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NOTE

Activity of Cu^{2+} Ions on the Tetrahedral and Octahedral Sites of Spinel Oxide Catalysts for CO Oxidation

In studies of CO oxidation on substituted copper chromite spinel oxide catalysts it was observed that the catalytic activity of a normal $Cu[Cr_2]O_4$ spinel oxide catalyst decreases as the Cu^{2+} content of the catalyst decreases, either by substitution with a divalent ion, i.e., Cu_{1-x} Mg_x $[Cr_2]O_4$, or by reduction of Cu^{2+} to Cu^{1+} (1). Crystallographic studies have shown that $Cu[Cr_2]O_4$ changes from normal to partially inverse when Cr^{3+} is replaced by Al^{3+} (2). Thus, in aluminum-substituted copper chromite catalysts, copper is present on both tetrahedral and octahedral sites of the spinel lattice, i.e., Cu_{1-x} Al_x $[Cu_xCr_{2-(x+y)}$ $Al_y]O_4$. ESCA studies have shown that upon Al substitution some of the tetrahedral Cu^{2+} ions are reduced to Cu^{1+} and this causes a reduction in the catalytic activity of the catalysts (1). The present work was taken up to compare the activity of Cu^{2+} on tetrahedral sites with that on octahedral sites of the spinel oxide catalyst. For this, CO oxidation studies were carried out on the inverse spinel $CuFe_2O_4$ and on the normal spinel $CuRh_2O_4$ catalysts.

In $Cu[Rh_2]O_4$, similar to $Cu[Cr_2]O_4$, Cu ions occupy the tetrahedral sites exclusively (3), while those in $CuFeO_4$, i.e., $(Cu_{0.09}$ $Fe_{0.91})$ $[Cu_{0.91}Fe_{1.09}]O_4$, occupy mainly octahedral sites (4). The variation in specific activity with absolute temperature (T) between 373 and 723 K of the three catalyst samples, which have surface areas of 1.5 ($CuRh_2O_4$), 2.0 ($CuCr_2O_4$), and 1.1 ($CuFe_2O_4$) m^2/g, is shown in Fig. 1. A comparison of the catalytic activities of these spinel oxide catalysts with the activity of $CuCr_2O_4$ suggests that the mechanism of oxidation on $CuFe_2O_4$ and $CuRh_2O_4$ is similar to that on $CuCr_2O_4$. Moreover, the activity of $CuRh_2O_4$ is comparable to that of $CuCr_2O_4$ but the activity of $CuFe_2O_4$ is considerably lower. In this catalyst Cu is present mainly on the octahedral sites, which may be responsible for the lower activity of this catalyst.

Thus it appears that the activity due to Cu ions on octahedral sites is less than that of Cu ions on tetrahedral sites. This is contrary to the reports in earlier studies (5) where it was indicated that the catalytic activity of a metal ion is generally higher when it is present on octahedral sites than when it is present on tetrahedral sites. However, some recent studies have shown that Cu on the tetrahedral site of the spinel lattice is more stable and can act as a better catalyst (6).

Thermal studies carried out on these catalysts show that $CuCr_2O_4$ and $CuRh_2O_4$ are reduced relatively easily to $Cu_2Cr_2O_4$ and $Cu_2Rh_2O_4$, respectively, than $CuFe_2O_4$ is reduced to $Cu_2Fe_2O_4$. This suggests that Cu^{2+} ions on tetrahedral sites are more susceptible to reduction to lower oxidation states. This was also indicated in the ESCA studies on $CuCr_{1-x}$ Al_xO_4, in which the Cu^{1+} ions formed by reduction are all present on the tetrahedral sites. Furthermore,

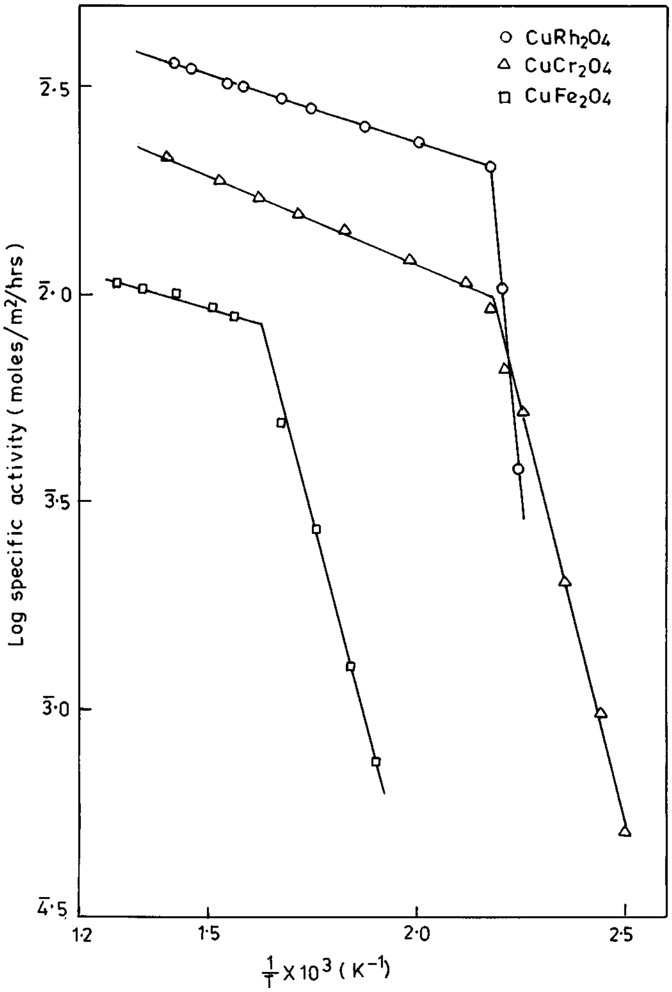

FIG. 1. Log specific activity vs $1/T$ for $CuRh_2O_4$, $CuCr_2O_4$, and $CuFe_2O_4$.

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Cu^{1+} has the same electronic configuration as $Zn^{2+}(d)^{10}$ and hence would have a definite preference for tetrahedral sites like Zn^{2+} (7). Thus, the tendency of tetrahedral Cu ions to be readily reduced probably makes them catalytically more active than octahedral Cu ions. However, at lower temperatures, the relative activities of the octahedral site cations cannot be ascertained, although from Fig. 1 it appears that the activities of $\mathrm{Rh} \approx \mathrm{Cr} > \mathrm{Fe}$.

From these results, it may be concluded that in oxidation reactions on copper spinel oxide catalysts, the catalytic activity is higher when copper is present on the tetrahedral sites of the spinel lattice.

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