

The kinetic regularities of selective carbon monoxide oxidation over mixed oxide catalysts based on Cu, Co, Fe

Volodymyr Veselovskyi, Tatyana Zakharova,
Olena Ischenko

Physical Chemistry Chair, Chemical Department,
Taras Shevchenko National University of Kyiv, UKRAINE,
Kyiv, Volodymyrska street 64,
E-mail: veselovskyi.v@gmail.com

Abstract – The kinetics of CO and H₂ oxidation over mixed oxide catalysts based on transition metals (Cu, Co, Fe) were tested in the CO-PROX reaction. The experimental results showed that the CO oxidation rate was essentially independent of H₂ and O₂ concentrations, while the H₂ oxidation rate was practically independent of CO and O₂ concentrations. It was shown that the experimental kinetic regularities of CO oxidation could be described by the Mars-van Krevelen equation. In the CO oxidation, the reaction orders were 1 and 0 with respect to the partial pressure of CO and O₂, respectively.

Key words – mixed oxide catalysts, oxides of transition metals (Cu, Co, Fe), delafossite CuFeO₂, spinel, oxidation processes, CO-PROX reaction, catalytic oxidation of carbon monoxide, purification of hydrogen.

I. Introduction

The problem of finding alternative energy sources remains actual, which is associated with the growing needs of humanity and with the environmental problems that arise with using conventional energy sources. An alternative energy source can be fuel elements (FE), which is characterized by high efficiency and environmental safety.

The ideal fuel for FE is hydrogen, which could be obtained by steam reforming, partial oxidation or autothermal reforming of hydrocarbons followed by CO steam reforming. However, such hydrogen-containing gas mixtures contain about 1 vol.% CO, which is quite easy adsorbed on highly porous platinum anode of FE, reducing the efficiency of the fuel cell [1-3]. Thus, before feeding the gas mixtures, which are enriched with hydrogen, it is necessary to clean them from the CO impurities. Selective catalytic oxidation of carbon monoxide (CO-PROX reaction) is one of the simplest and the most effective method of removing CO.

The oxides of transition metals were chosen for investigation in the process of purification hydrogen-rich gas mixture from CO due to their cheapness and prevalence.

In previous studies [1, 3] three bimetal systems of mixed oxide catalysts (Cu-Co, Cu-Fe and Co-Fe) were examined in the CO-PROX reaction. According to these results the most active samples are very attractive for more detailed investigation with the following implementation in real operating conditions. Thus, the main aim of current research is to study the detailed

kinetic regularities and to offer the reaction mechanism of the selective CO oxidation.

II. Experimental

Mixed oxides of transition metals (Cu, Co, Fe) were prepared by dissolution of 1 g of metals mixture powder (all are Aldrich products) taken in appropriate ratios in 15 ml of 12 M nitric acid. The solution was evaporated at temperature below 100 °C on a sand bath up to wet sediment formation. Then the sediment was calcined at 250 °C and transported into thermo-programmed desiccator where dried for 1 h at 100 °C in an air atmosphere. Hereafter the notation used for the samples is referred to the relative mass percentage of each metal in the catalyst used for its preparation, *i.e.* Cu₂₅Fe₇₅ is a sample that contains 25 mass.% of Cu and 75 mass.% of Fe.

The specific surface area (S_{sp}) was determined by means of nitrogen physisorption at 77 K. The PXRD patterns of ground samples were collected using a DRON-4-07 diffractometer (filtered CoK $\alpha_{1,2}$ -radiation, $\lambda = 1.7903 \text{ \AA}$). The chemical nature of the surface of mixed oxide catalysts taken after the catalytic tests was examined by thermal program desorption followed by mass spectrometry measurements (TPD MS). The sample (0.1 g) was placed into a quartz reactor connected with a quadrupole mass-spectrometer (MX-7304 A), evacuated before the desorption runs and then heated using a linear heating regime with 14°C/min rate. The morphology and elemental analysis of the catalysts were determined using a Jeol JSM-6490 scanning electron microscope equipped with an Oxford Inca 350 energy dispersive X-ray spectrometer. The microscope was operated at 20 keV. The elements content obtained by the SEM-EDX microanalysis was represented as the mass ratio.

The catalytic activity of the samples in the oxidation of carbon monoxide in the presence of hydrogen was studied in a flow-type reactor at atmospheric pressure by chromatographic control (chromatograph Shimadzu GC-2014) of the reaction mixture. The kinetics of heterogeneous catalytic processes was studied using a differential reactor with piston swirl. The feed rate of the reaction mixture was 100 cm³/min ($1,67 \cdot 10^{-6} \text{ m}^3/\text{s}$). Separation of gases (H₂, O₂, CO, CO₂) was performed on a column of 1m length, filled with molecular sieves 5A (dispersion of 40-60 mesh), the current strength of the detector was 100 mA. The determination of the kinetic characteristics of the CO oxidation catalysts was carried out in the temperature range 90-160 °C with the weight of the sample 0.5 g. The determination period of the reaction rate at each temperature was about 30 minutes.

III. Results and discussion

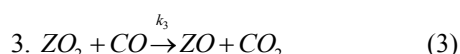
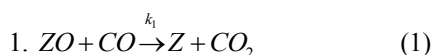
In order to study the detailed kinetic regularities as well to offer the reaction mechanism of selective oxidation of carbon monoxide over mixed oxide catalysts, the kinetic studies were performed for the most active samples from each bimetal oxide system and one less active sample, which were chosen based on the results of previous studies [1, 3].

From the data obtained it is clear that the reaction rate of CO oxidation depends linearly on the partial pressure of carbon monoxide, indicating the first reaction order with respect to CO. However, the rate of oxidation of CO is almost constant and independent of the partial pressure of O₂. Thus, the reaction order is the zeroth with respect to O₂.

The reaction order of the hydrogen oxidation is close to unity with respect to H₂ and is the zeroth with respect to O₂. It should be noted that the reaction rate of CO oxidation is independent of the partial pressure of H₂.

It should be noted that one of the most important factors is exactly the one that the CO oxidation is independent of the H₂ content in the reaction mixture. Other words, the mechanism of the carbon monoxide oxidation could be considered without the participation of hydrogen. Also it should be noted that the similarity of the nature of the kinetic curves for all the samples suggests that the reaction proceeds by the same mechanism.

Thus, it was suggested the following kinetic scheme of the reaction of selective CO oxidation:



where Z – reduced form of the active center of the surface of the oxide catalyst.

Thus, this scheme takes into account the possibility of oxygen adsorption both in the atomic (ZO) and in the molecular (ZO₂) forms. Also, it is assumed that in this scheme CO reacts directly from the gas phase. So, the experimental kinetic regularities of CO oxidation could be described by the Mars-van Krevelen equation.

This scheme corresponds to the following kinetic equation:

$$r = \frac{2k_2 p_{O_2} k_3 p_{CO}}{k_2 p_{O_2} (1 + \frac{k_3}{k_1}) + k_3 p_{CO}} \quad (4)$$

For the gaseous reaction mixtures with excess oxygen:

$$k_2 p_{O_2} (1 + \frac{k_3}{k_1}) \gg k_3 p_{CO} \quad (5)$$

Then:

$$r = \frac{2k_1 k_3 p_{CO}}{k_1 + k_3} = 2k_{ef} p_{CO} \quad (6)$$

where

$$k_{ef} = \frac{k_1 k_3}{k_1 + k_3} \quad (7)$$

According to the above equation, $k_{ef} = k_1$, if $k_1 \ll k_3$ or $k_{ef} = k_3$, if $k_1 \gg k_3$. So, k_{ef} is the rate constant of the

limiting stage of the interaction of CO with adsorbed oxygen in the atomic (step (1) of the scheme) or in the molecular (step (3) of the scheme) forms.

Appropriate effective activation energies are given in Table 1.

TABLE 1

THE KINETIC CHARACTERISTICS OF THE REACTION OF SELECTIVE OXIDATION OF CARBON MONOXIDE IN THE PRESENCE OF HYDROGEN FOR THE INVESTIGATED MIXED OXIDE CATALYSTS

Samples	E_{ef} , kJ/mol
Cu ₁₅ Co ₈₅	13.7±0.2
Cu ₈₅ Co ₈₅	33.0±0.3
Cu ₂₅ Fe ₇₅	56.5±2.2
Co ₃₅ Fe ₆₅	58.0±0.6

From the results shown in the table, it is clear that the most active catalyst Cu₁₅Co₈₅, which was prepared from 15 wt.% Cu and 85 wt.% Co, is characterized by the lowest effective activation energy and contains, according to Powder X-ray diffraction data analysis, a mixture of spinels: Co₃O₄ and CuCo₂O₄.

Conclusion

Based on the above mentioned data, one can draw the following conclusions. The reaction rate of CO oxidation is not dependent on H₂. The experimental kinetic regularities of CO oxidation could be described by the Mars-van Krevelen equation. The carbon monoxide oxidation on the mixed oxide catalysts is described by the first reaction order with respect to CO and by the zeroth reaction order with respect to O₂. The hydrogen oxidation is described by the near to the first reaction order with respect to H₂ and the zeroth reaction order with respect to O₂.

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