration of Cu species with the size of about 20 micrometers.

Tab.1. Composition of fresh and used hopcalite catalysts.

Catalyst	Crystalline phase proposed
Commercial hopcalite (fresh)	amorphous
Commercial hopcalite (spend)	$CuMn_2O_4$, $CuMnO_4$, CuO, Mn_2O_3, Mn_3O_4
0.5% Au-hopcalite (fresh)	$CuMn_2O_4$
0.5% Au-hopcalite (spend)	$CuMn_2O_4$, $CuMnO_4$, CuO, Mn_2O_3, Mn_3O_4, MnO_x, $Mn(OH)_2$

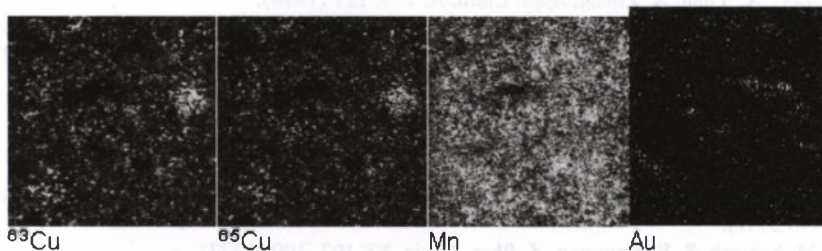^{63}Cu ^{65}Cu Mn   Au

Fig. 7. ToF-SIMS surface images of used 1% Au-Cu-Mn hopcalite.

4. CONCLUSIONS

- Addition of Au improves activity of commercial hopcalite but does not prevent its thermal deactivation, it is probably connected with non-homogenous Au distribution,
- Higher activity of Au modified hopcalite can be connected with the presence of modified $Cu^{2+}+Mn^{3+} \Leftrightarrow Cu^{+}+Mn^{4+}$ centres.

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