CALCULATION OF THE HEAT OF SURFACE CLUSTER FORMATION AND OXYGEN ADSORPTION ON COPPER-MAGNESIUM OXIDE CATALYSTS BY THE INTERACTING BONDS METHOD

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The heat of copper cluster formation on MgO surface has been calculated by the interacting bonds method. Oxygen adsorption on these catalysts is discussed.

Методом взаимодействующих связей рассчитаны теплоты образования кластеров меди на поверхности окиси магния. На этих катализаторах рассмотрена адсорбция кислорода.

The calculation of the heat of copper cluster formation in the bulk MgO lattice by the interacting bonds method (IBM) is discussed in Ref. /1/. In the present study the results obtained earlier are used to calculate thermodynamic data referring to the surface, viz. the heat of formation of surface copper clusters and oxygen adsorption on them.

All calculations were performed for the (100) plane of the NaCl lattice, which has the smallest surface energy and, hence, should be the most developed in polycrystalline samples.

Dissociative adsorption of oxygen is considered in one-center (MO) form, since according to Ref. /2/, this form is the most active in the catalytic reactions of complete oxidation.

The heat of formation of surface copper clusters from an infinitely dilute solid solution of CuO in MgO (ΔH₅) was calculated using the following thermodynamic scheme
1. \[ n\{\text{CuO}_6\} \text{Mg}_n\text{O}_{n-6n} \rightarrow n\text{Cu} \text{(g)} + 6n\text{O} \text{(g)} + \{ \} \text{Mg}_{n-n} \text{O}_{n-6n} \] (\(\Delta H_1\))

2. \[ \{\text{Mg}_n\text{O}_m\} \text{Mg}_{n-n} \text{O}_{n-m} \rightarrow n\text{Mg} \text{(g)} + m\text{O} \text{(g)} + \{ \} \text{Mg}_{n-n} \text{O}_{n-m} \] (\(\Delta H_2\))

3. \[ \{ \} \text{Mg}_{n-n} \text{O}_{n-m} + n\text{Cu} \text{(g)} + m\text{O} \text{(g)} \rightarrow \{\text{CuO}_n\} \text{Mg}_{n-n} \text{O}_{n-m} \] (\(\Delta H_3\))

4. \[ \{ \} \text{Mg}_{n-n} \text{O}_{n-6n} + n\text{Mg} \text{(g)} + 6n\text{O} \text{(g)} \rightarrow n\text{MgO} \] (\(\Delta H_4\))

\[ n\{\text{CuO}_6\}_6 \text{Mg}_{n-n} \text{O}_{n-6n} \rightarrow \{\text{CuO}_n\}_n \text{Mg}_{n-n} \text{O}_{n-m} \] (\(\Delta H_s = \sum_{i=1}^{4} \Delta H_i\))

where

\[ \{\text{CuO}_6\} \text{Mg}_{n-1} \text{O}_{n-6} \] is a copper ion with its nearest-neighbor oxygen environment in the infinitely dilute solid solution of CuO in MgO;

\[ \{ \} \text{Mg}_{n-1} \text{O}_{n-6} \] is the corresponding bulk cluster vacancy in the MgO lattice;

\[ \{ \} \text{Mg}_n\text{O}_m \] is a section of the MgO surface with \(n\) atoms of Mg and \(m\) atoms of oxygen associated with the former;

\[ \{ \} \text{Mg}_{n-n} \text{O}_{n-m} \] is the corresponding cluster vacancy on the MgO surface;

\[ \{\text{CuO}_n\} \text{Mg}_{n-n} \text{O}_{n-m} \] is the copper cluster on MgO surface under study.

The heat of atomization (or of the reverse processes) of the stages \(\Delta H_i\) involved in the scheme were calculated by a method similar to that employed for calculating the heat of formation of copper clusters in the MgO lattice. The bond coefficients in the crystal bulk found in Ref. /1/ were used.

The above thermochemical scheme permits calculation of the \(\Delta H_s\) values for isolated surface copper ions and nine copper clusters whose structures and composition are listed in Table 1.

The calculation has shown that the emergence of isolated surface copper ions from the bulk of an infinitely dilute solution is accompanied by a maximum heat evolution (Table 1, No. 1). Hence, at low concentrations of copper and as long...