Nitrogen Chemisorption on Reduced Cobalt Oxide with K₂O as Promoter

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Summary Nitrogen chemisorption occurs slowly on re- cobalt oxide, when K_2O is present as a promoter and when duced cobalt oxide at 200 and 300°, and much more rapidly when K_2O is present as a promoter.

THE effect of promoters on iron catalysts have been studied, in connection with the mechanism of ammonia decomposition¹⁻⁴ and synthesis,⁵ and adsorbed states of nitrogen.⁶⁻⁸ Cobalt is known to be inactive as a catalyst for nitrogen chemisorption at high temperatures, although it belongs to the same group of the periodic table as iron.⁹⁻¹¹ We report evidence for nitrogen chemisorption on reduced

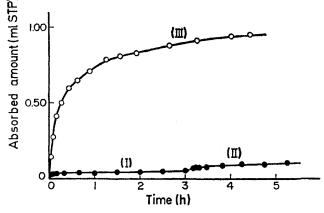


FIGURE. Nitrogen adsorption as a function of time. (I): Adsorption on unpromoted catalyst at 250° and 102 Torr. (II) Change of adsorption temperature; from 250 to 300.° Catalyst used: 4 g (as oxide). (III): Adsorption on promoted catalyst at 200° and 100 Torr. Catalyst used: 8 g (as oxide).

it is not.

Cobalt carbonate was precipitated by adding a solution of ammonium carbonate to that of cobaltous chloride and then heated (at 320° in air) to give Co_3O_4 . The promoted catalyst was prepared by soaking this oxide in 1N KOH solution for 24 h at room temperature and then drying at 120° for 12 h. These two forms of Co_3O_4 (*i.e.* the unpromoted and promoted forms) were degassed in vacuo at 200° and then reduced at 300° for 72 h under purified hydrogen^{3,4} (flow rate: 200 ml STP min⁻¹). The unpromoted catalyst alone was further reduced at 400° for 24 h, because it did not show appreciable nitrogen adsorption at 200°.

Adsorption of nitrogen was studied volumetrically at pressures of 30-150 Torr. Prior to each adsorption run, the catalyst was reduced overnight as described above, and then evacuated to 10^{-6} Torr. The surface areas of the catalysts (in reduced form) were determined by the BET method with Ar. The areas of unpromoted and promoted catalysts were 1.20 m² g⁻¹ and 1.16 m² g⁻¹, respectively.

The Figure shows nitrogen adsorption as a function of time. The unpromoted catalyst showed low adsorption at 250° and 300°, 102 Torr while the promoted catalyst adsorbed nitrogen even at 200°, 100 Torr. For both catalysts, the amount of nitrogen adsorbed increased at high temperature, indicating chemisorption. The initial rate of adsorption on promoted catalysts at 200° was higher than that for the unpromoted catalysts at 250°. As in the case of iron catalysts, nitrogen adsorption on cobalt is thus enhanced by the presence of a small amount of K_2O .

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