

THERMODYNAMIC EVALUATION OF NON-EQUILIBRIUM COMPOSITIONS AND ACTIVITY OF MULTICOMPONENT CATALYSTS IN REDOX REACTIONS

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Abstract

The analysis of structural state and energetic properties of active catalyst component in oxide copper-containing catalytic system has been performed on the basis of comparing the data of thermochemical, X-ray diffraction and catalytic activity determinations. The analysis of thermochemical data obtained makes it possible to evaluate changes in lattice energy and the nearest coordination sphere energetic parameters of copper cations during the formation of solid solutions. The high degree of correlation of catalytic properties and the formation enthalpy of solid solutions can be explained by the fact that alongside with the factors influencing the catalytic activity it is the strength of cation–cation interaction that is the most important.

Keywords: carbon oxide conversion, catalytic activity, formation enthalpy, oxide solid solutions

Introduction

The development of new catalysts and the prediction of their life require long and expensive industrial tests. The application of thermochemical methods for the study of catalysts allows a significant increase in the research of effective catalysts and sorbents. Many authors consider that only on the basis of a definite amount of information on thermodynamic parameters of multicomponent systems one can predict the period of the effective stable activity of catalysts [1–3].

Copper-containing oxide catalysts used during the formation of hydrogen and some alcohols differ because their catalytic activity and stability in work depend greatly upon the phase structure. The phase structure of such catalysts can be represented by individual oxides of metals, and non-equilibrium, metastable compounds – solid solutions as well. These compounds have required catalytic properties.

Experimental

The samples were prepared by coprecipitation of copper, zinc and magnesium by neutralizing the solutions of their nitrates with sodium carbonate solution at pH=7. The conditions of coprecipitation were selected to afford the maximum degree of the interaction of compounds. During the thermal treatment of coprecipitated systems (for CuO–ZnO $T=250^{\circ}\text{C}$, for Cu–Mg samples $T=300^{\circ}\text{C}$) a solid oxide solution was formed.

The analysis of structural state and energetic parameters of an active component in copper-containing catalysts in the samples being formed has been carried out on the basis of comparing the data of thermochemical, X-ray diffraction and catalytic activity determinations.

The formation enthalpy of solid solutions of copper and zinc oxides, copper and magnesium oxides is measured in the calorimeter with an isothermal shell at the dissolution of a sample in 10% H_2SO_4 . The values of thermochemical parameters were calculated as the difference between experimentally obtained enthalpy of catalyst composition dissolution and the mechanical mixture of oxides.

The catalytic activity of specimen was estimated as the rate of test reactions during carbon oxide conversion. The catalyst was loaded into reactor and reduced by a gaseous mixture (50 vol% H_2 , 50 vol% Ar). The tested catalyst was heated at speed 4 degree per minute up to 220°C . At this temperature the catalyst was reduced within 1 h. The initial gaseous mixture for reaction had the structure (vol%): CO – 12; CO_2 – 9; H_2 – 55; Ar – rest. A ratio of water vapour and the sum of dry gases equals $0.7 \div 1$. The gaseous mixture was passed through the catalyst at volumetric speed 5000 l h^{-1} . The catalytic activity of samples was estimated according to the reaction rate constant by the equation:

$$K = \frac{\ln\left(\frac{100}{100-x}\right)^{(1+n)}R}{60g_c} \quad (1)$$

where R – dry gases flow rate, $\text{ml}^3 \text{ min}^{-1}$; x – CO conversion ratio, %; n – the water vapour and the sum of dry gases ratio; g_c – catalyst samples mass, gr.

Results and discussion

The isolated cations or copper clusters dissolved in zinc or magnesium oxide crystalline lattice is the active component of oxide copper-containing catalyst [1]. The catalysts are more often heterogeneous and consist of a phase of a solid solution and that of individual oxides. The X-ray analysis data of Cu–Zn and Cu–Mg catalysts testify to the availability of the crystal and X-ray amorphous phases of copper, zinc and magnesium oxides (Fig. 1). X-ray amorphous phase in its turn contains a phase of a solid solution of copper in zinc or magnesium oxides and the phases of low temperature oxides with a high level of defects in a crystalline lattice which do not give a pre-

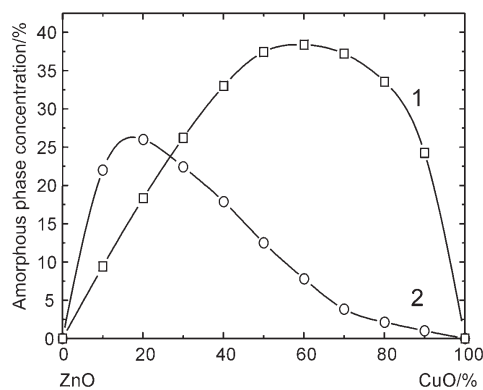


Fig. 1a Change of phase structure in co-precipitated copper–zinc oxide system. The content of X-ray amorphous phase. 1 – CuO; 2 – ZnO

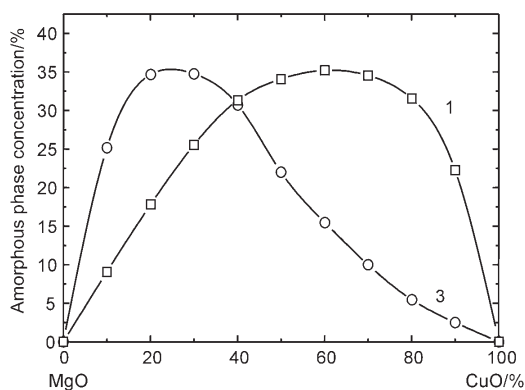


Fig. 1b Change of phase structure in co-precipitated copper–magnesium oxide system. The content of X-ray amorphous phase. 1 – CuO; 3 – MgO

cise diffraction picture. Thus, the X-ray phase analysis data do not allow to determine the concentration of a solid solution.

The data on the parameters changes of a thin crystalline structure calculated on the basis of X-ray structural analysis testify that in the 10 to 50% concentration range for CuO maximum distortions of copper and zinc oxides crystal lattice are observed. The structural distortions of a copper oxide lattice are higher, than those of zinc oxide. When CuO concentration is decreased less than 50%, the crystallite size is reduced to the values less than 10 nm, and the microdeformations are increased up to 2% and above. When the concentration of copper oxide is less than 40%, the interference picture of CuO phase is not fixed (Fig. 1).

The crystal structures of pure oxides, for example, copper and zinc oxides (Fig. 2) differ greatly. In CuO (tenorite) the copper cations form 4 bonds with an anion of oxygen with the length $d=0.195$ nm and the energy $E_{\text{Cu-O}}=145$ kJ mol⁻¹ and 1

Cu–Cu bond with the length $d=0.29$ nm and the energy $E_{\text{Cu-Cu}}=159$ kJ mol⁻¹. The enthalpy of a CuO crystal lattice is a sum of 4 Cu–O bonds energy and the energy of Cu–Cu metal bond.

$$E_{\text{CuO}}=4E_{\text{Cu-O}}+E_{\text{Cu-Cu}}=4\times 145+159=739$$
 kJ mol⁻¹ (2)

Zinc oxide crystallizes in a hexagonal structure of wurtzite (Fig. 2a). The ions of zinc are in tetrahedral vacancy of the most dense oxygen packing with the lengths of bonds $d=0.195$ nm and energy $E_{\text{Zn-O}}=215$ kJ mol⁻¹. The enthalpy of a ZnO crystal lattice is a sum of 4Zn–O bonds energy.

$$E_{\text{ZnO}}=4E_{\text{Zn-O}}=4\times 215=860$$
 kJ mol⁻¹ (3)

The formation of the solid solution phase is accompanied by the distortions in individual oxide structures. That results in the growth of a crystal lattice energy of the system being formed. To some extent the crystal lattices of both oxides are subjected to distortions. The oxide, the structure of which is changed a greater extent, is considered to be dissolved in an oxide – solvent matrix. For a theoretical evaluation of energy, which is needed for a solid solution formation, it is necessary to find out, what structural distortions in the system formed can happen.

For a thermodynamic evaluation of probable directions of restructuring the processes in CuO (tenorite), ZnO (zinkite) and MgO (periclas) during the formation of a

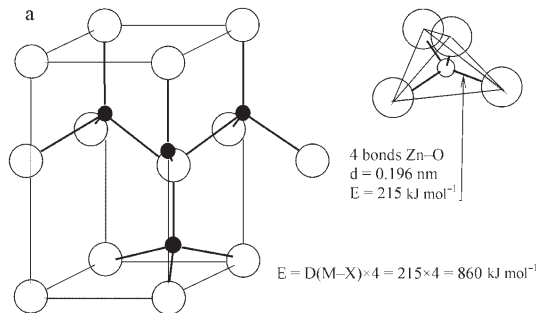


Fig. 2a Crystalline structure and energetic parameters of CuO

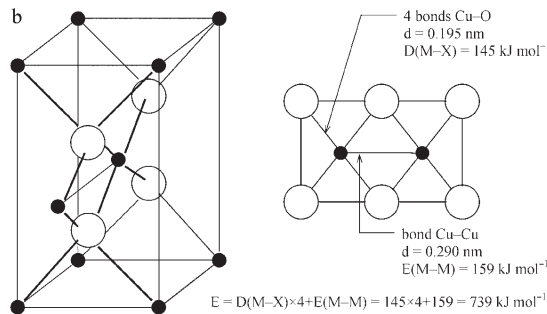
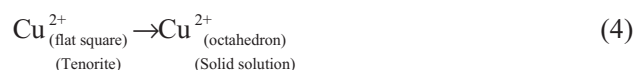


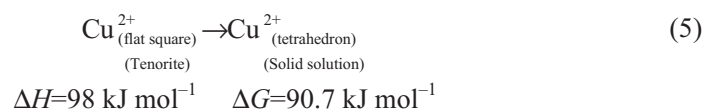
Fig. 2b Crystalline structure and energetic parameters of ZnO

solid solution the values of structural transitions energy in oxygen polyhedrons of various co-ordination are used:

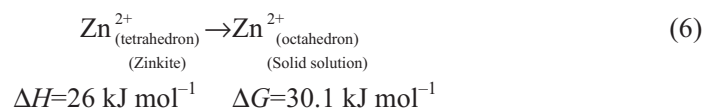


The Cu(II) ion in tenorite crystal lattice is in flat square environment by oxygen anions [4]. But sometimes the co-ordination number for a copper ion in tenorite equals 4+2, taking into account 2 remote oxygen anions ($d=0.278$ nm). Thus, the flat-squared co-ordination of a copper ion is an intermediate structure between tetrahedral and octahedral co-ordinations. The character of Gibbs energy change testifies, that the Cu(II) transition from flat square to octahedral environment is connected with smaller expenditure of energy as compared with the transition into tetrahedral co-ordination.

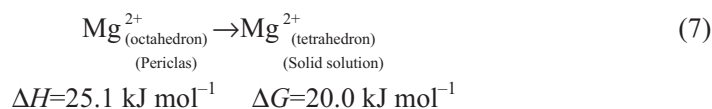
The copper ion transition into tetrahedral co-ordination at dissolution in oxides of zinc and magnesium is improbable because of high value of Gibbs energy and the enthalpy [4].



The zinc ions in a zinkite crystal lattice are in tetrahedral co-ordination. The change in an oxygen polyhedron in zinc oxide during the formation of a solid solution is improbable due to significantly high energy transition values from tetrahedral co-ordination into octahedral.



The magnesium ions in a periclas crystal lattice are in octahedral co-ordination. As in the case of zinc oxide, the change in an oxygen polyhedron in magnesium oxide during the formation of a solid solution is improbably due to rather high energy transition values from octahedral co-ordination into tetrahedral.



The thermodynamic evaluation of reorganising the co-ordination oxygen polyhedrons of copper(II) and zinc(II) ions shows, that metastable solid solutions ($\Delta G > 0$) are most likely to be formed, in which the structural changes in the nearest anion environment of copper ions are energetically more preferable as the enthalpy and Gibbs energy for Cu^{2+} (flat square, tenorite) \rightarrow Cu^{2+} (octahedral, solid solution) process are minimum.

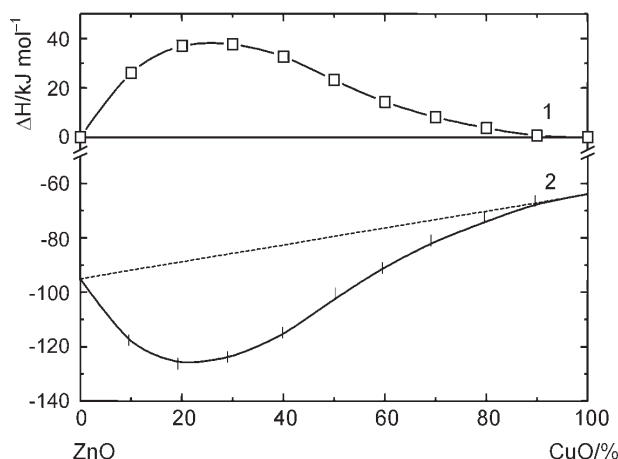


Fig. 3 Enthalpy of dissolution and formation of a solid solution in copper–zinc oxide system. 1 – $\Delta H_f(\text{Cu,Zn})\text{O}$; 2 – experimental data of dissolution in sulphuric acid

From the data given above it follows that thermodynamically the formation of solid solutions based on zinc oxide in CuO–ZnO system, and those based on magnesium oxide in CuO–MgO system is most probable.

The research of solid solutions structure in CuO–ZnO and CuO–MgO systems by electron paramagnetic resonance, electronic spectroscopy and X-ray-photoelectronic spectroscopy methods [1] confirms that in zinc(II) and magnesium(II) oxides the copper(II) has octahedral positions. High copper concentrations in the structure of the nearest environment of oxygen anions produce axial distortions of an octahedron, and flat square environment of Cu(II) is formed. Simultaneously with the increase of distortions the far order of a solid solution is destroyed, which results in the appearance of copper(II) oxide phase.

The formation enthalpy of a solid solution ($\Delta H_{f,\text{solid solution}}$) is determined as the difference of the dissolution enthalpy of mechanical mixture of oxides ($\Delta H_{\text{solv,CuO}}^0 C_{\text{CuO}} + \Delta H_{\text{solv,ZnO}}^0 C_{\text{ZnO}}$) and the dissolution enthalpy of an investigated system ($\Delta H_{\text{solv,catalyst}}^0$).

$$\Delta H_{f,\text{catalyst}} = \Delta H_{\text{dissolv,CuO}} C_{\text{CuO}} + \Delta H_{\text{dissolv,ZnO}} C_{\text{ZnO}} - \Delta H_{\text{dissolv,catalyst}} \quad (8)$$

The dependence of the formation enthalpy of a catalyst is of extreme character. The maximum value of the formation enthalpy in Cu–Zn oxide system is achieved when the content of CuO in ZnO is 20–30 mass% and equals $36 \pm 4 \text{ kJ mol}^{-1}$ (Fig. 3); when the concentration of CuO in MgO is 25–40 mass% the formation enthalpy equals $45 \pm 4 \text{ kJ mol}^{-1}$ (Fig. 4). In high CuO concentration range in both systems the formation enthalpy of a solid solution is sharply decreased and when CuO content is above 80%, $\Delta H_{f,\text{solid solution}}$ equals zero.

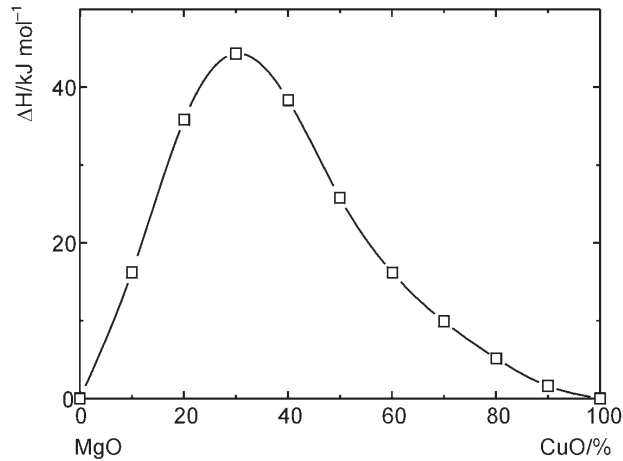


Fig. 4 Enthalpy of solid solution formation in oxide copper–magnesium system

The formation of a solid solution of copper ions in zinc and magnesium oxides was verified by thermochemical research of solid solutions in the CuO–ZnO and CuO–MgO systems in a broad range of concentrations.

The calculation of solid solution formation energy is conducted with the allowance for enthalpies of co-ordination change of Cu(II) cation (ΔH_K), the enthalpy is stipulated by a high dispersibility of the components (ΔH_S), and the enthalpy of a cation – cation bond destruction in a copper oxide.

The contribution of the copper(II) ion transfer from flat square environment into octahedral co-ordination (ΔH_K) with the registration of a molar fraction of the dissolved copper oxide (C_{CuO}) in the integral thermal effect of solid solution formation (ΔH_1) is 10–20% (3–6 kJ mol⁻¹).

$$\Delta H_K = \Delta H_1 C_{CuO} \quad (9)$$

For a correct evaluation of the enthalpy of low-temperature solid solution formation in CuO–ZnO and CuO–MgO systems it is necessary to take the energy achieve fine crystalline structure state (ΔH_S) into account. The influence of the crystallite size (D) on the dissolution enthalpy is calculated on the basis of the values of surface energy (E_s), molecular mass (M) and density (ρ):

$$\Delta H_S = \frac{6E_s M}{\Delta D\rho} \quad (10)$$

The calculation was based on the assumption that ΔH_S value is proportional to a specific crystallite surface, multiplied by the surface energy. The surface energy for copper oxide is taken $E_{s,CuO} = 0.6 \text{ J m}^{-2}$ and for zinc oxide $E_{s,ZnO} = 0.7 \text{ J m}^{-2}$. The calculations show that with the decrease of the crystallite size (D) from 100 to 10 nm the enthalpy of dissolution for CuO is increased 0.5 kJ mol⁻¹, and for ZnO – 0.7 kJ mol⁻¹ [5].

The analysis of the structure and the bonding energy for copper and zinc oxides shows that alongside with a cation–anion interaction it is necessary to take the interaction arising directly between the cations (Fig. 2b) into account. Among the considered oxides the oxide of copper exhibits the strongest cation–cation interaction. The energy of a cation–cation interaction in oxides of zinc and magnesium is small and it was not taken into account in the calculation. The number of cation–cation destructed bonds during CuO–ZnO and CuO–MgO solid solutions formation is proportional to the molar fraction of the dissolved component (C_{CuO}).

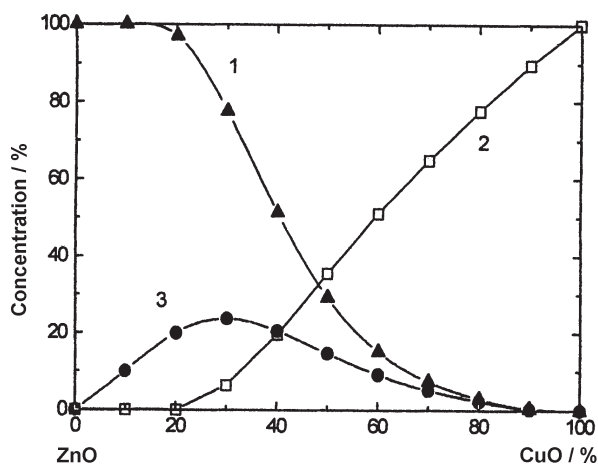


Fig. 5 Influence of reagents parity on copper ions dissolution degree in zinc oxide; 1 – degree of copper ions dissolution in zinc oxide; 2 – part of unsolved copper; 3 – part of dissolved copper

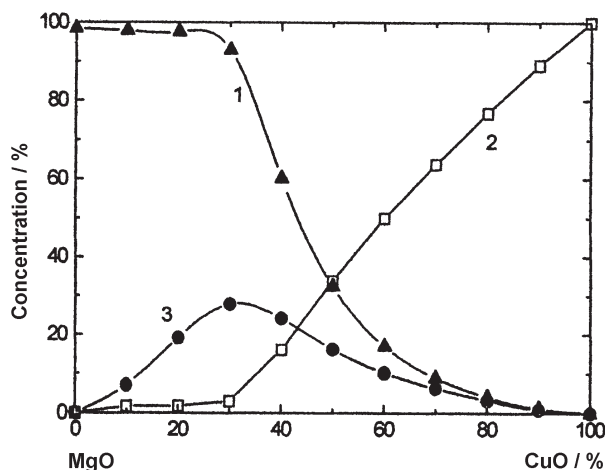


Fig. 6 Influence of reagent parity on copper ions dissolving degree in magnesium oxide; 1 – degree of copper ions dissolution in magnesium oxide; 2 – part of unsolved copper; 3 – part of dissolved copper

$$\Delta H_{\text{Cu-Cu}} = E_{\text{Cu-Cu}} C_{\text{CuO}} \quad (11)$$

Taking into consideration the above given model of solid solution formation it is possible to calculate energetic parameters, using the data of thermochemical measurements, the degree of dissolution of a copper oxide in the second oxide lattice according to the formula:

$$\Delta H_{\text{f solid solution}} = \Delta H_{\text{k}} C_{\text{CuO}} + \frac{6E_{\text{SCuO}} M_{\text{CuO}}}{\Delta D_{\text{CuO}} \rho_{\text{CuO}}} + \frac{6E_{\text{SZnO}} M_{\text{ZnO}}}{\Delta D_{\text{ZnO}} \rho_{\text{ZnO}}} + E_{\text{Cu-Cu}} C_{\text{CuO}} \quad (12)$$

The calculations of the dissolved copper(II) quantity in solid solutions for copper–zinc and copper–magnesium catalysts, according to the formula given above are shown in Figs 5, 6. The highest concentrations of dissolved copper for both systems can be obtained when CuO contents in a specimen is from 20 up to 40%.

The values of the enthalpy of solid solution formation and catalytic activity depending on CuO/ZnO and CuO/MgO ratio have a high degree of a correlation. The maximum rate constant in CO oxidation reactions with water vapour for the oxide copper–zinc composition is obtained at 20–25% CuO concentration in a solid solution and equals $10.4 \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$ (Fig. 7). The similar dependence is obtained for Cu–Mg catalyst.

On the basis of the calorimetric data the thermodynamic analysis of solid solutions of copper and zinc oxides, copper and magnesium oxides obtained by a co-precipitation method is conducted. The evaluation of energetic expenditures of reorganising the nearest co-ordination environment of cations and the changes of fine crystalline structure parameters is given. It is established, that at 20–30% CuO contents the formation enthalpy of a solid solution from oxides reaches the maximum value and equals 35–37 kJ mol⁻¹, for Cu–Mg catalyst the maximum value of the enthalpy is ob-

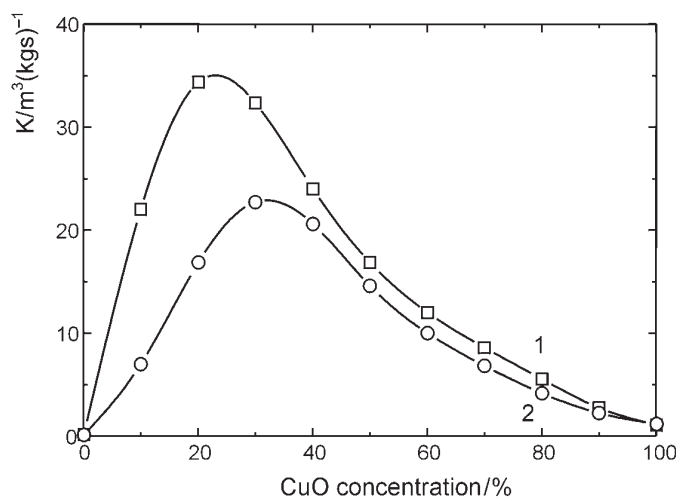


Fig. 7 Catalytic activity of copper–zinc (1) and copper–magnesium (2) oxide catalysts in water gas reaction

tained at 25–40% CuO concentration and equals 40–45 kJ mol⁻¹. It is shown, that the relation of the formation enthalpy of a solid solution and the catalytic activity on CuO/ZnO and CuO/MgO ratio have similar character of changing.

The total energy of a solid solution formation consists of three parts. The reorganization of the nearest co-ordination environment of copper ions in total energy of solid solution formation is 10–15%. The change of thin crystalline structure parameters is 0.5–2% of total energy. The greatest contribution into the enthalpy of a solid solution formation is made by the energy a cation–cation interaction between Cu(II) ions and it makes 80–90%.

Thus, the conducted researches show that the concentration of isolated atoms of copper dissolved in zinc or magnesium oxide, greatly influences the formation enthalpy of a solid solution and its catalytic activity.

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