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Note

Thermoprogrammed reduction of cobalt oxide catalysts

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The gas chromatographic technique of thermoprogrammed reduction has proved very useful for determination of the reducibility of oxide catalysts such as NiO and CuO[1].

The present note reports the use of this technique for Co_3O_4 and Co_3O_4–SiO_2 and Co_3O_4–γ-Al_2O_3 catalysts, prepared as described previously[2,3]. (Co_3O_4–γ-Al_2O_3 was prepared analogously to Co_3O_4–SiO_2.) The system used is shown in Fig. 1.

Before the thermoreduction process each catalyst was standardized by heating at 573°K in a stream of argon deoxidized by a method described earlier[4,5]. A mixture containing 92% of argon and 8% of hydrogen, flow-rate 10 cm³/min, was intro-

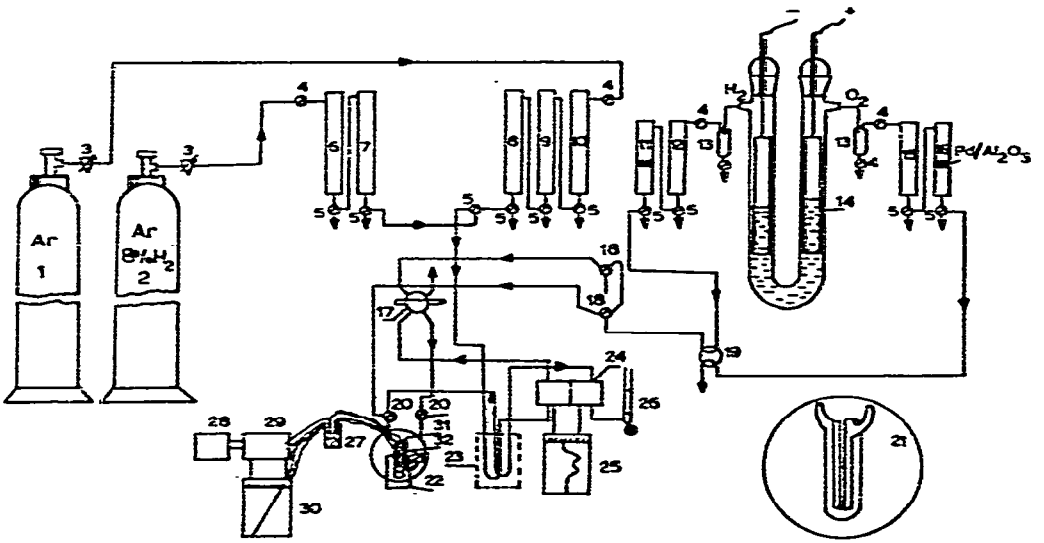

Fig. 1. Apparatus for thermoprogrammed reduction investigations. 1 and 2 = Cylinders with compressed gases; 3 = precisely controlled valves; 4 = straight-run valves; 5 and 18 = three-way valves 10, 12 and 13 = drying columns; 7, 8, 9, 11 and 16 = columns with deoxidation catalyst; 13 = electrolyser protection; 14 = electrolyser; 17 = six-way dosing valve; 19 = four-way valve; 20 = reactor valves; 21 = reactor; 22 = furnace; 23 = thermostat of gases coming into and leaving the katharometer; 24 = katharometer; 25 = registrator; 26 = foamometer; 27 = "cold end" of thermocouple; 28 = millivoltmeter with a digital reading; 29 = temperature programme; 30 = temperature recorder; 31 = controlling thermocouple; 32 = measurement thermocouple.

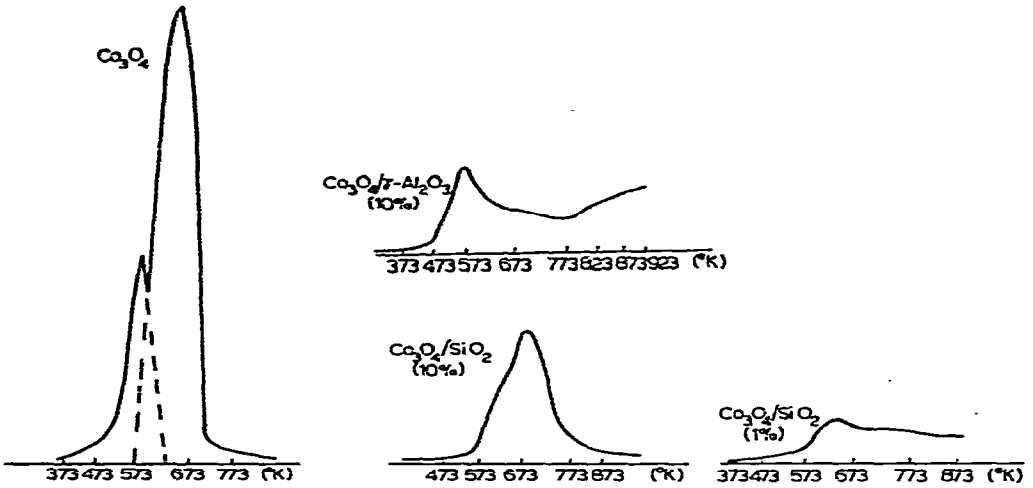

Fig. 2. Examples of chromatograms for selected catalysts.

duced and the heating started, at a linear rate of temperature increase of 10°/min. Examples of chromatograms for selected catalysts are presented in Fig. 2.

For pure Co_3O_4 the reduction process starts in the temperature range 453–503°K. Two clear maxima suggest a two-stage process. Surface analysis of both peaks indicates that reduction to CoO takes place first and then metallic cobalt is formed. The maxima correspond to the temperatures 593 and 663°K, respectively. The reduction is complete in the temperature range 733–773°K.

For supported catalysts the course of the process is different. For the catalyst Co_3O_4–SiO_2, containing 10% of active phase (calculated for cobalt metal) the process starts at *ca.* 553°K. The reduction maximum is reached at *ca.* 693°K and the process is completed in the range 825–873°K. Thus the temperature ranges are 30–50° higher than those for pure Co_3O_4. At 673°K the degree of reduction is *ca.* 40%.

For a catalyst containing 1% of active phase the process is still incomplete at 873°K. A maximum is reached at *ca.* 643°K (corresponding perhaps to the reduction stage $Co_3O_4 \rightarrow CoO$).

The chromatogram of the reduction of Co_3O_4–γ-Al_2O_3 (10% active phase) indicates that it is more difficult to reduce than Co_3O_4–SiO_2. The process is still incomplete at 923°K.

To sum up:

(1) Reduction of pure Co_3O_4 occurs in two stages, $Co_3O_4 \rightarrow CoO$ and $CoO \rightarrow Co$.

(2) A support clearly decreases the reducibility of Co_3O_4.

(3) Interactions of the active phase of Co_3O_4 with a support are stronger for γ-Al_2O_3 than for SiO_2.

(4) Reducibility of the Co_3O_4–SiO_2 catalyst increases with the increase of the supported active phase.

(5) The results are in a satisfactory agreement with the investigations carried out by the pulse method[2,3].

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