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Gas phase ozone decomposition over co-precipitated Ni-based catalysts

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The effect of nickel content in the catalyst was investigated in this work in regard to the catalytic activity, stability and mechanical strength of the mixed metal oxides generated by thermal treatment of co-precipitated Ni-Cu-Al samples as catalyst precursors in the reaction of ozone decomposition. The impact of the silver present as a promoter on the catalytic activity was also examined. The catalytic activity of the metal oxide catalysts was estimated by monitoring of the inlet and outlet ozone concentrations and calculating the conversion degree of ozone into molecular oxygen. It was established that at room temperature all the catalysts demonstrate stable and almost constant conversion degree in the course of time on stream. It was found out that all tested catalyst samples have activity in ozone decomposition but the maximal conversion degree (more than 90%) was observed with the catalyst sample impregnated with 3% Ag_2O.

The properties of the catalysts were characterized by using various physical methods such as PXRD, TEM and SEM.

Keywords: Ni-Cu-Al metal oxide catalysts, Ag promoter, Co–precipitation, Ozone decomposition

INTRODUCTION

Ozone is widely used in the industrial and environmental processes more specifically in semiconductor manufacturing, deodorization, disinfection and water treatment [1]. Ozone in the atmosphere protects the Earth's surface against UV radiation, but on the ground level it is accepted to be one of the criteria for air contamination [2].

An effective method for purification of toxic gases containing ozone is the heterogeneous catalytic decomposition [3]. The most effective catalysts for this process are those containing platinum and platinum group metals, however, these metals are very expensive and this fact is limiting their application on a large-scale. Hence, efforts are made to replace precious metals by low cost non-noble transition metals and metal oxides of Mn, Co, Ni, Cr, Ag, Cu, Ce, Fe, V and Mo supported on high specific surface area carriers such as γ-Al_2O_3, SiO_2, TiO_2, ZrO_2 and charcoal [4]. It has been reported that the transition metals oxides exhibit high catalytic activity in the decomposition of ozone [5]. Among them, the catalysts based on manganese oxide demonstrate the highest activity in the ozone decomposition reaction [3].

The behaviour of silver-containing catalysts in the above mentioned reaction is the subject of several insightful publications. Silver- and nickel-based catalysts deposited on γ-Al_2O_3 by the impregnation method have been evaluated for the removal of toluene in different plasma catalytic systems. It was reported that NiO/Al_2O_3 catalyst displayed a higher enhancement of CO_2 selectivity and ozone decomposition efficiency [6].

Ru-Mn-promoted Ni-based catalysts and commercial Ni-based catalysts have been compared in the reaction of catalytic steam reforming of toluene in the temperatures range 673–1073 K. Generally, it was found out the conversion of toluene and the H_2 content in the product gas increased with the temperature increase [7].

The performance of cassava rhizome gasification has been carried out at high temperatures ranging from 873 up to 1073 K in the presence of Ni/α–Al_2O_3 and it was reported that the higher temperature improved the conversion of this material into fuel gas [8].

Efficient degradation of 2,4-dichlorophenoxyacetic acid in aqueous solutions has been achieved on NiO/SiO_2 catalysts in the presence of ozone [9]. In this work NiO nanoparticles have been deposited on the silica surface by impregnation and liquid phase photodeposition in the presence of acetone or benzophenone. The most promising method of preparation appeared to be the sensitized photodeposition allowing a higher reduction degree of the precursor Bis(2,4-pentanedionato)nickel(II) after short irradiation time interval. The authors claim that according to the results on catalytic ozonation of 2,4-dichlorophenoxyacetic acid, the initial specific activity of the photodeposited catalyst was almost 7 times higher compared with that of the impregnated catalyst sample.

The influence of NiO addition on the activity of cement containing catalyst has been studied in the reaction of ozone decomposition [10]. It was found

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out that the addition of NiO to the catalyst system improves its catalytic properties.

In another paper [11] the ability of Ni–Zn ferrite magnetic catalyst in decomposition of dye model contaminants by photocatalytic ozonation has been investigated. Formate, acetate and oxalate anions have been detected as dominant aliphatic intermediates and nitrate, sulfate and chloride ions have been detected as mineralization products of dyes. The results demonstrated that the photocatalytic ozonation using Ni-Zn ferrite magnetic catalyst was a very effective method for dye degradation.

A literature survey suggests that Ag- and Ni-containing catalytic compositions show high activity in the ozone decomposition and most of them have been obtained from impregnated precursor samples [12].

The aim of this paper was to investigate the activity, stability and mechanical strength of the mixed metal oxides promoted by thermal treatment of co-precipitated Ni-Cu-Al samples as catalyst precursors in the reaction of ozone decomposition. Two effects have been observed to have impact on the catalytic activity of the oxide compounds: the nickel content and the silver promoter. For this purpose, two Ni-Cu-Al samples with composition 10%NiO-5%CuO-85%Al_2O_3 and 20%NiO-5%CuO-75%Al_2O_3 were synthesized. Studying the influence of the silver addition by co-precipitation or conventional impregnation method on the catalytic activity of the materials would enable to select the optimal catalyst composition with the most advantageous characteristics in the ozone decomposition reaction.

EXPERIMENTAL

Sample preparation

All precursor samples were obtained by co-precipitation at 60°C and constant pH=9.0, using '*pro analysi'* purity grade nitrate salts of the corresponding metals: $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $AgNO_3$, and Na_2CO_3 as a precipitating agent. A fixed volume of distilled water was poured in a laboratory synthesis reactor, heated to 60°C, and adjusted with 0.9 M Na_2CO_3 solution to reach pH=9.0. The mixed nitrate solution (total metal concentration of 0.5 M) and the precipitant were introduced drop-wise simultaneously controlled by two peristaltic pumps during vigorous stirring. The resulting slurry was aged for 60 min in the mother liquor under continuous stirring at 60°C and pH=9.0. Then it was filtered off, washed thoroughly with distilled water until neutral pH value of the filtrate was obtained and absence of NO_3^- ions - the latter was tested using solution of diphenylamine in H_2SO_4. The obtained precipitates were further dried at 100°C for 20 h.

The co-precipitated precursors were thermally treated in an air atmosphere at 450°C for 2.5 h before running the catalytic activity test. The calcined products were labeled as Ni10, Ni10Ag and Ni20, where 10 and 20 denote the percentage of NiO in the solids, respectively, and Ag indicate the presence of Ag modifier (Table 1).

The calcined sample Ni10 was impregnated with aqueous solution of $AgNO_3$ in such quantity as to receive a sample having 3.0 wt % Ag_2O in its composition. After drying at 100°C, the sample was once more calcined at 450°C for 2.5 h.

Table 1. Sample notation and chemical composition of the studied samples

Sample	Chemical composition						
	(wt. %)				(molar ratio)		
	NiO	CuO	Al_2O_3	Ag_2O	Ni^{2+}/Al^{3+}	Cu^{2+}/Al^{3+}	M^{2+}/Al^{3+}
Ni10	10.0	5.0	85.0	–	0.08	0.04	0.12
Ni10Ag	10.0	5.0	82.0	3.0	0.08	0.04	0.12
Ni20	20.0	5.0	75.0	–	0.18	0.04	0.22

Sample characterization

Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer employing CuKα radiation (λ = 0.15406 nm), operated at U = 40 kV and I = 40 mA. The crystalline phases were identified using Joint Committee on Powder Diffraction Standards (JCPDS) files. The microstructure of the catalyst was observed using a high-resolution transmission electron microscope (HRTEM JEOL 2100).

A scanning electron microscope (SEM) JSM-5510 of JEOL was used for morphology observations.

The ozone conversion degree measurements were carried out in a tubular glass reactor (6×150 mm) charged with 0.1 g of fixed catalyst bed. The experiments were performed at feed flow rates of 6.0 l h^{-1} and inlet ozone concentration of 10 000 ppm. The ozone was generated by passing dry oxygen through a high-voltage silent-discharge ozone generator. The inlet and outlet ozone concentrations were monitored using a BMT 964 UV absorption-type of ozone analyzer.

RESULTS AND DISCUSSION

The time–conversion degree dependence measured in the course of 180 min time interval over the studied catalysts is represented in Fig. 1. One can see that the conversion degree is stable and it remains almost constant with time on stream at room temperature of the catalyst bed. The conversion degree results reveal that the high-loading Ni catalyst (Ni20) demonstrates higher ozone decomposition value (~90%) than that of the low-loading catalysts Ni10 (~77%).

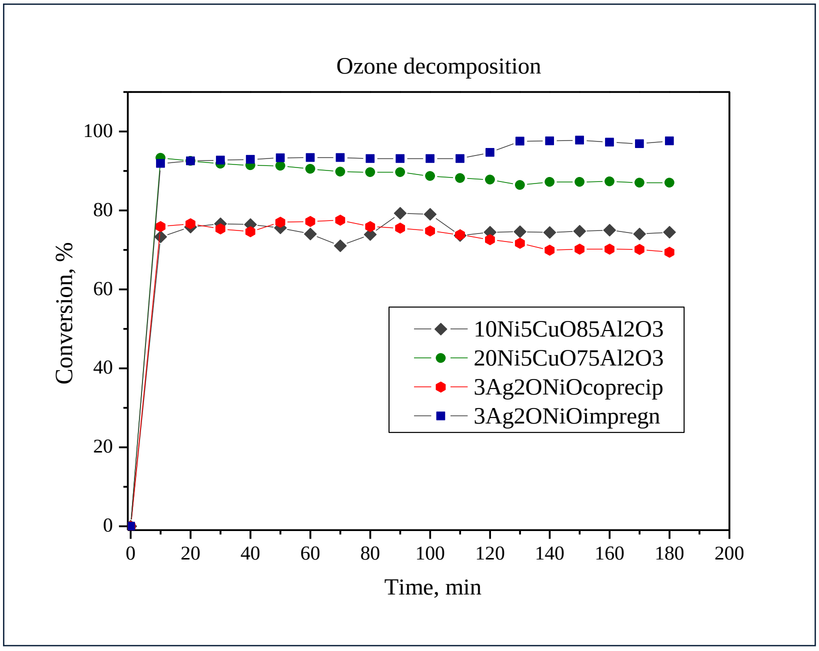

Fig. 1. Ozone conversion as function of ozonation time for the metal oxide catalysts

These results could be explained by considering the most probable mechanism of ozone decomposition including formation of superoxide or peroxide particles on the catalytic surface (Fig. 2). According to this reaction mechanism, ozone is adsorbed on catalytically active site (*), then O–O bond is cleaved, O_2 is released and atomic oxygen-containing active site O* is formed as a result (1). These surface sites react again with ozone molecules impinging from the gas phase (2), O_2 is released and an active site containing molecular oxygen O_2* is created, and then subsequently it is desorbed (3):

$$O_3 + * \rightarrow O_2 + O^* \qquad (1)$$

$$O_3 + O^* \rightarrow O_2^* + O_2 \qquad (2)$$

$$O_2^* \rightarrow O_2 + * \qquad (3)$$

Fig. 2. Mechanism of catalytic ozone decomposition

It could be supposed that during ozone decomposition on transition metal oxides such as NiO-CuO-Al_2O_3 there occurs formation of intermediate ionic particles possessing either superoxide or peroxide features. The formation of charged chemisorbed oxygen species is accompanied by oxidation of the respective number of cations in the oxide crystal lattice to a higher oxidation state. In our case this will be the oxidation of Ni^{2+} to Ni^{3+} ions, namely:

$$O_3 + Ni^{2+} \rightarrow O^{2-} + Ni^{3+} + O_2$$

$$O_3 + O^{2-} + Ni^{3+} \rightarrow O_2^{2-} + Ni^{3+} + O_2$$

$$O_2^{2-} + Ni^{3+} \rightarrow Ni^{2+} + O_2$$

The probable reaction scheme of ozone decomposition consists of electron transfer from the Ni^{2+} ion to ozone, resulting in formation of higher oxidation state Ni^{3+} species and peroxide particles O_2^{2-}, followed by reduction of Ni^{3+} species back to Ni^{2+} ion by desorption of peroxide particle to form oxygen ($O_2^{2-} \rightarrow O_2 + 2e^-$) closing the catalytic cycle.

The proposed scheme illustrates the electron transfer ensuring the catalytic ozone decomposition and the necessity of having optimal ratio of the Ni^{2+}/Ni^{3+} ions and reversible redox $Ni^{2+}\leftrightarrow Ni^{3+}$ transition. The probability of this kind of association is realized in Ni20 catalyst. Its relatively higher activity could be ascribed to the higher nickel content in this oxide sample, where some Ni^{2+} ions are partially oxidized into Ni^{3+} oxidation state, enough to form redox Ni^{2+}/Ni^{3+} couple, hence to realize the reversible redox mechanism of $Ni^{2+}\leftrightarrow Ni^{3+}$ transition. The lower nickel content in Ni10 catalyst reduces the number of active sites available on the catalyst surface.

An attempt was made to improve the activity of Ni10 catalyst by introduction of silver in the Ni-Cu-Al sample, either by co-precipitation or by impregnation of the calcined Ni10 sample.

The catalytic system containing Ni10 (10%NiO-5%CuO-85% Al_2O_3) demonstrates lower degree of ozone decomposition than that of the respective oxide system impregnated with 3.0wt% Ag_2O, pointing to the high redox properties of Ag in the ozone decomposition [13].

The morphology of the catalytic surface was studied by high resolution transmission electron microscopy (Fig. 3). TEM images reveal an aggregated bundle-like particles and each aggregate is consisting of numbers of nanowires/rods**,** which are created in the solid solution metal oxide.

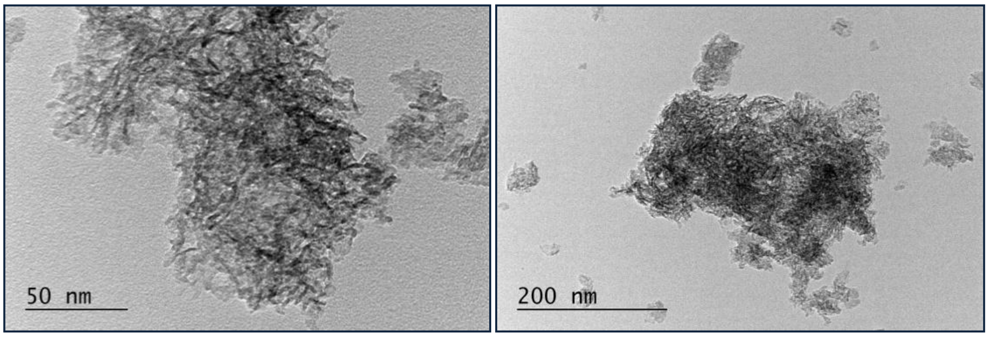

Fig. 3. TEM images of 20Ni catalyst at different magnifications

PXRD patterns of the synthesized metal oxide systems were used for detecting the resultant phases (Fig. 4). The diffractograms reveal that calcination of the co-precipitated precursors at 450°C gives rise to oxide compositions with broad diffraction lines. The recorded badly organized reflections are corresponding to the non-stoichiometric spinel-like $NiAl_2O_4$ (JCPDS 00-010-0339) and $CuAl_2O_4$ (JCPDS 01-078-0556) phases. The formation of spinel-like Ni- and Cu-aluminate phases could be explained based on the weight content of Ni and Cu in the samples or rather accounting for the superior Al concentration, corresponding to M^{2+}/Al^{3+} molar ratio from 0.12 to 0.22 (Table 1). It is well-known that the stoichiometric aluminate spinel $M^{2+}Al_2O_4$ presents a molar ratio M^{2+}/Al^{3+} equal to 1:2 [14]. It is necessary to mention that the most intensive peaks of $NiAl_2O_4$, $CuAl_2O_4$ and γ-Al_2O_3 overlap due to the almost identical positions of the various reflections that hamper the accurate identification of the corresponding phases. In addition, the possibility of a mixed spinel $(Cu,Ni)Al_2O_4$ formation should not be ignored. Moreover, characteristic patterns of γ-Al_2O_3 (JCPDS 00-010-0425) are observed. However, some low intensity reflections of γ-Al_2O_3 phase are absent in the diffractogram of sample Ni20 (higher nickel loading). Reflections of both single NiO and CuO phases are not registered.

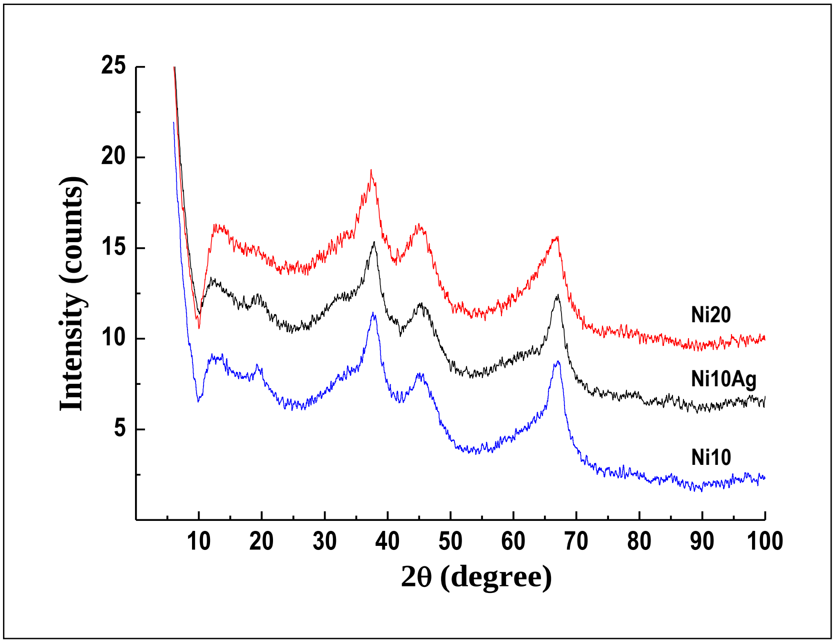

Fig. 4. XRD patterns of nickel, copper, aluminum and silver metal oxide catalysts.

Ag_2O oxide phase was not observed in the PXRD patterns of silver modified sample (Ni10Ag). This result is not unexpected because $AgNO_3$ decomposes at 440°C into metallic silver, nitrogen, oxygen, and nitrogen oxide [15]. However, the diffraction lines typical of metal silver (JCPDS 00-004-0783) phase did not appear in the diffractogram of the Ni10Ag sample, most probably due to the small amount of silver or very finely dispersed silver phase.

In general, the observed broadening of the diffraction lines indicates that the calcined oxide compositions are poorly crystallized materials, whose average particle size determination is practically impossible.

A wide area of the surface of Ni10 catalyst was scanned by SEM. The illustrations are represented in Figure 5. The so obtained SEM images are exhibiting nanorods-well dispersed particles as well as rounded–like particles agglutinated on mesoporous spheres [16].

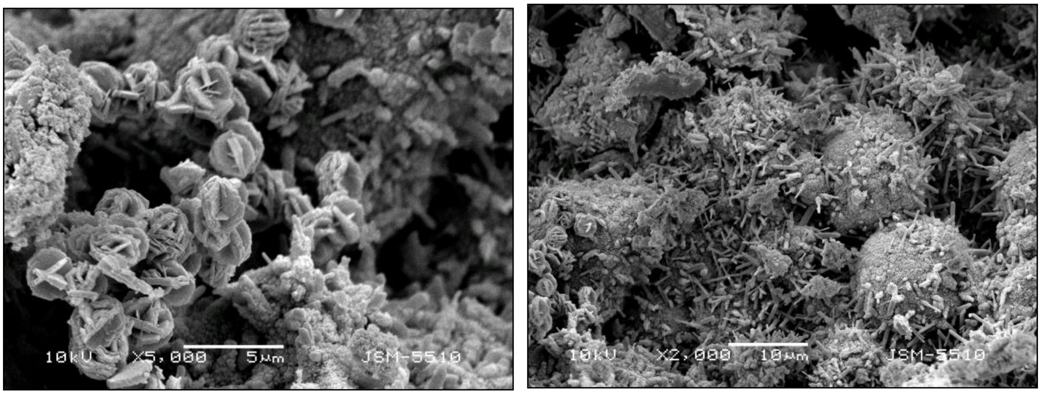

Fig. 5. SEM micrographs of Ni10 catalyst at different magnifications.

The morphology of these particles evidences porous structure of the catalytic surface. The SEM studies are indicative of the influence of the applied preparation method of heterogeneous catalysts with surface roughness which increases the effective surface area of the material. This is essential for the dissociative adsorption of O_3 on the catalytic surface in order to form chemisorbed atomic oxygen in concentrations sufficiently high to promote oxidation.

CONCLUSIONS

The co–precipitation method turned out to be a very suitable technique for preparation of highly active $NiO–CuO–Ag_2O–Al_2O_3$ catalyst for ozone decomposition.

It was found out that all treated catalytic simples have considerable activity in ozone decomposition but the maximal conversion degree (more than 90%) was observed with the catalyst sample impregnated with Ag_2O.

The SEM analysis proves the significant role of sample surface morphology in the process of ozone decomposition on the surface of $NiO–CuO–Ag_2O–Al_2O_3$ solid solution oxide catalyst.

The strong synergistic effect due to the formation of $NiO–CuO–Ag_2O–Al_2O_3$ solid solution oxide gave rise to larger number of adsorbed ozone molecules and preferable low temperature redox catalytic cycle, which make a great contribution to its superior activity.

It can be summarized that the ozone decomposition activity increases with the nickel content. This fact is ascribed to the availability of optimal Ni^{2+}/Ni^{3+} ion pair ratio. A probable scheme is proposed about ozone decomposition composed by the redox couple Ni^{2+}/Ni^{3+} and reversible redox $Ni^{2+}\leftrightarrow Ni^{3+}$ transition.

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РАЗЛАГАНЕ НА ОЗОН ВЪРХУ СЪУТАЕНИ НИКЕЛ СЪДЪРЖАЩИ КАТАЛИЗАТОРИ В ГАЗОВА ФАЗА

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(Резюме)

В настоящата работа беше изследван ефекта на количеството никел върху активността, стабилността и якостта на смесени метални оксиди получени чрез термична обработка на съутаени Ni-Cu-Al образци като прекурсори на катализатори за реакцията на разлагане на озон. Също така беше изследвано и влиянието на среброто като промотор на каталитичната активност. Каталитичната активност на метал оксидните катализатори беше определена чрез регистриране на озонните концентрации на вход и изход от реактора и изчисляване конверсията на озон до молекулен кислород. В хода на реакцията беше установено, че при стайна температура всички катализатори работят стабилно. Също така беше намерено, че всички третирани каталитични образци притежават активност в реакцията на разлагане на озон, но най-висока конверсия (над 90%) показва катализатора импрегниран с Ag_2O.

Свойствата на катализаторите бяха потвърдени чрез използване на различни физични методи за охарактеризиране като ПРД, ТЕМ и СЕМ.