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BRIEF COMMUNICATIONS

Catalyst for Melamine Production

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Abstract—A novel electrolytic method for preparing the catalyst (active aluminum oxide) for melamine synthesis and a process for catalytic synthesis of melamine from urea are proposed.

Melamine (1,3,5-triamino-2,4,6-triazine) is a valuable precursor in production of plastics, lacquers, and adhesives exhibiting high mechanical strength, stability in hot water and in organic solvents, low electrical conductivity, and high thermal stability. These materials based on melamine–formaldehyde resin are widely used in various branches of industry [1, 2].

To synthesize melamine from urea, we developed a catalyst, active aluminum oxide with the specific surface of about 300–400 $m^2 g^{-1}$.

A goal of this work was to develop a low-waste procedure for preparing the catalyst, by ensuring stable conditions of granule formation and improved quality of the target product.

We improved a process for production of $Al(OH)_3$ and γ-Al_2O_3 to increase the melamine content in the target product from 80 to 96–98%. Initially we took commercial aluminum hydroxide with the specific surface area of 80–120 $m^2 g^{-1}$. Impurities present in it (up to 0.1 wt % Na_2O, 0.1 SiO_2, and 0.4 Fe_2O_3) adversely affected the quality of the γ-Al_2O_3 obtained (the melamine yield was about 80%). To remove them, commercial aluminum hydroxide was reprecipitated from chemically pure grade HNO_3, washed to remove ammonia, molded, dried, and calcined. The thus prepared γ-Al_2O_3 provided the melamine yield of up to 88.5% and had the specific surface area of 160–170 $m^2 g^{-1}$, which is insufficient for commercial production of melamine.

Nevertheless, the above study showed that purification of alumina increases the process selectivity. However, the above purification procedure is unacceptable, because the increase in the number of reprecipitation stages complicates the technology and increases the washwater amount. Therefore, we developed a method for preparing $Al(OH)_3$ from pure metallic aluminum by electrolytic precipitation. The precipitate was molded in grains by a sol–gel process and then was thermally treated to obtain granulated γ-Al_2O_3 [3].

Two electrodes (200 × 120 × 15-mm plates) made from metallic aluminum (99.9 wt % Al) were placed parallel to each other at a distance of 10–15 cm in a glass vessel filled with distilled water containing 2–4 wt % NH_4NO_3 as an electrolyte; dc electrolysis was performed at I = 27 A and U = 65 V.

A gel-like $Al(OH)_3$ precipitate was formed on the anode. The pulp was separated at the solid : liquid ratio of 1 : 8 by centrifuging, and a substance with the solid : liquid ratio of 1 : 4 and pH 7 was obtained. Concentrated chemically pure grade HCl was added to decrease pH to 3–4. A transparent thixotropic colloid of basic aluminum chloride (BAC) was thus obtained by the reaction [4]

$$2Al(OH)_3 + HCl \rightarrow Al_2(OH)_5Cl + H_2O \qquad (1)$$

with the Al_2O_3 content of 50 $g\,dm^{-3}$; it was aged at room temperature for 12–24 h.

A drop-oil method was used to mold granules. A molding mass was poured in a cone-shaped vessel and fed through a pipette 1.5 mm in diameter at a rate of 2–3 drops s^{-1} into a molder, a cylinder filled with a two-phase liquid (3–4-cm layer of kerosene to form drops and 25% aqueous solution of urea to form three-dimensional gel structure; the layer thick was sufficient for neutralization of granules for 3–4 min). In the first stage, granules were dried for 1 day in air. In the second stage, they were dried in a vacuum drier for 2–3 days at 40°C. Then the temperature was elevated at a 10 deg h^{-1} rate to 150°C, and at this tem-

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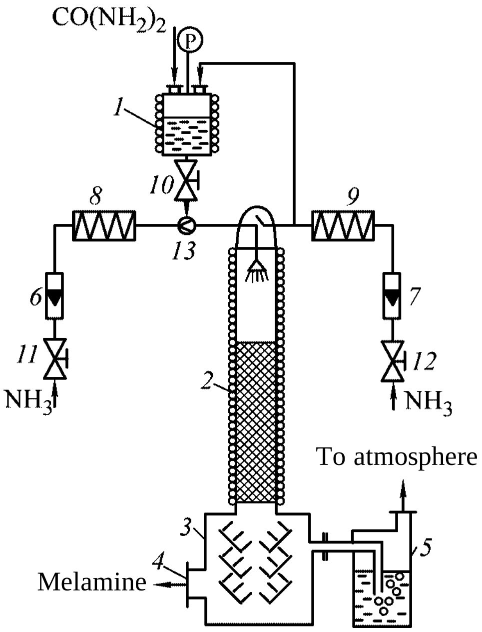

Scheme of the pilot setup for melamine production from urea: (*1*) melter, (*2*) catalytic reactor, (*3*) sublimer with packings for collecting product, (*4*) hatch for unloading the target product, (*5*) bubbler with ammonia water, (*6*, *7*) rotameters, (*8*, *9*) ammonia heaters, (*10*–*12*) valves, and (*13*) injector.

perature the granules were kept for 4 h. In the third stage, granules were calcined in a muffle furnace according to the following schedule: heating at a rate of 20 deg h^{-1} from 150 to 200°C, 50 deg h^{-1} from 200 to 500°C, 100 deg h^{-1} from 500 to 900°C; keeping at 900°C for 4 h; and gradual cooling and sampling. Production of the catalyst was tested in a pilot setup (see figure).[1]

The urea melt is fed from a melter *1* at 140–160°C under a pressure of 0.8 MPa into the reactor *2*. Ammonia heated to 350–500°C is also fed at the melt to gas wt ratio of 1 : (7–9). In the reactor, the melt is entrained with the gas and decomposes by the reaction

$$CO(NH_2)_2 \rightarrow HNCO + NH_3. \quad (2)$$

A mixture of cyanic acid and ammonia is fed to the catalyst bed, where melamine is formed by the reaction

$$6HNCO \rightarrow C_3H_6N_6 + 3CO_2 \quad (3)$$

at a pressure of 0.1–0.2 MPa.

The reaction products are sublimed in vessel *3* at 180–200°C. Melamine as a white finely dispersed powder is unloaded through hatch *4*. An $NH_3 + CO$ gas mixture from the sublimer is bubbled through water in vessel *5*, where ammonia partially dissolves. The urea conversion amounts to 97–98%, and the yield of the target product is 98% [5].

CONCLUSION

The developed procedure for preparing granulated γ-Al_2O_3 provides high specific surface area of the catalyst (up to 300–400 $m^2\,g^{-1}$) and elevated selectivity with respect to the target product, melamine (yield 96–98%).

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[1] The pilot setup was developed in Novomoskovsk Institute, Mendeleev Russian University of Chemical Engineering.