

14 kcal/mole). However, addition of palladium or ruthenium does not yield more stable catalysts.

### The Activity of Copper Polychelates and Their Monomer Analogs in Reactions with Hydrazine

N. P. KEYER, L. F. RUBTSOVA,  
G. F. GERASIMOVA, E. K. MAMAYEVA,  
V. I. DINDOYN, AND V. F. ANUFRIYENKO  
*Institute of Catalysis, Siberian Department,  
Academy of Sciences, USSR*

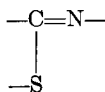
The authors have studied the decomposition of hydrazine in the presence of copper polychelates derived from  $\alpha$ -thiopicoline anilides. Infrared and ESR spectrometry indicate that the hydrazine decomposition is accompanied by the decomposition of the chelate complex and reduction of the copper to metal. The initial reaction of the hydrazine with the copper complex is governed by the magnitude of the effective change on the cation (this change is a function of the nature of the ligand section not immediately adjacent to the copper). The catalytic activity of the complex decreases with the increase of the negative effective charge on the chelate-held copper. The first stage of the reaction is noncatalytic; subsequent stages are catalytic, and the active site is the copper atom.

The rate of decomposition of the polymers in the reaction with hydrazine exceeds that of monomeric complexes, and its magnitude is dependent on the degree of order in the polymer.

### Infrared Spectroscopic Study of Reactions of Hydrazine with Copper Complexes Derived from Thiopicoline Anilides

V. I. DINDOYN AND N. P. KEYER  
*Institute of Catalysis, Siberian Department,  
Academy of Sciences, USSR*

The authors have obtained the infrared spectra and have assigned the specific absorption bands of several thiopicoline anilides, as well as of products from reactions of hydrazine or deuteriohydrazine (in gas phase) with copper chelate complexes derived from these anilides. It is shown that these reactions result in the decomposition of the chelate bond and, in most cases, the addition of one of the hydrazine hydrogens to the nitrogen of the chelate group



Changes of intensity of infrared absorption lines were used to calculate the relative rates of

decomposition of the complexes as a function of the substituents on the organic moiety.

### The Mechanism of CO Oxidation over Lanthanum Oxide

L. A. SAZONOV AND E. V. ARTAMONOV  
*Institute of Catalysis, Siberian Department,  
Academy of Sciences, USSR*

The mechanism of CO oxidation over lanthanum oxide at 300°–420°C was studied with the help of  $^{14}\text{C}$ . Below 300°C, the activation energy  $E_1 = 3$  kcal/mole, and the product  $\text{CO}_2$  is completely adsorbed on the oxide surface. Between 300° and 400°C, the controlling stage ( $E_2 = 19$  kcal/mole) is  $\text{CO}_2$  desorption, and above 400°C it is the rate of the chemisorption ( $E_3 = E_1 = 3$  kcal/mole). It is postulated that CO oxidizes via an intermediate complex involving  $\text{CO}_3^{2-}$ , and the activation energy for the dissociation  $\text{CO}_3^{2-} \rightarrow \text{CO}_2 + \text{O}^{2-}$  is 40 kcal/mole.

### The Catalytic Activity of Iron, Cobalt, and Nickel Oxides in Isotopic Exchange in Carbon Dioxide

V. G. AMERIKOV, G. K. BORESKOV,  
AND L. A. KASATKINA  
*The Mendeleev Chemical Engineering  
Institute, Moscow*

The isotopic exchange of oxygen in  $\text{CO}_2$  was investigated between  $-78^\circ$  and  $+350^\circ\text{C}$  at  $\text{CO}_2$  pressures ranging from 4 to 200 mm Hg. The catalysts were  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , or  $\text{NiO}$ , which were degassed in a vacuum at 350°C and then kept under  $\text{CO}_2$  or  $\text{O}_2$  until establishment of a steady state. Under these conditions the exchange reaction is very fast and requires a very low activation energy. Its rate depends on the history of the catalyst.

### The Mechanism of Pyridine Reaction with NiO Surfaces

Z. A. MARKOVA AND YU. N. RUFOV  
*Institute of Chemical Physics,  
Academy of Sciences, USSR*

The authors present the infrared spectra of pyridine adsorbed on NiO and their change upon adsorption of oxygen. These spectra, as well as data on adsorption and charging of the surface by pyridine and oxygen, are used in postulating a mechanism of adsorption of pyridine on NiO.