Catalyst for HCN synthesis by Andrussov's method, modified by aluminium oxide

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Received 17 September 1996; accepted 18 December 1996

The properties of a Pt–10% Rh gauze catalyst, modified by coating its surface with alumina film containing dispersed platinum metals, have been studied. The conversion, process yield and morphological changes of the surface of the modified catalyst are compared with those of a standard gauze applied in the HCN synthesis. For the first time it has been demonstrated, basing on HRTEM observations, that formation of a Pt–Al intermetallic compound on the surface of the gauze catalyst occurs under the conditions of HCN synthesis by Andrussov's method.

Keywords: Pt–10% Rh gauze catalyst, Pt–Al intermetallic compounds, HCN synthesis

Hydrogen cyanide (HCN) can be obtained by dehydrogenation through synthesis from methane and ammonia in the presence of platinum supported on α-Al_2O_3 at a temperature of 1423–1473 K, or by oxidation, from methane and ammonia as well, but with addition of air (often enriched with oxygen) in the presence of a catalyst, platinum–rhodium gauzes, at a temperature of 1290–1350 K [1–3]. An industrial plant, employing the latter method – also called Andrussov's method – has been working in Poland for many years. A mixture composed of the reagents in the mole ratio $CH_4/NH_3 = 1.0$–1.3 is used, while the ratio of air to combustible compounds is $(N_2 + O_2)/(CH_4 + NH_3) = 2.8$–3.0. The process can be intensified by using oxygen-enriched air. The products of the reaction, apart from hydrogen cyanide, are carbon monoxide and hydrogen. The normally used catalytic layer consists of five PtRh gauzes and corundum granules arranged as follows: wire-gauzes 0.16 and 0.076 mm in diameter, corundum layer, wire gauze 0.076 mm, corundum layer and then again wire gauzes 0.076 and 0.016 mm. The bed is sealed up from the reactor's side with a thick platinum gauze.

High consumption of expensive platinum metals and the potentiality of improving the HCN yield encouraged us to search for solutions which would enable lowering of platinum losses while maintaining the high efficiency of the process. The fact that the process of HCN synthesis from ammonia and methane occurs in the presence of platinum catalyst supported on α-Al_2O_3 [1] prompted us to undertake studies on modification of PtRh gauzes by spreading an alumina coating containing dispersed Pt and Rh metals on their surface [4,5].

Investigations were conducted in an experimental installation placed in a side stream unit of the industrial plant producing HCN (a reactor of 48 mm in diameter). The working parameters of the experimental installation were the same as in the industrial reactor, i.e. the pressure was 0.119 MPa, gas mixture velocity 1.5 m/s (0.1 MPa, 273 K). The investigations of different catalyst beds consisting of gauzes and a catalyst on the corundum carrier had been carried on continuously for at least 200–300 h each time. Activation of the catalyst was realised with stable composition of the mixture while from periodical (every 2 h) analysis of the gas products composition the mass balance was calculated.

The industrial synthesis mixture CH_4–NH_3–air ($CH_4/NH_3 = 1.26$ and $(N_2 + O_2)/(CH_4 + NH_3) = 2.88$) was normally used. Additional experiments with separately prepared synthetic mixtures enriched with oxygen with the composition $CH_4/NH_3 = 1.0$–1.5 as well as $(O_2 + N_2)/(CH_4 + NH_3) = 1.78$–1.86 were also carried out.

The parent substance for preparation of the alumina coating was aluminium hydroxide produced by hydrolysis of aluminium isopropoxide in excess of boiling water under vigorous stirring. A sol of quasi-spheroidal particles was then obtained by peptization of the 5 wt% dispersion of aluminium hydroxide by 1.5 wt% solution of HNO_3 (mol ratio: 0.05 mol HNO_3/1 mol Al_2O_3) at 360 K for 20 h.

Platinum metals were introduced into the sol in the amount of 1–4 wt% as a solution of H_2PtCl_6 and $RhCl_3$ (ratio Pt : Rh was 9 : 1). The surface of the gauzes was

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covered with such a spheroidal alumina sol exhibiting good coating-forming properties. After heating at 873 and 1353 K the obtained coatings consisted of γ- and α-(with traces of θ) Al_2O_3 with specific surface $S_{BET} = 220$ and 39 m^2/g, pore volume $V_p = 0.39$ and 0.01 cm^3/g and pore average size $r_{av} = 30$ and 56 Å respectively, containing dispersed platinum metals. The thickness of the coatings ranged from 2 to 6 μm, depending on the concentration of the sol used. It appeared that the coating of average thickness 4 μm, containing 1% dispersed platinum metal (calculated to Al_2O_3), was optimum and brought about many advantageous phenomena as [5,6]:

– it allowed to initiate the process without preactivation of the gauzes;

– after about 50 h of work much higher conversion and efficiency of the process could be reached, as indicated in figures 1a and 1b;

– mechanical resistance of the gauzes increased, what assisted in reduction of losses of platinum metals.

The advantageous properties of the modified catalyst have been acknowledged during exploitation in the industrial system.

The surface morphology of the coated gauzes after work in the process of HCN synthesis is decidedly different from the morphology of the standard gauzes. The coating causes reconstruction of the surface to a shape of flat walls with sharp edges of cuttings, whereas under the same conditions the surface of the standard gauzes is developed irregularly with many grooves and cauliflower accretions [5]. It indicates a different mechanism of surface etching in both cases. After three months of exploitation the presence of alumina coating on the gauzes was still observed (by using SEM and EDAX analysis).

Attempts of HCN synthesis were also carried out with a catalyst consisting of a corundum filler in the shape of granules coated with platinum metals, identically like gauzes. Such a catalyst exhibited too weak an activity and a short life under the conditions of the process. However, when used together with PtRh gauzes it gave very good results. By using a layer consisting of four PtRh gauzes and 78 g catalyst on the corundum carrier more than 8.5 vol% of hydrogen cyanide, i.e. about 0.5% more than on the bed of standard gauzes, had been obtained in gas reaction products. The ceramic catalyst, containing about 0.015% PtRh at the begining took over platinum metals removed from the gauzes during the work, reaching the concentration of 0.8 wt% after twelve months of work [6].

In earlier works [5,6] we put forward the hypothesis that during the catalytic reaction intermetallic compounds of the type Pt_xAl_y can be formed on the surface of the gauzes. Observations carried out with a high-resolution electron microscope (Philips CM20 Super-Twin) confirmed the presence of particles of the intermetallic compound Pt_3Al. Two particles of this compound exhibiting lattice fringes of 3.9 Å, corresponding to $Pt_3Al(100)$ lattice planes, are shown in figure 2. The particles are oriented on α-Al_2O_3 crystal in a special way ((100) planes are perpendicular to the surface) and are covered with a nonuniform amorphous overlayer. Electron diffraction patterns obtained from these particles could be interpreted as consistent with a primitive cubic lattice ($a = 3.88$ Å) in [120] orientation. These results are consistent with the Pt_3Al structure as determined by Hud and Klemm [7] ($a = 3.876$ Å, space group Pm3m, structure as in Cu_3Au).

The formation of Pt_3Al under the conditions of HCN synthesis by Andrussov's method takes place by reaction of platinum metal with alumina under (per

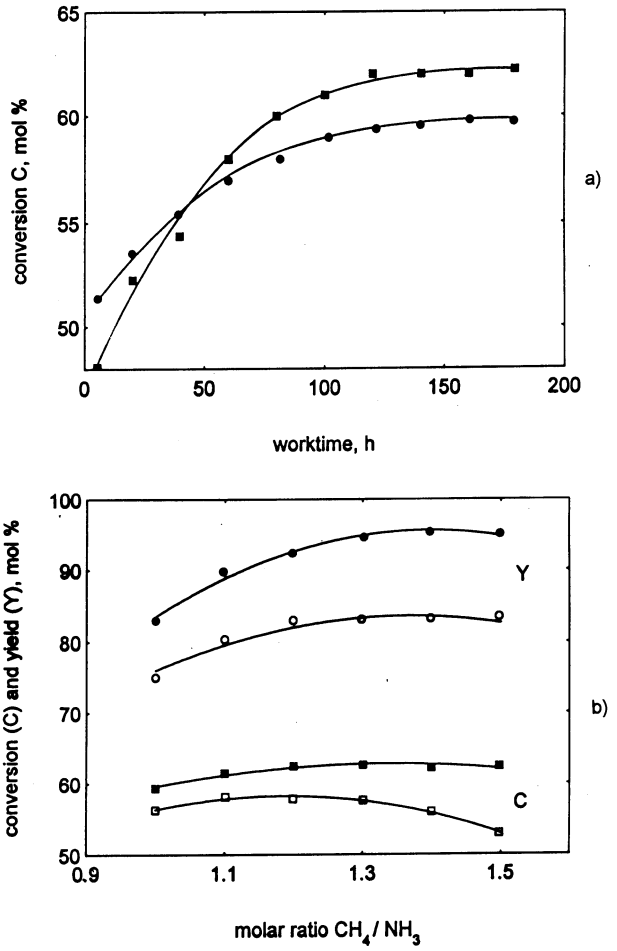

Figure 1. (a) Dependence of the ammonia conversion C to hydrogen cyanide upon the worktime of the gauzes with CH_4–NH_3–air mixture, with the mole ratio $CH_4/NH_3 = 1.26$; $(N_2 + O_2)/(CH_4 + NH_3) = 2.8$; (●) standard gauzes, (■) gauzes coated with 1 wt% $PtRh/Al_2O_3$. (b) Dependence of conversion C and process yield Y upon the mole ratio CH_4/NH_3 with the mole ratio $(N_2 + O_2)/(CH_4 + NH_3) = 1.78$; (○, □) standard gauzes, (●, ■) gauzes coated with 1 wt% $PtRh/Al_2O_3$. In consideration of the nomenclature concerning HCN synthesis accepted in the literature, the conversion and yield of the process were calculated from the following formulae, which are usually defined as yield and selectivity: $C = [(V_{HCN})_p/(V_{NH_3})_o] \times 100\%$, $Y = \{(V_{HCN})_p/[(V_{NH_3})_o - (V_{NH_3})_p]\} \times 100\%$, where $(V_{NH_3})_o$, $(V_{NH_3})_p$ are the volumes of ammonia in raw materials and products, and $(V_{HCN})_p$ is the volume of hydrogen cyanide in products.

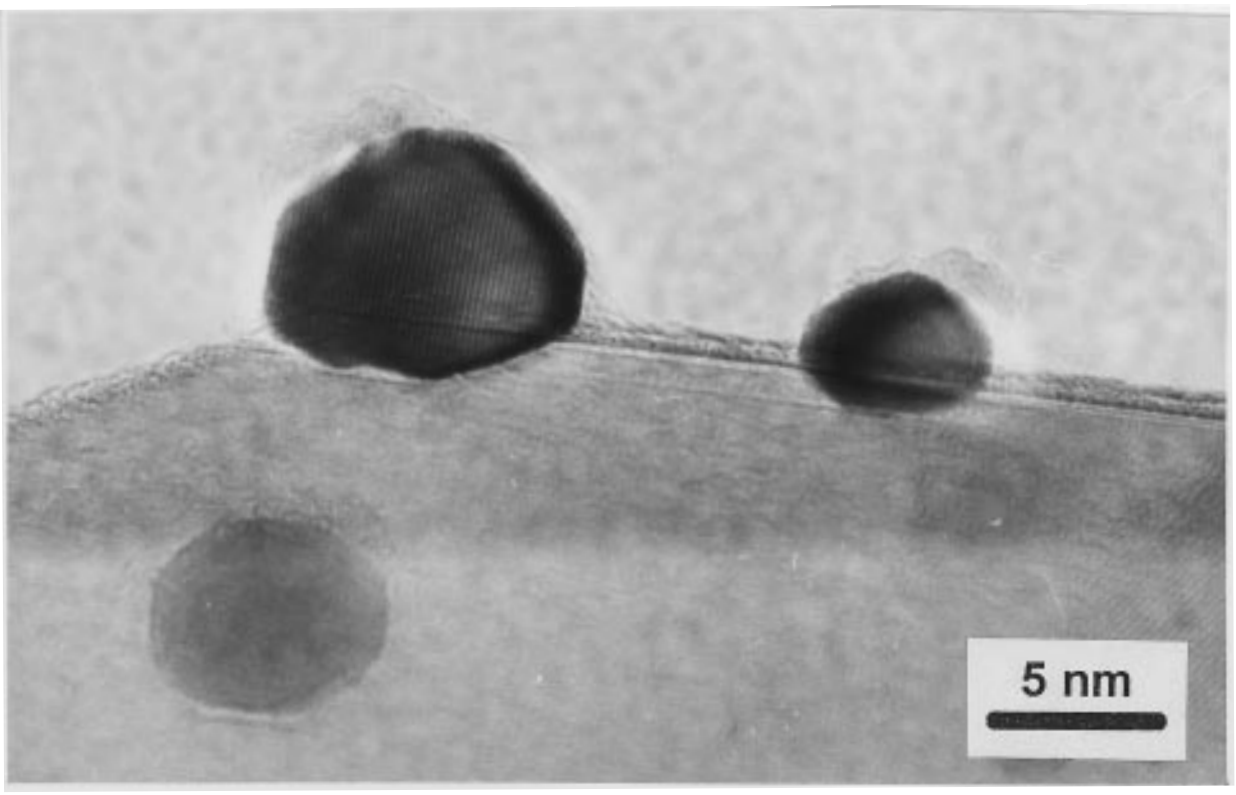

Figure 2. High-resolution image of Pt_3Al particles formed in Pt–alumina coating.

saldo) reducing conditions (all oxygen is consumed during reaction). Therefore it can be compared to the formation of Pt–Al intermetallic compounds from Al_2O_3 and Pt in hydrogen atmosphere described in the literature [8] and in the endothermic process of hydrogen cyanide synthesis from ammonia and methane carried out in the presence of a catalyst on a carrier but at temperatures ~ 100 K higher than those used in the process by Andrussov's method [1]. A corrosive reaction of Pt with alumina at the temperature of about 1473 K in inert gas (argon) and vacuum [9,10] was also reported.

The obtained results show that increased activity of PtRh catalysts modified by aluminium oxide can be caused not only by catalytic etching leading to different morphology of the gauze surface but also by the presence of Pt–Al intermetallic compounds formed as a result of strong metal–carrier interactions occurring under the conditions of HCN synthesis.

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