Synthesis and investigation of highly dispersed active phases of intermetallic and supported SHS-catalysts

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Abstract. In the present study, the active phases (AP) of an Fe–Ni–Co–Mn catalyst produced from SHS-intermetallics (a), a catalyst prepared via formation an intermetallic layer on a mesh surface of chromium-nickel stainless steel (b), and of a Co–Mn catalyst prepared via SHS on silica gel support (c), were isolated and characterized by SEM and XRD. The catalysts studied were highly active in the process of deep oxidation and catalysts (b) and (c) were highly active in the process of CO₂ methanation as well. All AP had oxo-metallic composition and were formed from nanoscale components, but if the structure of these components for catalyst (a) was the same as on the surface of the catalyst, the structures of AP components for catalyst (b) significantly differed from the surface structures. In addition, AP sediment grain nanostructures of catalyst (c) differed from those of catalysts (a) and (b).

1. Active phases of intermetallic catalysts

Previously, a new class of polymetallic catalysts based on complex multicomponent intermetallic compounds, which are the product of self-propagating high-temperature synthesis (SHS), was developed. To obtain the catalysts, intermetallic alloys are crushed, leached in an alkali solution (NaOH, KOH) and stabilized by treatment with a solution of hydrogen peroxide. When leaching and stabilizing, the higher intermetallic phases reduce to disordered nanostructured oxo-metallic formations that form the catalytically active phase (AP) on the support from the remaining unleached lower intermetallic phases. The catalysts have high activity and selectivity in oxidizing and reducing processes, their specific surface reaches 50 m²/g [1–3].

Figure 1. SEM image of AP precipitate of 50%Fe–35%Ni–10%Co–5%Mn catalyst.
In the process of obtaining of the catalysts a small amount of AP forms a highly dispersed suspension, slowly precipitating from the reaction medium. This suspension was isolated and examined by scanning electron microscopy (SEM). Figure 1 presents the morphology of sediment powder and fine structure of an individual grain of AP of the Fe–Ni–Co–Mn catalyst of deep oxidation.

As can be seen in figure 1, the sediment granules are chaotic aggregates of the nanostructures of AP, apparently formed in the process of precipitation from an alkaline medium and subsequent washing and stabilization. It follows from table 1 that the grains of AP are oxo-metallic formations with an admixture of residual alumina (point 4). The nanostructures that make up the grains of precipitated AP are identical to those on the surface of the catalyst granules [3].

| Spot | O | Al | Mn | Fe | Co | Ni |
|------|---|----|----|----|----|----|
| 1    | 38.8 | 4.6 | 18.7 | 25.1 | 5.6 | 7.2 |
| 2    | 48.2 | 11.2 | 2.2 | 17.8 | 4.4 | 16.2 |
| 3    | 16.4 | 9.5 | 6.6 | 44.7 | 10.3 | 12.4 |
| 4    | 68.3 | 20.8 | 3.4 | 6.5 | - | 1.0 |

Catalysts closely related to the studied class of catalysts were obtained by activating polymetallic support such as stainless steel by forming an intermetallic layer on the surface with its subsequent leaching and stabilization as described above. The intermetallic layer was formed in the process of diffusion saturation of the surface with aluminum at \( T \approx 620 – 640 \) °C. If intermetallic compounds of other catalytically active metals are added to aluminum, catalysts with AP promoted with these metals can be obtained. The results of testing such catalysts in the processes of deep oxidation of CO and propane, as well as hydrogenation of CO\(_2\), are presented in figures 2 and 3.

**Figure 2.** Conversion of CO and propane vs. temperature in the process of deep oxidation on activated chromium–nickel stainless steel wire mesh, promoted with Co and V. Composition of gas mixture (in % vol): propane – 0.2, CO – 0.7, O\(_2\) – 2, N\(_2\) the rest. GHSV = 120000 h\(^{-1}\).

**Figure 3.** Concentrations of CO\(_2\), CH\(_4\) and CO vs. temperature in the process of CO\(_2\) hydrogenation on activated chromium–nickel stainless steel wire mesh, promoted with Co. Composition of gas mixture (in % vol.): CO\(_2\) – 2.3, H\(_2\) – 9.2, He the rest. GHSV = 3000 h\(^{-1}\).

As can be seen in figure 2, 50% of CO conversion is achieved already at \( T < 200 \) °C, and 50% of propane conversion is achieved at \( T < 275 \) °C. The maximum yield of methane in the hydrogenation of CO\(_2\) is 1.42% at \( T = 350 \) °C and total conversion of CO\(_2\) equal to 59.6% (figure 3).

Figure 4 shows micrographs (SEM) of the powder and a separate grain of the sediment of the stabilized AP precipitated from the leach solution. As in the previous case, the sediment grains are composed of formations of various shapes, sizes and composition, the elemental composition of the surface of which is shown in table 2.
The XRD results shown in figure 5 also indicate a highly defective, largely amorphized structure of aggregates consisting mainly of oxide phases with an admixture of metallic iron. Note that, in contrast to the previous case, the morphology of individual components of the grains differs markedly from the structures found in the composition of AP on surface of activated support [4].

Table 2. EDS results of the AP particle precipitate of stainless steel based catalyst in figure 4 (wt %).

| Spot | O   | Al  | Cr  | Mn  | Fe  | Ni  |
|------|-----|-----|-----|-----|-----|-----|
| 1    | 21.6| 18.9| 7.8 | -   | 48.2| 3.4 |
| 2    | 26.1| 15.8| 6.8 | -   | 48.0| 3.2 |
| 3    | 44.9| 11.0| 3.5 | -   | 35.5| 5.2 |
| 4    | 36.0| 12.8| 3.6 | 1.2 | 45.3| 1.1 |

Figure 5. XRD pattern of AP precipitate of stainless steel based catalyst.

2. Active phases of supported catalysts

A number of catalysts on various supports (γ-Al₂O₃, zeolites, silica gel, and halloysite) with AP based on Co, Ni, and Mn, obtained in low-temperature combustion mode, was studied. The supports were impregnated with a calculated amount of a mixture of solutions of metal nitrates (oxidizers) and urea (fuel), dried and heated in an argon atmosphere prior to the initiation of a combustion wave. The temperature in combustion wave reached 300–310°C. As in the previous case, the catalysts were washed and treated with a hydrogen peroxide solution to stabilize the phases of free metal. Their catalytic properties were studied in the processes of deep oxidation and hydrogenation of CO₂. Figures 6 and 7 show the results of testing samples of catalysts with nickel–cobalt and nickel AP on various supports.
Figure 6. Conversion of CO and propane vs. temperature in the process of deep oxidation on (10%Co+10%Ni)/ZSM-5 catalyst. Composition of gas mixture (% vol): propane – 0.2, CO – 0.7, O₂ – 2, N₂ the rest. GHSV = 120,000 h⁻¹.

Figure 7. Concentrations of CO₂, CH₄ and CO vs. temperature in the process of CO₂ hydrogenation on Ni10%/haloizite catalyst.
Composition of gas mixture (% vol): CO₂ – 3.9, H₂ – 11.8, He the rest. GHSV = 12,000 h⁻¹.

It is possible to note the high activity of the catalyst (10% Co + 10%Ni)/ZSM-5 in the process of deep oxidation, especially CO, for which complete conversion was achieved already at 200°C. The conversion of CO₂ in the process of hydrogenation on the catalyst 10% Ni/haloisite at a temperature of 350°C amounted to 82% with a selectivity to methane of 100%.

The study of the phase composition of AP on the surface of the catalysts is complicated by the fact that the high intensity of the support peaks in the X-ray diffraction spectra masks the weaker and more broadened peaks of AP. For a more detailed analysis of the structure and composition of AP, cobalt-nickel catalysts based on silica gel were synthesized. The catalysts were boiled in a solution of NaOH to dissolve the support and separate AP. The morphology and elemental composition of the washed precipitate of AP of (10%Co + 10%Ni)/SiO₂ catalyst is shown in figure 8 and table 3, respectively.

Figure 8. SEM image of AP precipitate of 10%Co + 10%Ni/SiO₂ catalyst.

Table 3. EDS results of AP precipitate particles of (10%Co + 10%Ni)/SiO₂ catalyst in figure 8 (wt %).

| Spot | O  | Si | Co  | Ni  |
|------|----|----|-----|-----|
| 1    | 7.4| 1.0| 47.1| 44.6|
| 2    | 21.2| 2.7| 40.4| 35.6|
| 3    | 18.8| 2.2| 33.6| 45.3|
| 4    | 4.7 | 0.7| 45.1| 49.5|
| 5    | 25.9| 4.5| 33.7| 35.8|
| 6    | 36.8| 3.7| 27.8| 31.7|
The isolated AP, as can be seen in figure 8, is a rather large (about 1 mm) debris fraction obtained by drying a bulk, poorly precipitating sediment with a large amount of residual water. The formation of such a structure is facilitated by the presence in the composition of the sediment (table 3) of a small amount of, apparently, hydrated silicon oxide, which plays the role of a binder. As follows from the high-resolution image in figure 8, these particles are formed (presumably in the process of precipitation) from granules with dimensions of the order of tens of nm and are highly porous formations. This fact is also confirmed by the nature of XRD spectrum (figure 6). The composition of the active phase, as follows from figure 6, contains both the phases of free metals (Co, Ni) and their oxides.

![Figure 9. XRD pattern of AP precipitate of (10%Co + 10%Ni)/SiO\(_2\) catalyst.](image)

From the foregoing, it can be concluded that the proposed methods for the synthesis of catalysts, both on the basis of intermetallic compounds and those produced in the combustion process on supports, make it possible to obtain catalysts with highly dispersed, nanostructured AP. All studied AP have oxometallic composition. Due in large part to these facts, such catalysts are highly active both in the process of deep oxidation of CO and hydrocarbons, and in the process of hydrogenation of CO\(_2\).

References
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