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Physical Chemistry

Thermodynamic Analysis of CoO, NiO, CuO, FeO Interaction with Methane

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ABSTRACT. Complete thermodynamic analysis of reduction of CoO, NiO, CuO, FeO by methane is presented. Initial structures have been chosen on the basis of the following reactions: 1. $CoO_{(cd)} + CH_{4(gas)}$; 2. $NiO_{(cd)} + CH_{4(gas)}$; 3. $4CuO_{(cd)} + CH_{4(gas)}$; 4. $4FeO_{(cd)} + CH_{4(gas)}$; 5. $4FeO_{(cd)} + 2CH_{4(gas)}$.

The calculations are performed at atmospheric pressure in the temperature range 300-1500 K with application of computer program ASTRA-4.

The basic results are presented in the form of diagrams (dependence of the contents of components on temperature). *© 2010 Bull. Georg. Natl. Acad. Sci.*

Key words: *oxide, reduction, methane.*

Complete thermodynamic analysis (CTA) of the reduction of CoO, NiO, CuO, FeO by methane is accomplished. We have not found any data on CTA of these systems in the literature.

The thermodynamic modelling was performed on computer by application of ASTRA-4 programme [1] at the general atmospheric pressure (101 kPa) and the temperature range of 350-1500K.

Initial structures are chosen on the basis of the following reactions:

1. $CoO_{(cd)} + CH_{4(gas)}$;
2. $NiO_{(cd)} + CH_{4(gas)}$;
3. $4CuO_{(cd)} + CH_{4(gas)}$;
4. $4FeO_{(cd)} + CH_{4(gas)}$;
5. $4FeO_{(cd)} + 2CH_{4(gas)}$.

H_2O, C, Co, CoO, Co_3O_4, $Co(OH)_2$, Ni, NiO, $Ni(OH)_2$, Cu, CuO, Cu_2O, $CuCO_3$, Cu_2O_3, $Cu(OH)_2$, Fe, FeO, Fe_2O_3, Fe_3O_4, $Fe(OH)_2$, $Fe(OH)_3$, Fe_3C have been considered among the probable condensed components. Gaseous: O, O_2, O_3, H_2, OH, HO_2, H_2O_2, H_2O, C, C_2, C_3, C_4, C_5, CO,CO_2, C_2O, C_3O_2, CH, CH_2, CH_3, CH_4 (Because of the great number of gaseous connections of the C-H-O system only some of them are specified) Co, CoO, $Co(OH)_2$, CoH, Ni, NiO, $Ni(OH)_2$, NiH, Cu, CuH, $Cu(OH)_2$, Fe, FeO, FeOH, FeO_2.

The basic results of the complete thermodynamic analysis (CTA) are presented in diagrams.

Fig.1 shows the dependence of the component's contents (concentration) in the system on the temperature for reaction 1. It is obvious that the process of reduction begins below 350 K and this reaction ends completely at 450 K (cobalt is completely restored).

In 350-1500K temperature range a change of the quantity of components is observed in the gas phase. It is clear from the diagram that below 350 K the system contains Co, unrestored CoO and gaseous components (CH_4 and H_2). At this point to eduction of condensed carbon also starts. A preliminary thermodynamic analysis of dissociation of methane (CH_4) has shown that below 400 K there takes place its partial dissociation with release of H_2, and above 400 K - of condensed carbon. It is most likely that these components (H_2 and

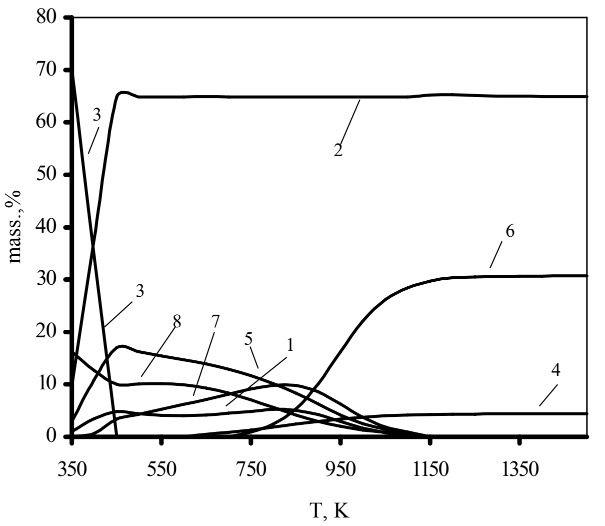

Fig.1. Dependence of the components contents (concentration) in system on the temperature for reaction 1: 1-C, 2-Co, 3-CoO, 4-H_2, 5-H_2O, 6-CO, 7-CO_2, 8-CH_4.

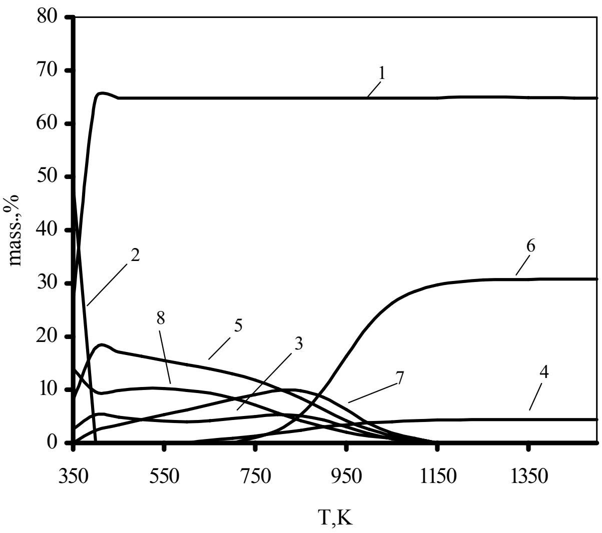

Fig.2. Dependence of the components contents (concentration) in system on the temperature for reaction 2: 1-Ni, 2-NiO, 3-C, 4-H_2, 5-H_2O, 6-CO, 7-CO_2, 8-CH_4

C) restore CoO and formation of H_2O and CO_2 takes place in the system. The quantity of H_2O sharply increases up to 450K (the end of the reduction process) and that of CO_2 – up to 800 K. Above these temperatures the quantity of H_2O and CO_2 in the system decreases and at 1150 K these connections disappear completely. H_2 and CO in the gas phase appear at ~ 600K and ~700 K respectively. With the rise of temperature the quantity of H_2 smoothly increases up to ~1050 K, and the quantity of CO sharply increases up to ~1150 K. With an increase of temperature the concentration of CH_4 decreases and at ~1150K disappears completely.

The thermodynamic analysis has shown that above 1150K the basic reaction proceeds with release of metal Co and gaseous CO and H_2, which is in good agreement with [2]:

$$CoO_{(cd)} + CH_{4(gas)} = Co_{(cd)} + CO_{(gas)} + 2H_{2(gas)};$$

A similar picture is observed at reduction of NiO by methane (Fig. 2). Comparing the results of the thermodynamic analysis of the reduction of NiO and CoO it is possible to conclude that restoration process of NiO comes to an end at lower temperatures (~ 400K) than in the case of CoO. Above 1150K the basic reaction of reduction of NiO also proceeds with release of metal Ni and gaseous CO and H_2:

$$NiO_{(cd)} + CH_{4\,(gas)} = N_{(cd)} + CO_{(293)} + 2H_{2\,(gas)};$$

Complete thermodynamic analysis (CTA) of the reduction of copper oxide (CuO) by methane (CH_4) for reaction 3 has been carried out.

Fig. 3 shows the dependence of the components contents (concentration) in the system on the temperature for reaction 3. It is seen that the process of reduction proceeds and completely ends below 300 K. In the form of gas phase only CO_2 and H_2O are educed and their quantity in 400-1500 K temperature range does not change. The basic reaction proceeds with the formation of metal Cu and gaseous - CO_2 and H_2O:

$$4CuO + CH_4 = 4Cu + CO_2 + 2\,H_2O$$

According to the experimental data, the reduction process of copper oxide proceeds at 100ºC.

Fig.4 shows the dependence of the components contents (concentration) in the system on the temperature for reaction 4. The reduction process here proceeds below 400 K, with educed Fe, whose quantities reduce to ~750 K; further, it rises up to ~1300 K and achieves a maximum (43mass. %). FeO in the system is

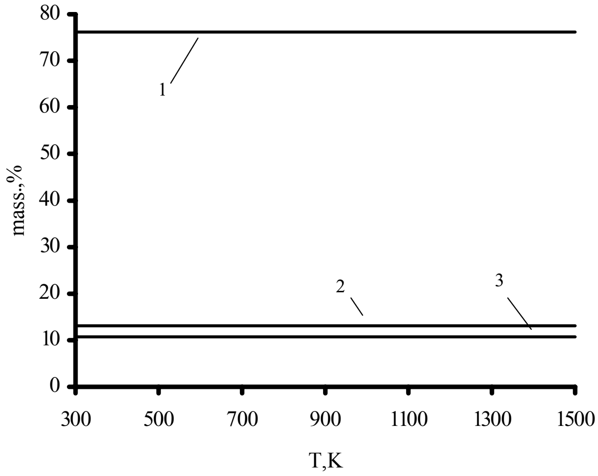

Fig. 3. Dependence of the components contents (concentration) in system on the temperature for reaction 3: 1-Cu; 2-CO_2; 3-H_2O

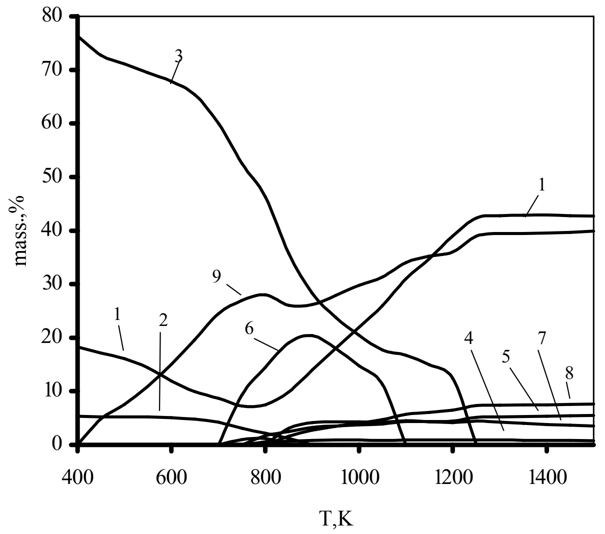

Fig.4. Dependence of the components contents (concentration) in system on the temperature for reaction 4: 1-Fe, 2-CH_4, 3-Fe_3O_4, 4-H_2, 5-H_2O, 6-Fe_3C, 7-CO_2, 8-CO, 9-FeO

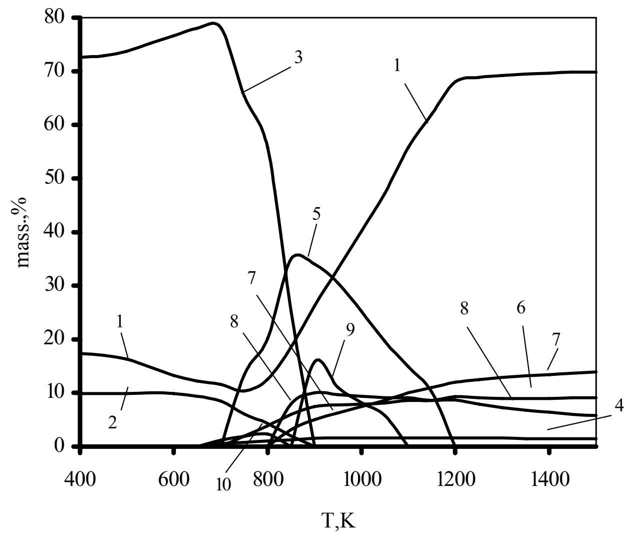

Fig. 5. Dependence of the components contents (concentration) in system on the temperature for reaction 5: 1-Fe, 2-CH_4, 3-Fe_3O_4, 4-H_2, 5-Fe_3C, 6-H_2O, 7-CO, 8-CO_2, 9-FeO, 10-C

educed below 450 K, quantity of which rises, achieving ~ 40mass.%. Fe_3O_4 in the system decreases and fully disappears below ~1250 K. Iron carbide is in a narrow temperature range (~750 – 1100 K). It is seen from the diagram that the reduction process does not occur up to the end - probably because of the shortage of a reducer.

The structure of the gas phase changes at 400-1500K temperature range. It is clear from the diagram, that below and above 400 K gaseous CH_4 is educed in the system, completely disappears at ~850 K. Above ~800K CO, CO_2, H_2O, H_2 are educed in the gas phase.

A similar picture is observed at reduction of iron in accordance with reaction 5. The only difference here is that the reduction process comes to an end at ~1200 K (or iron is reduced completely) (Fig. 5).

ფიზიკური ქიმია

CoO, NiO, CuO, FeO-ს მეთანთან ურთიერთქმედების თერმოდინამიკური ანალიზი

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ნაშრომში წარმოდგენილია CoO, NiO, CuO, FeO-ს მეთანით აღდგენის სრული თერმოდინამიკური ანალიზი შემდეგი რეაქციებისათვის: 1. $\mathbf{CoO_{(კ)} + CH_{4(აირი)}}$; 2. $\mathbf{NiO_{(კ)} + CH_{4(აირი)}}$; 3. $\mathbf{CuO_{(კ)} + CH_{4(აირი)}}$; 4. $\mathbf{4FeO_{(კ)} + CH_{4(აირი)}}$; 5. $\mathbf{4FeO_{(კ)} + 2CH_{4(აირი)}}$.

ანგარიში შესრულებულია ატმოსფერულ წნევაზე 300-1500 K ტემპერატურულ შუალედში ASTRA-4 კომპიუტერული პროგრამის გამოყენებით.

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