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Active Oxygen in Oxide Catalytic Systems for Environmental Catalysis

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Summary. The effect of the synthesis conditions of individual and modified with Mn Ni- and Co-oxide systems on the content and the mobility of their active oxygen has been studied by means of chemical and IR spectral analyses. The results obtained show that the main part of the active oxygen in Ni-oxide system is located on the catalyst's surface (O_s* is approximately 73% of the total active oxygen), while Co-oxide system is characterized by much lower surface active oxygen content. Ni- and Co-oxide systems modified with Mn have comparatively higher active oxygen content as compared to the individual ones. Data of the IR spectral analysis reveal that Mn, as a modifying component, affects the mobility of the active oxygen, the latter contributing to the activity of oxide systems in oxidation processes. The high content of loosely bonded active oxygen formed during the synthesis determines a high catalytic activity of the studied samples in reactions of complete oxidation in the low temperature region.

Keywords. Oxides; Active Oxygen; Heterogeneous catalysis; IR spectroscopy; Depletive oxidation.

Introduction

The most reliable and perspective methods for decontamination of toxic compounds in wastewaters and gas emissions of various chemical industries are based on heterogeneous catalytic reactions. The latter allow to achieve a complete oxidation of toxic substances. These reactions are practically irreversible, the latter allowing the harmful substances to be completely transferred into harmless products under mild conditions, using suitable catalytic systems. The catalyst is the main factor in catalytic reactions. It should satisfy a number of requirements, the more essential among them being as follows: to exhibit high catalytic activity in the operating temperature interval; to run the process selectively; to have high thermal stability; to be stable against catalytic poisons (the most contaminants in waste waters and gas emissions); to be easily regenerated.

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A number of catalytic systems suitable for complete oxidation have been studied in detail [1]. They include noble metals (Pt, Pd) [2, 3], individual oxides of transition metals [4–7], and complex oxide systems (ferrites, cobaltites, chromites, molybdates, *etc*.) [8–11]. Heterogeneous catalytic oxidation on transition metal oxides is more complicated than that running with participation of metal catalysts. The reason is that in oxidation on oxide systems oxygen is present both as a reactant in the gas phase and as a constituent of the catalyst and being a component of the catalyst it can also participate in catalytic reaction. As a reactant in catalytic reaction oxygen can take part in the latter either as electrophilic particles O_2, ${O_2}^-$ or O^-, or as nucleophilic particles O^{2-}. Correspondingly, the processes of catalytic oxidation can be classified in two groups: (i) electrophilic oxidation running through activation of oxygen on the catalyst surface with generation of electrophilic oxygen species; (ii) nucleophilic oxidation including activation of the substrate molecule as a first step, followed by interaction with the nucleophilic lattice oxygen of oxide catalyst [12, 13]. It is established that a complete substrate oxidation always occurs in the presence of electrophilic oxygen species O^- and ${O_2}^-$ on the catalyst surface [14]. Nucleophilic oxidation runs with participation of the O^{2-} ions from the oxide lattice. They do not possess oxidizing ability but as nucleophilic reactants attack the activated molecule of the substrate yielding partially oxidized products. Electrophilic oxygen species can also be generated on the surface of oxide catalyst even in the absence of oxygen in the gas phase resulting in the experimental conditions of the synthesis of the catalysts [13]. This means that not only oxygen from the gas phase but also the oxide oxygen can produce electrophilic oxygen that exhibits high reactivity and is responsible for the complete substrate oxidation. The fact that on interaction of various substances with transition metal oxides in the absence of gaseous oxygen a complete oxidation occurs instead of expected high selectivity to partially oxidized products supports this suggestion.

The possible decontamination of strongly toxic substances in wastewaters and gas emissions to harmless products based on their catalytic oxidation on suitable catalytic systems at low temperature is the major motive in preparation and characterization of such catalysts. The scientific basis for synthesis of catalytic systems for heterogeneous oxidation of toxic compounds (including catalytic poisons as well) to non-toxic products is based on the idea to produce an active phase of high dispersity; with high active oxygen content; with high degree of oxidation and octahedral coordinaton of metal ions; with low energy of the M–O bond on the surface; and with presence of OH-groups in the catalyst composition. The preparation of catalysts answering the above listed requirements is strongly dependent on both initial compositions and on experimental conditions of the synthesis procedure.

Oxides of nickel, cobalt, and manganese belong to the most important catalysts for complete oxidation among the transition metals oxides. Their high catalytic activity in the field of air pollution control and control of organic pollutants in wastewaters has been reported in a large number of papers [15–22]. Depending on the method of preparation, nonstoichiometric higher oxides of these metals (individual or mixed ones) could be obtained as a result of incorporation of over stoichiometric (*i.e.* active) oxygen in their composition. Consequently, an improvement of their catalytic behavior could be expected.

The high active oxygen content in oxide catalysts enlarges markedly their possible application. Apart from catalysts for complete oxidation they could be used: as oxygen storage capacity promoters in automotive exhaust-treatment catalysts similarly to CeO_2 and MnO_2 [23]; for depletive oxidation of substrates; as reagent for organic synthesis.

The present paper aims at studying the effect of experimental conditions of synthesis of individual and modified with Mn Ni- and Co-oxide catalytic systems on the active oxygen content and its mobility using chemical analytical methods and IR spectroscopy.

Results and Discussion

Data about active oxygen content – total (O^*) and surface ($O_s{}^*$) – in freshly synthesized catalytic systems are summarized in Table 1.

Data presented in Table 1 reveal that the applied method of synthesis favors the preparation of oxide catalytic systems with high active oxygen content. This oxygen exhibits high reactivity and is responsible for the complete catalytic oxidation of the substrate at low temperatures. Incorporation of over stoichiometric (*i.e.* active) oxygen into oxide systems is a consequence of chemosorption of the nascent oxygen (produced on decomposition of the oxidant used in strongly alkaline medium) on the precursor surface in the course of synthesis. This provides an emergence of structural defects associated with the formation of metal ions in a higher oxidation state than that characteristic of the corresponding stoichiometric oxides that act as active catalytic sites. These all are factors favoring the occurrence of donor catalytic reactions.

It is obvious that modification of individual Ni- and Co-oxide systems with Mn leads to an increase of the total active oxygen content in the catalyst composition. The reason is the fact that Ni-Mn-fresh and Co-Mn-fresh oxide systems are bicomponent catalysts comprising higher oxides of Ni and Co, respectively, and γ-MnO_2 with greatly defected structure provided by incorporation of the over stoichiometric oxygen in its composition. The surface active oxygen content of individual and mixed catalytic samples is not noticeably differentiated, the latter implying a similar catalytic activity in reactions of complete oxidation. This has been experimentally established by the authors in reactions of low temperature liquid phase oxidation of phenol [24]. It is seen from Table 1 that in Ni-oxide system the sur-

Table 1. The active oxygen content of the studied oxide systems

Oxide system	Active oxygen content			
	Total (O^*)		Surface ($O_s{}^*$)	
	(%)	($g\ at \cdot g^{-1} \cdot 10^3$)	(%)	($g\ at \cdot g^{-1} \cdot 10^3$)
Ni-fresh	5.33	3.33	3.89	2.43
Ni-Mn-fresh	7.71	4.82	3.92	2.45
Co-fresh	6.40	4.00	2.56	1.60
Co-Mn-fresh	8.80	5.51	2.64	1.65

face active oxygen constitutes about 73% of the total active oxygen, while in Co-fresh sample the $O_s{}^*$ is only 40% of the total one. An anologous relationship is observed with mixed oxide systems, but a decrease in the relative percentage content of O^* is observed at commensurable values of Ni and Co content (in g-at metal/g of catalysts) in both individual and modified catalytic samples. This gives grounds to suggest that the active oxygen bonded to manganese ions is mainly located in the lattice of oxide systems, while the surface active oxygen is bonded to Ni and Co ions.

Results obtained about the effect of temperature of the thermal treatment of catalytic systems on the active oxygen content reveal that the Ni-oxide system loses its active oxygen at temperatures higher than 393 K. The amount of O^* in Co-oxide systems thermally treated up to 473 K remains unchanged and is sharply reduced on heating of the sample above 573 K ($O^* \sim 1\%$). Incorporation of Mn in the individual oxide systems leads to increase of their thermal stability. At that Ni-Mn-fresh sample preserves 62% of its total active oxygen content on heating up to 823 K, while Co-Mn-fresh sample preserves 56%. This extends the possibilities for practical application of the modified catalytic systems in reactions of complete oxidation of toxic substances in gas phase that require higher reaction temperatures.

The bonding energy of oxygen to metal ions on the catalyst surface is the main factor providing the activity of oxide catalysts. With decrease of the bond strength between the surface cation and oxygen the catalytic activity is increased and the selectivity of the process against products of complete oxidation is enhanced. IR spectral characterization of catalytic systems can provide information about the way of oxygen bonding to metal ions on the surface of oxide catalysts as well as about energy uniformity and reactivity of catalytic systems.

Figures 1–4 demonstrate the IR spectra of fresh, thermally treated, and reduced after depletive oxidation of the substrate (sulfide ions in aqueous phase and methanol in gaseous and aqueous phase) catalytic samples. In details the results regarding

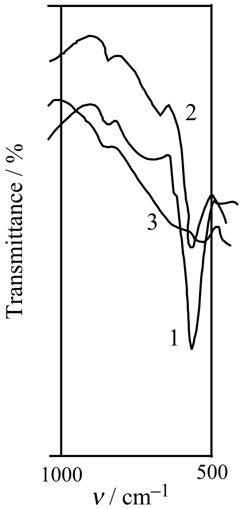

Fig. 1. Relative intensity of the band at 573 cm^{-1}: *1* Ni-fresh; *2* Ni-fresh, heated to 363 K; *3* Ni-fresh, heated to 423 K

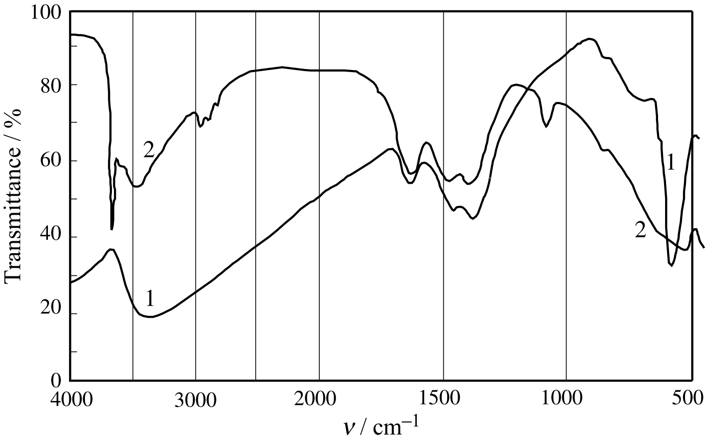

Fig. 2. IR spectra of Ni-fresh (1) and after depletive oxidation of CH_3OH in gaseous phase (2)

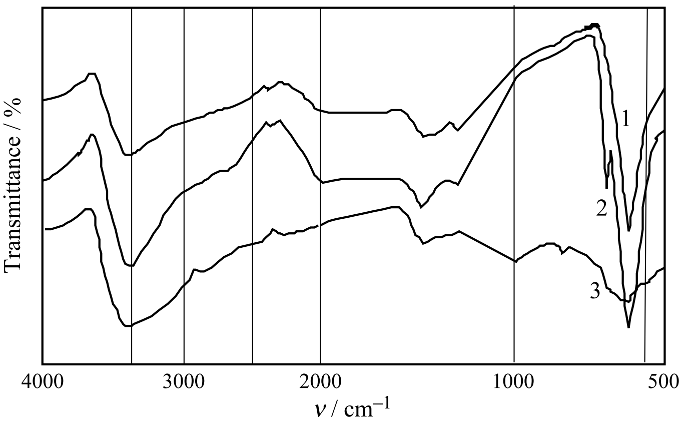

Fig. 3. IR spectra of Co-oxide system: *1* Co-fresh; *2* after depletive liquid phase oxidation of sulfides ($C^0S^{2-} = 0.130\,g \cdot dm^{-3}$); *3* after depletive liquid phase oxidation of sulfides ($C^0S^{2-} = 13.0\,g \cdot dm^{-3}$)

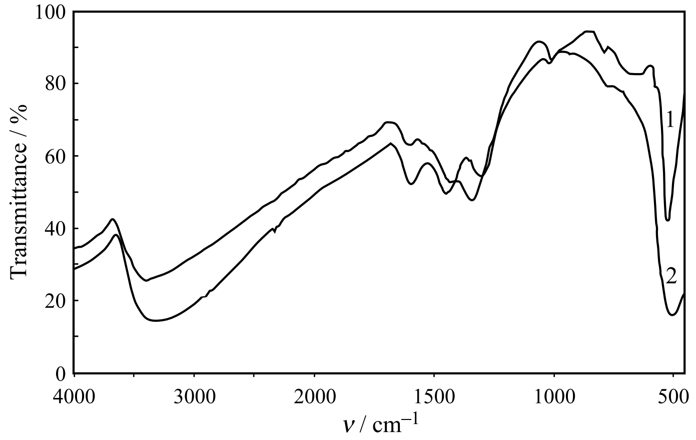

Fig. 4. IR spectra of Ni-fresh (1) and Ni-Mn-fresh (2)

aqueous phase catalytic oxidation of sulfide ions over Ni- and Co-oxide systems, as well as data about catalytic oxidation of methanol in gaseous and aqueous phase using Ni-oxide system are published in Refs. [25–27].

The presence of a wide and intense absorption band at $573\,cm^{-1}$ (Ni-fresh), $567\,cm^{-1}$ (Ni-Mn-fresh), $586\,cm^{-1}$ (Co-fresh), and $579\,cm^{-1}$ (Co-Mn-fresh), respectively, is a characteristic feature of the IR spectra of studied freshly prepared oxide systems. The discussed band (recorded at frequences higher than that associated with the vibrations of the M–O bond in corresponding hydroxides) is provided by stretching vibrations of the M–O bond on the surface of catalytic sample and indicates the presence of active oxygen.

According to literature data absorption bands associated with vibration of surface cation-oxygen bonds posses a number of peculiarities. The authors have established the latter as well [28]:

- The intensity of the cited absorption band is proportional to the active oxygen content in the sample;
- a decrease in relative intensity of the band is observed in the course of thermal treatment of the fresh oxide systems at various temperatures (Fig. 1); moreover, the increase of temperature along with the decrease of intensity, brings about a shift of the band's maximum to lower frequencies;
- the intensity of the band decreases (up to its complete disappearance) resulting in the interaction between the fresh sample and substrate (Figs. 2 and 3).

The presence of a single absorption band in the IR spectra of fresh oxide systems, typical of stretching vibrations of the surface cation-metal bond is an evidence of the energy uniformity of oxygen on the surface of synthesized samples [29]. On the other hand the frequency region in which the band appears in spectra of studied individual and modified Ni- and Co-oxide systems (between 600 and $900\,cm^{-1}$) suggests a covalent character of the bond between active oxygen and metal cations on the sample surface. This character provides a low energy of the surface cation-oxygen bond and higher catalytic activity of oxide systems, respectively.

IR spectral characterization of mixed Ni-Mn- and Co-Mn-oxide systems reveals that incorporation of Mn as a modifying additive to individual catalytic samples influences the position and integral intensity of the absorption band provided by stretching vibrations of the cation-oxygen bond on the surface. Modification of the Ni-fresh and Co-fresh samples with Mn causes both a bathochromic shift of the band (Fig. 4) thus ascertaining the reduced strength of the M–O bond on the surface, and an increase of the integral intensity, the latter confirming the strengthening of the ionic character of the bond. Data of IR spectral analysis gave grounds to assume that Mn as modifying additive affects the mobility of reactive oxygen that is an important factor providing the activity of oxide systems in oxidation processes.

The surface oxygen reactivity in oxide catalysts can be approximately evaluated based on the relationship between the rate of substrate interaction with surface oxygen in the absence of oxygen in gas phase (depletive oxidation). Activation energy of this interaction can be regarded (with some approximation) as oxygen bonding energy in the oxide catalysts [1]. In this regard a depletive oxidation of CO in gas phase was carried out on Ni-fresh and Co-fresh samples by passing CO

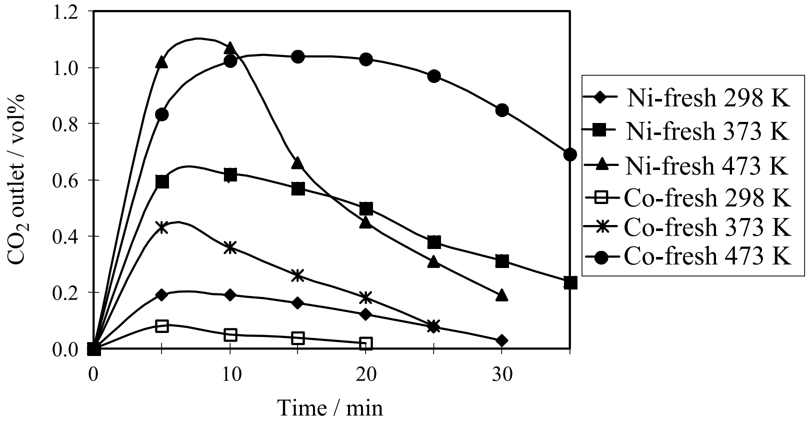

Fig. 5. Depletive oxidation of CO over Ni- and Co-oxide systems

(1.15 vol%) through the catalyst layer in Ar stream at temperatures 298, 373, and 473 K. The results of this experiment are presented in Fig. 5.

It is seen from Fig. 5 that CO is oxidized even in the absence of gas-phase oxygen by oxide systems, that act as oxygen storage compounds. The amount of CO_2 produced at 298 K is negligible, the latter indicating that under these conditions only a small part of oxygen in the oxide exhibits reactivity. With increase in temperature the rate of depletive oxidation increases. Some difference in behavior of the systems is observed. The amount of the active oxygen, participating in oxidation of CO on a Ni-fresh sample at 373 and 473 K (calculated from integral peak intensity) equals to $7.45 \cdot 10^{-3}$ and $9.43 \cdot 10^{-3}$ g, respectively. The amount of CO_2 produced on depletive oxidation of CO on a Co-fresh sample at 473 K is markedly larger than that produced at 373 K. This suggests that not only surface active oxygen of the Co-oxide but also active oxygen in the bulk participate in oxidation at higher temperatures. These results are in agreement with data of chemical analysis of fresh samples about the content of total and surface oxygen. They confirm the conclusion, that the active oxygen in the Ni-oxide system is located mainly on the surface, while in Co-oxide the surface oxygen comprises only 40% of the total active oxygen.

The activation energies of depletive oxidation of CO on the studied oxide systems are calculated to be $15.9\,\mathrm{kJ\,mol^{-1}}$ for Co-oxide and $10.9\,\mathrm{kJ\,mol^{-1}}$ for Ni-oxide. These low values give grounds to conclude that the synthesis conditions favor the preparation of oxide catalysts with high content of loosely bonded active oxygen the latter providing high activity and selectivity of the as-synthesized oxide systems with respect to reactions of complete oxidation.

Experimental

The catalysts were prepared by the oxidation-precipitation method in aqueous solutions, according to the procedure described in detail by *Christoskova et al.* in Refs. [30–32]. The applied method is based on the precipitation of metal hydroxides (as precursors) in strong oxidative medium created by NaOCl or $KMnO_4$, followed by thermal treatment of the solids at relative low temperatures (323–393 K). The catalysts obtained were characterized by means of IR, XPS, ESR, DTA, X-ray diffraction, and chemical analyses. Analytical data showed that the applied synthesis procedure yields amorphous and highly disperse active phases with non-stationary surface properties, which determine their high catalytic activity in reactions of complete oxidation at low temperatures [30–32].

The total active oxygen content (O^*) (the amount of excess oxygen in the oxide above that required by the lowest stable valence state) was determined by a direct iodine method [33]. About 0.1 g of catalyst is accurately weighed and added to 25 cm^3 dilute (1:10) sulphuric acid containing 2 g potassium iodide in a flask supplied with a ground stopper. After complete dissolution of the sample, the solution is allowed to stand for 10 min and the liberated iodine is titrated with 0.1 *N* sodium thiosulfate solution using starch as indicator.

The surface active oxygen content ($O_s{}^*$) was determined by the procedure described in the paper of *Ushijima et al.* [34]. A known amount of catalyst sample (0.1 g), 15 cm^3 of buffer solution (*pH* 7.1), and about 2 g KI were placed in a closed vessel. The latter was vigorously shaken for 7 h. The reaction mixture was then filtered, washed with methanol, acidified with 0.1 *M* HCl, and the liberated iodine titrated with 0.01 *N* sodium thiosulfate solution using starch as indicator.

The infrared spectra were recorded with a 1750 model Perkin Elmer FTIR spectrophotometer in KBr tablets. The tablets were prepared according to a procedure described elsewhere [35]. The applied procedure yielded IR spectra free of undesirable bands of adsorbed water (water may be adsorbed during mixing and preparing of tablets).

Depletive oxidation of CO was carried out in flow equipment under the following conditions: the rate of the gas flow – 4.3 $dm^3\,h^{-1}$; the inlet concentration of CO in the gas flow – 1.03 vol%; the mass of the catalyst – 0.24 g for Ni-oxide system and 0.30 g for Co-oxide system, respectively; volume of the catalyst layer – 0.2 cm^3; carrier gas – Ar; temperature of the catalyst layer – 298–473 K. The concentration of CO and CO_2 was determined by means of gas analyzer Infralyt 2106. The rate of oxidation was evaluated by measuring the amount of CO_2 formed during the reaction.

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