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Dedicated to Professor Ionel Haiduc,
President of The Romanian Academy at his 70th anniversary

STUDIES ON SOME OZONE DECOMPOSITION CATALYSTS BASED ON NICKEL OXIDE

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ABSTRACT. In order to obtain some efficient ozone decomposition catalysts, nickel oxide powders or alumina-supported nickel oxide samples were prepared and characterised. The catalytic activity of NiO-based catalysts for O_3 decomposition, in correlation with their crystalline structure and surface characteristics is investigated.

Key words: catalysts; ozone decomposition; nickel oxide; alumina;

1. Introduction

Ozone is a toxic substance commonly found or generated in human environments (aircraft cabins, offices with photocopiers, laser printers). Moreover, ozone is used in many industrial applications as oxidising agent for example for bleaching, sterilization and wastewaters treatment. For this reason, catalytic ozone decomposition is of practical significance. It proceeds in the presence of precious metals or/and other transition metal oxides deposited onto alumina, and/or titania and/or silica support [1-6]. The catalysts composition and preparation technique as well as the carrier characteristics affect their physico-chemical properties and catalytc activitiy in the process of destruction of ozone in industrial waste gases [7,8].

In order to prepare some efficient ozone decomposition catalysts for environement protection, a complex study has been initiated in our group. In this respect, the preparation and characterisation of some alumina supported manganese, nickel, silver and/or copper based catalysts and their catalytic behaviour in ozone decomposition proccess was investigated. Our previous works showed that manganese oxide supported on gamma alumina is efficient for ozone destruction [9,10]. The present paper refers to the preparation and characterisation of some nickel based catalysts. The goal of the study is to establish the correlation between the catalytic activity and crystalline structure and surface area of catalysts.

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2. Experimental part

Nickel oxide-based catalysts were obtained by thermal dissociation of nickel nitrate. Sample **K70,** the un-supported NiO catalyst, was prepared from $Ni(NO_3)_2 \cdot 6H_2O$ (Merck) crystals calcined for 2 hrs at 500°C. Sample **K66,** the supported NiO/Al_2O_3catalyst, was prepared by impregnation method. The pre-heated support was immersed into 1.0 M solution of nickel nitrate (10 g Al_2O_3 extrudates in 25 ml nickel nitrate solution). After 24 hrs, the impregnated support was filtered, dried and calcined for 2hrs at 500°C.

All thus prepared materials have been 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 was measured for ozone decomposition process, 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 nickel-based catalyst was prepared by impregnation method and was 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 nickel 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 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 PDF file 100425, from Powder Data File database). The characteristic lines (311), (400) and (440) appear at 2θ = 37.20; 45.60 and 67.03 respectively. The unsupported catalyst, sample **K70,** is a black powder of NiO with cubic crystalline structure (cf. PDF 780423). The characteristic lines (-111), (111) and (-202) appear at 2θ =35.43, 38.62 and 48.81 respectively. XRD pattern of the supported catalyst, sample **K66,** is dominated by the diffraction lines of the gamma-alumina support. Additional lines of $NiAl_2O_4$ spinel (cf. PDF 780552) superimposed over the support bands are put in evidence. The characteristic lines (220), (311) and (400) of the cubic $NiAl_2O_4$ can be noticed at 2θ = 31.57, 36.39 and 44.80.

The infrared absorption spectra of precursor, support and catalysts are used to illustrate “the structural” purity of materials (Figure 2). FT-IR spectrum of γ-Al_2O_3 contains some specific absorption bands in the small wavenumber domain [ν (Al-O) ~ 598 cm^{-1}]. The bands assigned to NO_3 group and HO and HOH bonds of the entrained water can be noticed in precursor spectrum, sample **K70p**. During the precursor calcination stage, the specific $\nu_{asym}(NO_3)$~1385 cm^{-1} and $\pi(NO_3)$~ 824 cm^{-1} bands disapear, irrespective of the presence or absence of the support.

The surface area S_σ of materials was of 269 m^2/g for **S1**, 269 m^2/g for sample **K66** and 15.6 m^2/g for sample **K70**. The surface area of supported catalyst is determined by the γ-Al_2O_3 characteristics. The deposition of the catalytic active substance does not change the support porosity and surface area, which determines the specific properties of the catalyst. The supported NiO catalyst possesses a surface area of about 17 times larger then that of the un-supported material.

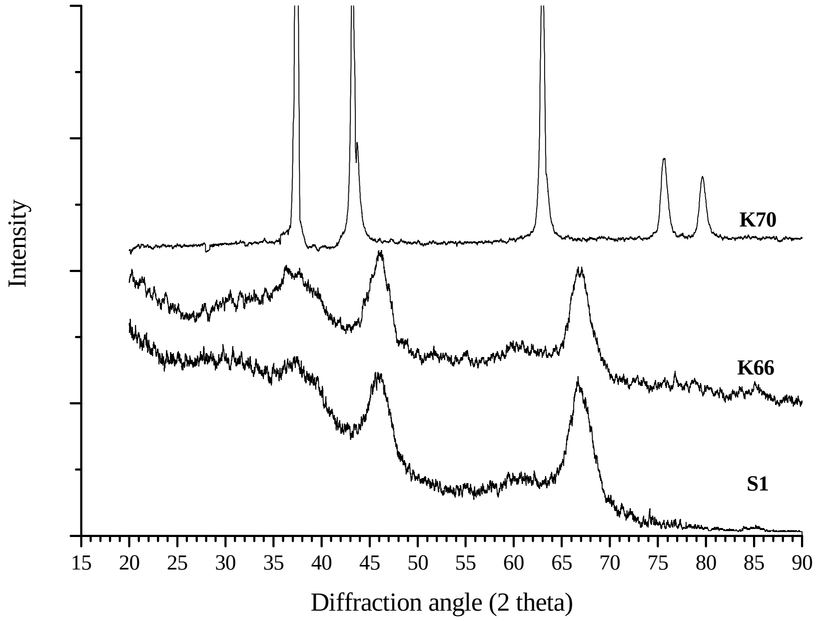

Figure 1. XRD patterns of Al_2O_3 -support (**S1**), NiO (**K70**) and NiO/Al_2O_3 (**K66**)

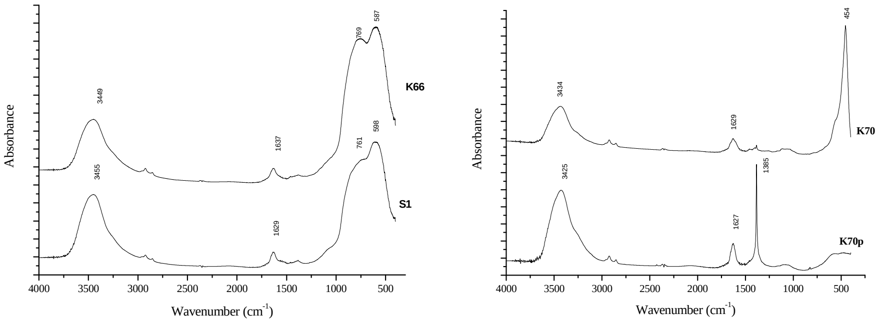

Figure 2. FT-IR spectra of Al_2O_3 -support (**S1**), NiO/Al_2O_3 (**K66**), NiO (**K70**) and $Ni(NO_3)_2\,6H_2O$ precursor (**K70p**)

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 η *=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 material amount.

The ozone conversion yield determined in identic experimental conditions (catalysts amount, space velocity, reagent concentration) is a direct measure of the catalytic efficiency of catalysts used for ozone decomposition. The time dependence of the conversion yield of investigated materials is presented in Figure 3.

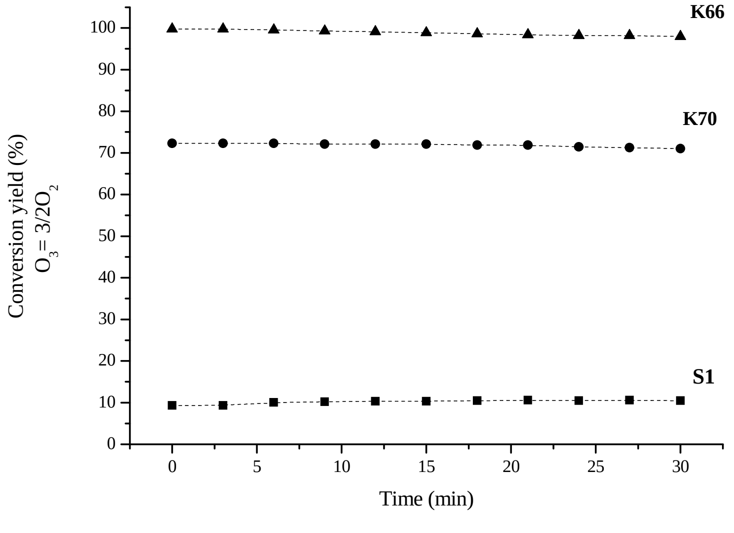

Figure 3. Catalytic efficiency of Al_2O_3-support (**S1**), NiO (**K70**) and NiO/Al_2O_3 (**K66**)

The sample **K66** (NiO/Al_2O_3) with very large surface area produces the decomposition of over 99% ozone in the first 6 testing minutes. The efficiency decreases to 97 %, in 30 minutes. The catalytic efficiency of un-supported **K70** catalyst is only 71% and decrease very little 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.

The catalytic efficiency of NiO-based catalysts is much higher then that of the corresponding MnO_2-based catalysts [10]. 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 the two kinds of catalysts is the presence of $NiAl_2O_4$ spinel generated by the interaction of nickel compound with the support. One can suppose that the high catalytic efficiency is associated with the presence of some active centres that involve the highly dispersed spinel material over the alumina surface.

4. Conclusions

Several nickel - based catalysts were prepared and characterised. The catalytic activity for ozone decomposition process in correlation with some peculiar physical-chemical characteristics was investigated. The major role of alumina support on the increase of catalyst – gas contact surface was put in evidence.

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