

## INFLUENCE OF ALUMINA ON SELECTIVITY OF COBALT CATALYST FOR OXIDATION OF AMMONIA

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Alumina has been tested as carrier of active component of cobalt catalyst for oxidation of ammonia to nitrogen oxide. Mutual diffusion of the carrier and the active component has been found to take place under the oxidation conditions. In surface layer of the active component  $\text{CoAl}_2\text{O}_4$  is formed which shows considerably lower selectivity (with respect to NO) than pure  $\text{Co}_3\text{O}_4$ . Time stability of the catalyst selectivity on alumina depends on temperature of its pre-treatment before introduction of the active component.

The best non-platinum catalyst for ammonia oxidation in production of nitric acid is that containing the active component based on  $\text{Co}_3\text{O}_4$  with or without addition of promoter<sup>1-8</sup>. However, in literature there are but sporadic notes about its application on industrial scale<sup>4</sup>. One of the reasons preventing the industrial application is its small mechanical strength: Tricobalt tetroxide recrystallizes under the conditions of ammonia oxidation, the granules fall to small particles which are taken along with the reaction mixture. Increase in mechanical strength could be obtained by spreading the active component on a suitable carrier. Besides that, the catalyst on a carrier is much cheaper due to lower content of the active component. So far, however, the non-platinum catalysts on carriers have exhibited lower selectivity than the pure active component with respect to NO (refs<sup>9,11</sup>).

The aim of this work was to test alumina as carrier of the active component of cobalt catalysts. At the same time influence of  $\text{Al}_2\text{O}_3$  on selectivity of pure  $\text{Co}_3\text{O}_4$  was studied. For this purpose we prepared samples of  $\text{Co}_3\text{O}_4$  containing 0 to 15% (by wt.)  $\text{Al}_2\text{O}_3$  and compared their selectivity with that of the catalysts containing  $\text{Co}_3\text{O}_4$  on alumina. Concentration changes of Al and Co at the surface and in the cut of the catalyst containing the alumina treated at 1200°C were followed by the method of electronic microanalysis<sup>12</sup> before and after a longterm use.

### EXPERIMENTAL

Pure  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$  containing 5 and 15% (by wt.)  $\text{Al}_2\text{O}_3$  were prepared by slow decomposition of cobalt(II) nitrate hydrate and its mixture with aluminium(III) nitrate, respectively, evaporation until dry at 400 to 450°C, and one hour annealing in air at 800°C. The resulting

solid was crushed to 1.5–2.5 mm particles. The specific surface determined by the method of Nelsen and Eggertsen<sup>13</sup> was *e.g.* 8.0 and 1.8 m<sup>2</sup>/g for a fresh sample and after six hours testing in a laboratory reactor, respectively.

The catalysts on carrier were prepared by repeated impregnation of Cherox 3300 alumina pretreated at 800–1200°C or cobalt spinel<sup>14</sup> with cobalt(II) nitrate solution and subsequent decomposition and one hour calcination at 820°C. Specific surface of the fresh samples did not depend on that of the pure carrier and varied within 1.5 to 0.5 m<sup>2</sup>/g.

The catalyst selectivity and activity were measured with a laboratory and a pilot-plant adiabatic reactor. At the laboratory conditions we tested the fresh samples and those after longterm use in the pilot plant. All the samples were measured under the same conditions. Diameter of the quartz reactor was 30 mm, and the flow rate was 0.5 m<sup>3</sup>/h of air–ammonia mixture (10.5% (by vol.) NH<sub>3</sub>) at atmospheric pressure. Height of the catalyst layer was 30 mm. The pilot-plant testing of time stability of selectivity of the catalyst on carrier was carried out at 0.7 MPa pressure in an adiabatic reactor of 140 mm diameter with 50 mm layer of catalyst particles in the form of 5 × 5 mm cylinders. The flow rate was 110 m<sup>3</sup>/h mixture with 10.5% (by vol.) NH<sub>3</sub>.

## RESULTS AND DISCUSSION

From the results of testing of pure Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> containing 5 and 15% (by wt.) Al<sub>2</sub>O<sub>3</sub> at 700 to 820°C (Fig. 1) it follows that the presence of Al<sub>2</sub>O<sub>3</sub> decreases yields of NO. With respect to that the resulting mixture did not contain any unreacted ammonia it can be presumed that the catalyst selectivity for the reaction ammonia → nitrogen increased. The negative effect of Al<sub>2</sub>O<sub>3</sub> on the yield of NO can be explained by formation of CoAl<sub>2</sub>O<sub>4</sub> in surface layer of the catalyst. The presence of spinel CoAl<sub>2</sub>O<sub>4</sub> can affect composition of surface layers of the catalyst, especially concentration of the chemisorbed oxygen, which is of decisive importance for selectivity of the oxidation processes<sup>15–17</sup>. Chemisorption of O<sub>2</sub> on *p*-type semiconductors follows<sup>15–21</sup> the scheme (1)–(5).

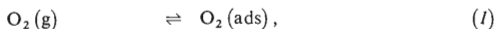
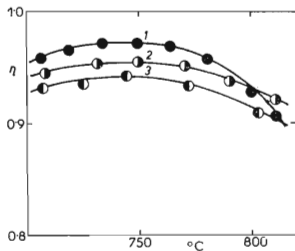
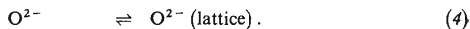
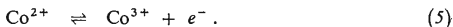


FIG. 1  
Selectivity of Pure Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> with  
Added Al<sub>2</sub>O<sub>3</sub>  
1 Co<sub>3</sub>O<sub>4</sub>; 2 Co<sub>3</sub>O<sub>4</sub> + 5% (by wt.) Al<sub>2</sub>O<sub>3</sub>;  
3 Co<sub>3</sub>O<sub>4</sub> + 15% Al<sub>2</sub>O<sub>3</sub>.





The cation  $\text{Co}^{2+}$  acts as the electron-donor in this case



Addition of  $\text{Al}_2\text{O}_3$  can have significant effect on position of Fermi level of  $\text{Co}_3\text{O}_4$  and, hence, also the equilibrium (5). Concentration decrease of "oxidable"  $\text{Co}^{2+}$  cations results in lowering of oxygen amount at the catalyst surface and, hence, lowering of the catalyst selectivity. Addition of  $\text{Al}_2\text{O}_3$  can also affect unfavourably the equilibrium<sup>22,23</sup> (1).

It is, however, difficult to give direct evidence of the existence of  $\text{CoAl}_2\text{O}_4$  at the catalyst surface. X-ray analysis practically cannot differentiate between  $\text{CoAl}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$ , and, furthermore,  $\text{CoAl}_2\text{O}_4$  is formed in such a thin layer that the changes do not make themselves felt in the volume of the X-ray analyzed layer.

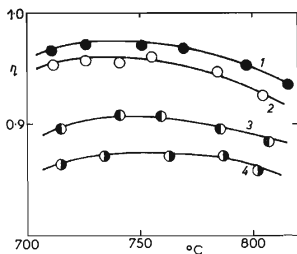


FIG. 2

Comparison of Selectivity of Fresh Catalyst and Catalyst After Use under Pilot Plant Conditions with Active Component Coated on Alumina (results of laboratory measurements)

1 Fresh catalyst on the alumina annealed at 850, 1000, 1200°C; 2 catalyst on the alumina annealed at 1000°C after 100 hours; 3 catalyst on the alumina annealed at 850°C after 24 hours; 4 catalyst on the alumina annealed at 850°C after 144 hours.

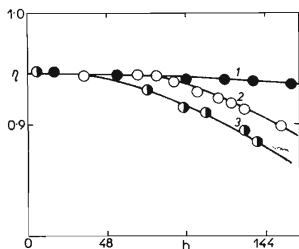


FIG. 3

Selectivity Change of Cobalt Catalyst on Carrier vs Time of its Use Measured at 0.7 MPa Pressure at 780°C

1 Active component ( $\text{Co}_3\text{O}_4$ ) on the spinel carrier; 2 active component ( $\text{Co}_3\text{O}_4$ ) on the alumina annealed at 1200°C; 3 active component ( $\text{Co}_3\text{O}_4 + 5\% \text{Al}_2\text{O}_3$ ) on the spinel carrier.

For comparison and possible indirect explanation of the selectivity decrease as a consequence of formation of the less active  $\text{CoAl}_2\text{O}_4$ , the active component was introduced on the carrier formed by a synthesized spinel. It was presumed that the reaction between the active component and  $\text{Al}_2\text{O}_3$  does not take place in this catalyst.

Fig. 2 gives results of the laboratory tests of the catalysts on alumina and effect of temperature of its pre-treatment on time stability of the catalyst selectivity. Figure 3 summarizes the results of measurements of time stability of selectivity carried out in the pilot plant reactor, *i.e.* at 0.7 MPa.

The found dependences show that fresh samples of the catalysts can give 95–97% conversion of  $\text{NH}_3$  to NO within 700 to 800°C, the temperature of alumina pre-treatment having no effect. After a certain time of action of the air–ammonia mixture, however, the individual samples showed considerable selectivity differences. Whereas selectivity of the catalyst having the active component on alumina decreased gradually within the followed time interval, that of the catalyst on spinel carrier<sup>14</sup> did not change.

Conversion degree of ammonia to NO decreased, in case of catalysts on alumina, with increasing temperature of the alumina pre-treatment. The greatest decrease (and also that after the shortest period) was observed with the catalysts on the alumina annealed at 850°C. With the catalysts on the alumina pre-treated at 1200°C observable selectivity lowering took place as late as after 100 hours of operation.

A particle of the catalyst with  $\text{Co}_3\text{O}_4$  on the alumina pre-treated at 1200°C was analyzed with an electronic microprobe before and after 145 hours of use in the pilot plant reactor. Concentrations of Al and Co at the surface and in the cut of the particle of 5 mm diameter are represented in Fig. 4.

It is surprising to find that even in a fresh sample the surface layer contains  $\text{Al}_2\text{O}_3$ . Probably the hot  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  dissolves a part of  $\text{Al}_2\text{O}_3$  during impregnation and calcination when it forms melt on the carrier surface. Thickness of the  $\text{Co}_3\text{O}_4$

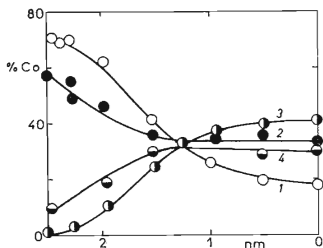


FIG. 4  
Dependence of Co and Al Concentrations  
on Radial Coordinate

Co concentration: 1 the fresh catalyst, 2 after 145 hours operation. Al concentration: 3 the fresh catalyst, 4 after 145 hours operation. ( $x$  — axis: mm)

surface layer formed by impregnation was 0.25 mm, and it contained 1 to 4% Al (i.e. 2 to 7.6% (by wt.)  $\text{Al}_2\text{O}_3$ ).

Co concentrations at individual points showed unambiguous decreasing trend toward centre of the particle, but the changes were not so smooth as in case of the fresh catalyst. The observed selectivity decrease can be explained by Co concentration decrease in the surface layer and by negative influence of the  $\text{Al}_2\text{O}_3$  which diffused into the active component during the use of the catalyst. This  $\text{Al}_2\text{O}_3$  can be present as  $\text{CoAl}_2\text{O}_4$  in the surface layer. The theory of formation of  $\text{CoAl}_2\text{O}_4$  is supported by results of Nishina and coworkers<sup>12</sup>. According to these authors  $\text{CoAl}_2\text{O}_4$  is formed at temperatures above 850°C. During oxidation of ammonia the catalyst surface temperature is substantially higher, and the time of 145 hours is sufficient for formation of  $\text{CoAl}_2\text{O}_4$ .

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