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Synthesis and characterisation of some copper oxide catalysts for ozone decomposition

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In the search for efficient ozone decomposition catalysts, cooper oxide powders and alumina-supported cooper oxide samples were prepared and characterised. The catalytic activity of CuO-based catalysts for O_3 decomposition, in correlation with some peculiar physical-chemical characteristics is investigated.

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1. Introduction

Ozone is used in a variety of oxidation processes, including disinfection of potable water, deodorization of air and waste gases and in the preservation of perishable goods. Because ozone is a toxic substance commonly found or generated in human environments (aircraft cabins, offices with photocopiers, laser printers, sterilizers) there is a continuous demand for efficient catalysts in the decomposition of residual ozone. The most used decomposition catalysts are precious metals or/and transition metal oxides deposited onto alumina, and/or silica support [1-5].

In order to prepare some efficient ozone decomposition catalysts, a complex study was initiated and developed [6,7,8]. The present paper reports our results referring to the preparation of copper based catalysts for O_3 degradation. In this purpose, copper oxide crystalline powders and alumina-supported copper oxide samples were prepared and characterised by several physical methods The goal of the study was to establish a correlation between the catalytic activity and crystalline structure and the specific surface area of catalysts.

2. Experimental part

Cooper oxide-based catalysts were prepared by the thermal dissociation of copper nitrate. Sample **K71**, the un-supported CuO catalyst, was prepared from $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) crystals calcined for 2 hrs at 500°C. Sample **K67**, the supported CuO/Al_2O_3 catalyst was prepared by impregnation method. The pre-heated support was immersed into 1.0 M solution of cooper nitrate (10 g Al_2O_3 extrudates in 25 ml cooper nitrate solution). After 24 hrs, the impregnated support was filtered, dried and calcined for 2 hrs at 500°C.

The as prepared materials were investigated by X-ray diffraction (DRON 3M Diffractometer; CuK_α radiation), FT-IR spectroscopy (JASCO-610 Spectrophotometer; KBr disks) and Brunauer- Emmett -Teller (BET) analysis (krypton adsorption isotherms). The catalytic activity for ozone decomposition process was measured by using a testing installation containing a thermostated Al- reactor (∅=4 mm). Ozone was prepared from oxygen, with a generator manufactured by S.C.RAAL S.A. Bistrița (Romania). The gas flow was 15 l/h and the measuring temperature was 25°C. Ozone concentration before and after passing through the catalyst layer (~0.06 g material) was determined with an OZOMAT analyser (ANSEROS).

3. Results and discussion

Alumina supported cooper-based catalyst was prepared by impregnation method and compared with the corresponding un-supported sample, in order to correlate the catalytic performances with the physical-chemical characteristics. The catalitic active substance, resulting from the thermal disociation of the adsorbed cooper nitrate, was formed on and inside the alumina grains. The influence of the substrate surface on the crystalline organisation, structural purity and catalytic activity of catalysts was illustrated by usual [6,7] investigations.

The crystalline structure of samples was evaluated on the basis of XRD patterns (Figure 1). The support, sample **S1**, shows the typical cubic crystalline structure of gamma-alumina (in agreement with Powder Diffraction Files PDF 100425). The characteristic lines/bands [311], [400] and [440] appear at 2θ=37.20; 45.60 and 67.03. The un-supported catalyst, sample **K71,** is a powder of CuO with monoclinic crystalline structure (in agreement with PDF 801268). The characteristic lines/bands [-111], [111] and [-202] appear at 2θ=35.43, 38.62 and 48.81. XRD pattern of the supported catalyst, sample **K67**, is dominated by the diffraction lines of the gamma-alumina support. Aditional lines of $CuAl_2O_4$spinel (in agreement with PDF 780556) superimposed over the support bands are put in evidence. The caracteristic lines [220], [311] and [400] of the $CuAl_2O_4$ cubic structure can be noticed at 2θ=31.44, 36.39 and 45.0.

The infrared absorption spectra of precursor, support and catalysts illustrate "the structural" purity of materials (Fig. 2). FT-IR spectrum of γ-Al_2O_3 contains specific absorption bands in the small wavenumber domain [ν(Al-O) = 730.9 cm^{-1}]. The bands assigned to NO_3 group and HO and HOH bonds due to the water could be noticed in the spectrum of the precursor (sample **K71p)**. During the precursor calcination stage, the specific $\nu_{asym}(NO_3)$ = 1384.6 cm^{-1} and $\pi(NO_3)$ = 823.5cm^{-1} bands disapear, irrespective of the presence or absence of a support .

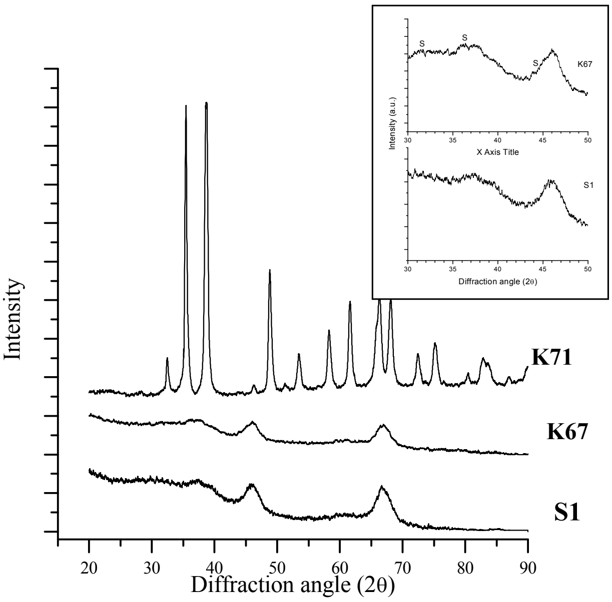

*Fig. 1. XRD patterns of Al_2O_3 -support (**S1**), CuO (**K71**) and CuO/Al_2O_3 (**K67**).*

The surface area S_σ of materials was of 269 m^2/g for S1, 317 m^2/g for sample K67 and 0.4 m^2/g for sample K71. The surface area of supported catalyst is determined by the γ-Al_2O_3 characteristics. The supported CuO catalyst possesses a surface area of about 800 times larger then that of the un-supported material.

The catalytic activity of samples was evaluated for ozone decomposition $O_3 \xrightarrow{k_1} 3/2\ O_{2,}$ on the basis of the conversion yield (η) expressed by $\eta = 100(C_o-C)/C_0$, where C_o and C is the O_3-concentration before and after passing through the catalyst layer, for a certain amount. The ozone conversion yield determined in identical experimental conditions (catalysts amount, space velocity, reagent concentration) is a direct measure of the catalytic efficiency of catalysts. The time dependence of the conversion yield of investigated materials is presented in Fig. 3.

The sample **K67** (CuO/Al_2O_3) with very large surface area produces the decomposition of over 92% ozone in the first 6 testing minutes.The efficiency decreases to 87%, in 30 minutes. The catalytic efficiency of the un-supported **K71** catalyst is only 21-22% and remains almost unchanged during the testing period. As expected, the alumina support itself, sample **S1**, induces a small ozone decomposition effect, probable due to the porosity/surface effect.

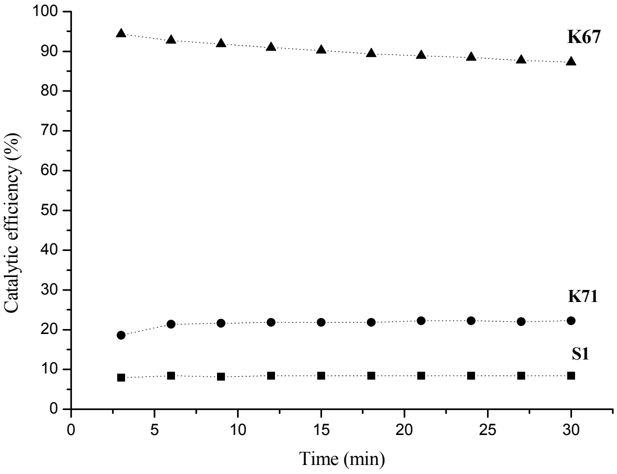

*Fig. 3. Catalytic efficiency of Al_2O_3 -support (**S1**), CuO (**K71**) and CuO/Al_2O_3 (**K67**).*

The catalytic efficiency of CuO-based catalyst is a little lower then that of NiO-based catalysts [7] but much higher then that of the corresponding MnO_2-based catalysts [6]. The catalytic efficiency is ~70% for MnO_2/Al_2O_3 while for NiO/ Al_2O_3 it is 99%. One of the major differences between these two kinds of catalysts is the presence of $NiAl_2O_4$ spinel or $CuAl_2O_4$ generated by the interaction of nickel/copper compound with the support (as illustrated by XRD patterns). One can suppose that the high catalytic efficiency is associated with the presence of active centres that involve the highly dispersed spinel material over the alumina surface.

4. Conclusions

Cooper-based catalysts were prepared, characterised and the catalytic activity for ozone decomposition process has been investigated. The major role of alumina support on the increase of catalyst – gas contact surface has been demonstrated by the experimental data.

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