THE ROLE OF MODIFIED ALUMINA SUPPORT FOR THE FORMATION OF ACTIVE Cu-Co OXIDE PHASE – AN XPS INVESTIGATION

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ABSTRACT

The present work considers the formation of an appropriate Cu-Co spinel structure, supported on pure Al₂O₃ and Al₂O₃ modified with MgO. The prepared catalyst samples have been characterized by X-ray photoelectron spectra (XPS), X-ray diffraction analysis (XRD) and AAS. The specific surface area has been determined by the BET method. The catalytic activity of the samples has been studied in the reaction of NO reduction by CO. The results show that the best Cu-Co spinel structure is formed in the case of catalyst based on alumina support in the presence of 8 % MgO.

Keywords: XPS, XRD, catalysts, spinel structure.

INTRODUCTION

The oxides of transition metals can fulfill the function of catalytically active components and they appear to be appropriate substitutes of noble metals in supported catalysts. The interaction between these oxides results in the formation of complex structures of spinel or perovskite type [1]. The catalytic activity can be promoted by using various supports or by introducing modifying additives in the support – such as MgO [2]. In a mixture of copper oxide and cobalt oxide starts formation of a phase of CuCo₂O₄ at 300°C, which remains stable up to 800°C [3]. When a mixture of copper oxide and cobalt oxide is supported on Al₂O₃, the cobalt oxide can react during the calcination process not only with the copper oxide but also with Al₂O₃ [4]. A number of properties of Al₂O₃ as catalyst support are closely connected with atomic defects or the so called “internal point defects”, and some of them are due to the doping additives such as CaO, MgO, La₂O₃, TiO₂, CuO, CeO₂ and others [5]. Among the doping additives the magnesia exerts a considerable effect upon the mechanical properties of Al₂O₃ [6].

The aim of the present investigation was to study the surface structure of mixed Cu-Co oxide, deposited on various supports, using XPS analysis. The task was to monitor the role of the modifying additives in the support upon the activity of the catalysts for NO reduction by CO. The formation of CuCo₂O₄ spinel has been studied using the following supports: Al₂O₃, Al₂O₃ - X %\text{mass MgO} (X = 4 and 8) and ceramic filter support.

EXPERIMENTAL

Preparation of catalysts

The studied catalyst supports are based on pure Al₂O₃, prepared by the precipitation method and treated thermally at 1000°C. The Al₂O₃ - MgO support has been
obtained by the method of wet mixing, whereupon the precursors used were boehmite and \((\text{MgCO}_3)_2\text{Mg(OH)}_2\cdot\text{SH}_2\text{O}\) and calcined at 1000°C for 4 hours. The composition of the prepared support is: \(\text{Al}_2\text{O}_3\) 92 to 96 % and \(\text{MgO}\) 4 to 8 %. Another support was also used—a ceramic filter, manufactured by the “Drache Umwelttechnik” GmbH, Germany containing mainly \(\text{Al}_2\text{O}_3\). The deposition of the active \(\text{Cu-Co}\) phase was carried out by impregnating the support, formed in advance, with an aqueous solution of a mixture of \(\text{Cu}\) and \(\text{Co}\) nitrates [7]. After supporting the active phase the catalysts were calcined at \(T=500°C\) for 3 hours. After the deposition of the \(\text{Cu-Co}\) active phase there follows the deposition of \(\text{CuO}\) on the support (ceramic filter) and after it—calcination at 500°C for 3 hours.

The so obtained catalyst samples are denoted as follows: KA – \(\text{Cu}_2\text{Co}/\text{Al}_2\text{O}_3\); KM1 – \(\text{Cu}_2\text{Co}/\text{Al}_2\text{O}_3\) – \(<4\%\) max \(\text{MgO}\); KM3 – \(\text{Cu}_2\text{Co}/\text{Al}_2\text{O}_3\) – \(<8\%\) max \(\text{MgO}\) and SN – \(\text{Cu}_2\text{Co}/\text{CuO}\) ceramic filter.

**Physical-chemical characteristics**

The structure and the phase composition of the so prepared catalyst samples have been identified by Bruker Advance X-ray apparatus using CuKα radiation and SolX Detector at 2θ ranging from 20 up to 80° at a scanning step of 0.04°. The specific surface area of the catalyst samples has been determined by the BET method. The chemical analysis of the catalysts was made on a FAAS M5 – Thermo Fisher.

**XPS characterization**

The X-ray photoelectron spectra (XPS) have been recorded using monochromatic radiation AlKα (1486.6 eV) on an electronic spectrometer VG ESCALAB MKII at base pressure 1×10⁻⁶ Pa and total resolution capability of the apparatus amounting to 1 eV. The charge effect has been corrected (calibrated) on the C1s peak (signal) related to a binding energy of 285 eV. The photoelectron spectra of C1s, O1s, Al2p, Cu2p, Co2p and Mg2p have been recorded and corrected by subtraction of the background of Shirley’s type and these have been evaluated quantitatively on the basis of the peak areas and the cross-sections of photoionization after Scoffield.

**Testing the catalytic activity**

The catalytic activity experiments have been carried out in a continuous flow catalytic reactor, described previously in [8]. A gaseous mixture has been used for this purpose consisting of NO + CO + Ar having component concentrations 1200 ppm CO, 1200 ppm NO and a reduction-oxidation potential (“redox” potential) \(\text{RO} = [\text{CO}]_{\text{red}}/\text{[NO]}_{\text{ox}} = 1 ± 0.05\) at a gaseous hourly space velocity \(W = 26,000\ h^{-1}\).

**RESULTS AND DISCUSSION**

**Physical-chemical characterization of the supports and the catalysts**

The most essential factors, which determine not only the structure of the supports, but also the structure and the texture of the catalyst samples, based on these supports, are the conditions of the synthesis of the supports. In order to obtain \(\text{Al}_2\text{O}_3\) having a stable structure and developed specific surface at high temperatures it is necessary to start with a precursor phase possessing fine dispersion. The \(\text{Al(OH)}_3\), which is the initial compound for obtaining \(\text{Al}_2\text{O}_3\), has been prepared by precipitation in a continuous regime, whereupon the basic parameters are constant and homogeneity of the medium is ensured. The alumina-magnesia supports, prepared by the mixing method are based on initial finely dispersed precursors: precipitated boehmit and basic magnesium hydroxyl-carbonate. The main physical-chemical properties of the supported catalysts are represented in Tables 1 and 2.

The introducing of the modifier \(\text{MgO}\) leads to lowering of the specific surface area and increasing the mechanical strength, while at the same time it exerts influence on the textural characteristics and causes acceleration of the phase transitions towards the higher-temperature modifications of the alumina and formation of spinel. The formation of a solid solution \(\text{Mg}_{0.33}\text{Al}_{0.67}\text{O}_4\) (JCPDS PDF 48 – 528) is much more distinctly expressed in the case of the support having a higher content of \(\text{MgO}\), which predetermines a faster transition towards a spinel phase. The absence of modifier in the support ensures a higher specific surface area of the catalyst sample and the presence of low-temperature modifications of \(\text{Al}_2\text{O}_3\), \(\delta + \theta\) \(\text{Al}_2\text{O}_3\) modifications (JCPDS PDF 11 – 517) + \(\alpha\) \(\text{Al}_2\text{O}_3\) (JCPDS PDF 10 – 173). The reflections of the active phase of the KA catalyst sample \(\text{CuCo}_2\text{O}_4\) – \(\text{Cu}_{0.92}\text{Co}_{0.08}\text{O}_4\) (JCPDS PDF 37 – 878) are weaker than those of the catalyst samples KM1 and KM3 – \((\text{Cu}_{0.43}\text{Co}_{0.57})\text{Co}_2\text{O}_4\) – (JCPDS PDF 25 – 270).
Table 1. Characterization of supports and catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Phase composition</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Mechanical strength (kg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>catalyst</td>
<td>support</td>
<td>catalyst</td>
</tr>
<tr>
<td>KA</td>
<td>Weak reflection</td>
<td>Strong reflection of δ, θ, α -</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>of CuCo₂O₄</td>
<td>Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>KM1</td>
<td>Mean reflection</td>
<td>Strong reflection of α - Al₂O₃</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>of CuCo₂O₄,</td>
<td>mean Mg₀.₃₈₈Al₂.₄₀₈O₄, strong</td>
<td>Mgo.₃₈₈Al₂.₄₀₈O₄</td>
</tr>
<tr>
<td></td>
<td>Mg₀.₃₈₈Al₂.₄₀₈O₄</td>
<td>α - Al₂O₃, weak</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>tenorite (CuO)</td>
<td></td>
</tr>
<tr>
<td>KM3</td>
<td>Intensive reflection of CuCo₂O₄, α - Al₂O₃, mean Mg₀.₃₈₈Al₂.₄₀₈O₄, tenorite (CuO)</td>
<td>Strong reflection of α - Al₂O₃, Strong reflection of Mg₀.₃₈₈Al₂.₄₀₈O₄</td>
<td>60</td>
</tr>
<tr>
<td>SN</td>
<td>Very weak reflection of CuCo₂O₄, strong α - Al₂O₃</td>
<td>Strong α - Al₂O₃, cristobalite – traces</td>
<td>1</td>
</tr>
</tbody>
</table>

The most poorly expressed is the active phase (Cu₀.₃Co₀.₇)Co₂O₄ - (JCPDS PDF 25 - 270) in the XRD pattern of the catalyst sample on the commercial support SN. The free phase of tenorite (CuO) (JCPDS PDF 48-1548) is more strongly expressed in the cases of higher content of MgO in the support. The chemical analysis data show that a better Co/Cu ratio has been achieved with the KM3 catalyst where the support contains 8% MgO.

**XPS results**

The XPS analysis (ESCA) has been applied in order to obtain information in regard to the composition on the surface of the so prepared catalyst samples. The atomic ratios on the surface (Table 3) have been calculated on the basis of the peak, taking into account the cross-section of scattering and the mean free path.

Due to the overlapping of the peaks of the internal electron levels of Cu₃p and Al₂p deconvolution of the complex peaks down to their components had to be applied in order to determine quantitatively the intensity of the Al₂p peak. The highest concentrations of copper and cobalt on the surface are observed with the SN sample (Table 3).

The XPS (ESCA) spectra of Cu₂p₃/₂ and Co₂p₃/₂ are presented in Fig. 1a, b, respectively for Cu-Co mixed oxide, deposited on various supports. The signal of Cu₂p₃/₂ of each catalyst sample appears as a wide asymmetric main peak at about 934.2 eV and an accompanying peak at higher binding energy, which is typical of the Cu²⁺ ions. The structure of the peak Cu₂p₃/₂ and the intensity ratio Iₚ/Iₚ₀ (where Iₚ refers to the satellite peak and Iₚ₀ refers to that of the main peak) compared to those of CuO and of the stoichiometric spinel Cu₀.₃Co₀.₇O₄ are quite different in each one of the studied samples. The value of Iₚ/Iₚ₀ in the case of mixed Cu-Co oxide catalysts on Al₂O₃ - 8% MgO is equal to that...

Table 2. Summary of Chemical results for the investigated catalysts.

<table>
<thead>
<tr>
<th>Composition, %</th>
<th>KA</th>
<th>KM1</th>
<th>KM3</th>
<th>SN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.2</td>
<td>3.6</td>
<td>2.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Co</td>
<td>3</td>
<td>3.1</td>
<td>3.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 3. Summary of XPS results for the investigated catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cu/Co</th>
<th>Cu/Al</th>
<th>Mg/Al</th>
<th>Co/Al</th>
<th>(Iₚ/Iₚ₀)Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>KA</td>
<td>2.5</td>
<td>0.07</td>
<td>0.03</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>KM1</td>
<td>1.74</td>
<td>0.08</td>
<td>0.13</td>
<td>0.04</td>
<td>0.47</td>
</tr>
<tr>
<td>KM3</td>
<td>0.38</td>
<td>0.07</td>
<td>0.22</td>
<td>0.20</td>
<td>0.67</td>
</tr>
<tr>
<td>SN</td>
<td>0.87</td>
<td>0.60</td>
<td>0.33</td>
<td>0.68</td>
<td>0.52</td>
</tr>
<tr>
<td>Cu₀.₃Co₀.₇O₄</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
<td>0.68</td>
</tr>
</tbody>
</table>
obtained for the stoichiometric spinel Cu$_{0.64}$Co$_{2.36}$O$_4$ (0.68). In the other case - the mixed Cu-Co oxide catalyst on CuO/ceramic support, this ratio has a value close to that obtained for CuO (0.56). The coordination geometry of the surface Cu$^{2+}$ ions can be established by determining the ratio between the intensities of the accompanying peak and of the main peak. Usually the ratio I$_y$/I$_m$ is decreasing when the number of oxygen ions, coordinated to the Cu$^{2+}$ ion, is increasing [9]. Taking into account this fact one can conclude that the low value of I$_y$/I$_m$ ratio is due to the presence of a large number of Cu ions in octahedral environment on the surface. It follows from here that in the case of catalyst samples having a low content of Cu the strongly dispersed copper oxide exists at one and the same time both in tetrahedral and in octahedral coordination environment, while in the catalyst samples with high copper content the octahedrally coordinated on the surface copper ion prevails.

The spectra of Co2p$^{3/2}$ show a main line at about 780 eV and accompanying satellite lines at 783 eV and 790 eV. The presence of a Co2p signal means that the surface of the samples in the general case consists of Co$^{2+}$ and Co$^{3+}$ in octahedral environment. The well expressed accompanying peak implies contribution of Co$^{3+}$ and the high-spin Co$^{3+}$, as the low-spin Co$^{3+}$ species, displays a poorly shaped satellite peak [10]. A low-intensity satellite peak is an indication that the Co ions are incorporated in the crystal lattice [11].

Now we can compare the ratio of intensities Cu/Co for the various catalyst samples with that of the stoichiometric spinel compound Cu$_{0.64}$Co$_{2.36}$O$_4$ (0.43). One can observe the presence of a larger quantity of Cu on the surface in the cases when the mixed Cu-Co oxide is deposited on supports: Al$_2$O$_3$ and Al$_2$O$_3$ modified with 4% of MgO. The catalyst samples KM1 and KM3, whose supports are modified with MgO, display a single-component photoelectron peak Mg2p at 50.3 eV close to the one, which has been reported in the current literature for MgO (50.2 eV) or MgAl$_2$O$_4$ (50.2 eV) [12]. The low values of the Mg/Al ratio in the XPS spectra are also evidence for a high degree of dispersion of MgO on the surface of Al$_2$O$_3$. The single-component oxygen peak at about 531.4 eV has been evaluated and attributed to the oxides. In the case of the SN sample spectrum the presence of other species was also observed, in addition to this peak, which proves the existence of separate phases of copper oxide and cobalt oxide.

**Catalytic activity of the samples**

The activity of the catalyst samples in the reduction of NO by CO has been monitored within the range of 100 - 400°C. The results are presented in Fig. 2. The lowest starting temperature of the reaction 200°C was
manifested by the KM3 catalyst sample, whereupon at 250°C a complete degree of reduction of NO by the CO is achieved. The difference in the behavior of the catalysts illustrates the influence of the modification of the support. It was found out in previous investigations [13] that Cu$_y$Co$_{3-x}$O$_4$ has been converted partially into Cu$^{2+}$, Co$^{3+}$, Co$^{3+}$, [Co$^{3+}$, Cu$^{2+}$]O$_4$ when y > 0 at x > 0.3. The Cu$^{2+}$ and Co$^{3+}$ cations are located in octahedral positions in the case of spinel at x > 0.3. So the stoichiometry of the spinel compound seems to be of substantial importance and the partial location of Cu$^{2+}$ in octahedral positions and the eventual displacement of Co$^{3+}$ cations from the octahedral positions results in promotion of the catalytic activity [14]. This is in accordance with the principle of bivalent catalytic sites [15, 16]. In the case of mixed oxides, calcined at 500°C, the increased catalytic activity is due to a large extent to the increased content of cobalt sites, which is confirmed once again by the XPS results.

CONCLUSIONS

The formation of deposited Cu-Co oxide phase has been studied on pure alumina and on modified alumina supports. The results from the XPS and the XRD investigations show that the best spinel form is obtained on alumina modified with 8 % MgO. The testing of the catalytic activity of the samples in the reduction of NO by CO illustrates the difference in their catalytic behavior. The highest activity is displayed by the KM3 catalyst sample, which confirms once again that the presence of MgO as modifying agent plays an important role in the formation of a stoichiometric Cu-Co spinel phase.
REFERENCES