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Structured reactors on a metal mesh catalyst for various applications

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ABSTRACT

The modified Bayer process allows coating of a metal mesh surface with a continuous aluminum hydroxide layer in the phase of bayerite. Subsequent calcination turns the aluminum hydroxide layer into a η-alumina layer. The method provides the uniform thickness of tens of microns for the alumina layer. Layers cracking, clogging of mesh cells are not observed. The alumina layer is formed by needle-shaped particles which coalesce to each other through common facets during crystallization. The alumina layer with high specific surface area is perfectly suitable as a support for various active components. A series of Fe-containing mesh-catalysts was tested in the NOx reduction with NH_3. Addition of Ce and W to Fe increases NOx conversion significantly. The FeCeW catalyst provides almost 100% of the NOx conversion at a space velocity of 40,000 h^{-1} in the range of 350–500 °C with a negligible quantity of N_2O. A series of Pt-containing catalysts was tested in the reaction of afterburning of hydrocarbons. Addition of tungsten oxide to the Pt/Al_2O_3 catalyst decreases T_{50} by 60 °C. An increase in the number of wire mesh leads to a drop of T_{50}. The mesh-catalyst provides better light-off performance than the honeycomb catalyst.

1. Introduction

The best-known application of metal meshes as a catalyst is associated with nitric acid production. Contact time with the catalyst in the process is one of the shortest contact time spans in industrial processes. Space velocity reaches a rather high value of 600,000 h^{-1} [1]. In this case, a substance of the metal mesh (Pt, Rh) itself is the catalyst. However, specific surface area of the metal meshes is very small restraining its application for extremely fast reactions. The metal meshes should be covered by a catalytic layer with a high specific surface area to be used in various other applications [2].

The advantages of the metal mesh used as a supports of catalysts are well-described in literature. A geometric surface area of the metal mesh substrates per unit volume reaches high values (up to 100 m^2/m^3) and becomes commensurate with the geometric surface of the modern honeycomb substrates [3,4]. It helps to provide high concentrations of a deposited catalyst per unit of a catalytic reactor. The metal mesh structures have ten times more mass transfer coefficient than that of honeycomb structures [5]. Radial substance transfer inside the mesh structure improves the uniformity of a gas flow [6]. The gas flow resistance of the mesh structures takes an intermediate position between beads and the honeycomb structures [7,8]. High thermal conductivity and mass transfer of the metal meshes provide a uniform distribution of a temperature field, except a local overheat of a catalyst that has a positive effect on the catalyst durability. Radial temperature gradient of the metal-mesh catalysts can be considered negligible [2].

High mechanical strength, possibility to vary the wire diameter, grid cell size and a distance between adjacent mesh layers provide wide opportunities to control the gas flow resistance, heat and mass transfer as well as the temperature distribution inside reactors. Along with high flexibility of the metal mesh, these advantages allow creating of the compact and effective catalytic reactors with a heating surface of various shapes.

A key problem of creating the mesh-catalyst is formation of a well-adhered catalyst layer with a high specific surface area and the uniform thickness over the entire surface. Some reviews on the methods of depositing catalyst on the structured surfaces, including the metal surface, are presented in literature [2,9,10]. In general, the formation of a catalytic layer includes some principal stages. One of them is the deposition of a support in a form of a layer with high specific surface area. Another is the deposition of the active components on the support. Both stages include drying and calcining steps to fix the support or active components. The most widespread methods of depositing the support are dip-coating (washcoating), spray-coating, electrophoretic deposition, chemical vapor

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deposition. Some of them are further subdivided depending on their specific conditions.

According to [11,12], electrophoretic deposition method demonstrates excellent results. The support layers are thick enough, cover the metallic surface entirely and without any cracks. A wide spectrum of coatings based on different compounds is described in literature, for instance, alumina [13], titanium oxide [11], zeolites [14]. It is generally accepted that dip-coating is one of the most suitable method for coating metallic structured substrates due to its versatile and simplicity [10]. This method allows creating of a variety of layers from of a large number of oxides. There are some typical challenges inherent to this method, for example, obtaining good adhesion, cracking of support, clogging, and layer thickness nonuniformity [15–21]. Sometimes all steps including drying and calcining are repeated to attain a desired layer thickness [6].

In some cases, a primer layer is used to improve adhesion between the support and the metallic surface, boehmite being suitable for this goal [22,23]. Creating a roughness on the metal surface also improves the adhesion. A preliminary treatment of the metal surfaces is employed to obtain the roughness. For instance, a certain roughness is generated on the external surface of Fe-Cr-Al alloys in a range of 900–1200 °C in oxidizing atmosphere [23,24].

Recently some articles have been devoted to the hydrothermal method [25–28]. The hydrothermal method provides an excellent opportunity to deposit oxides including complex ones.

The reviews listed above do not mention a method based on crystallization processes in liquid solutions. In this work the deposition of the alumina layer was obtained by crystallization of aluminum hydroxide from a sodium aluminate solution with a subsequent transformation of aluminum hydroxide into alumina by calcining. Crystallization of aluminum hydroxide from such solutions is a well-known process and constitutes the base of the Bayer process. Properties of the sodium aluminate solutions are well-studied and presented in numerous books and publications, for instance, in Ref. [29]. This work is focused on studying the properties of an alumina layer obtained as a result of controllable crystallization of aluminum hydroxide on a surface of a heat-resistant metal mesh. On the one hand, alumina is one of the most used supports for catalysts. On the other hand, the metal mesh structures are of great interest due to their advantages. So, another aspect of the work is studying some applications of the catalysts based on the resulting Al_2O_3/mesh system.

2. Experimental

2.1. Catalyst preparation

2.1.1. Deposition of the alumina layer on the metal mesh

A heat-resistant aluminum-containing steel mesh (Fechral gauze, GOST 3826-82, Soyuznikhrom Ltd., Russia) was used as the catalyst support. Chemical composition of steel mesh in mass.%: Al—5.1; Cr—22.15; sum of C, Ni, S, P, Ti, Mn, Si—1.0; Fe—balance. Two steel meshes with the number of wire mesh equal 18 and 35 (further referred to as M18 and M35, respectively) were used. The M18 mesh is made of the wire with a diameter of 0.4 mm and has the grid cell size of 1.0 mm. The M35 mesh is made of the wire with a diameter of 0.25 mm and has the grid cell size of 0.5 mm. Before depositing the catalyst, the meshes were calcined in air at 900 °C for 10 h to form a firm α-Al_2O_3 film similarly to that shown in Ref. [8].

The alumina layer was obtained using the known property of aluminum hydroxide to precipitate from supersaturated sodium aluminate solutions. This property is used in the Bayer process, which is the main industrial method to produce alumina [30]. In contrast to the Bayer process, where the aim is the precipitation of aluminum hydroxide in volume of the sodium aluminate solution in the form of separate particles of certain sizes, this process was adapted to provide formation of the aluminum hydroxide layer on the mesh surface. The process was carried out at a lower temperature and lower concentrations of reactants in the solution than those in the Bayer process. Temperature of the solution was kept at 25 °C by using a thermostat.

Dissolving of aluminum was used to reach supersaturation of sodium aluminate solution. Aluminum foil (99.9% pure) with a thickness of 60 μm was used. Before using the aluminum foil was cut into pieces of 10 by 10 mm. Dissolving processes can be represented by the equation:

$$2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2\,(g) \quad (1)$$

Hydrogen released during dissolution of aluminum passed up through the meshes and stirred the solution providing uniformity of the solution and a uniform coating the mesh surface with the hydroxide aluminum layer. Precipitation of aluminum hydroxide starts at a certain rate of concentration of sodium aluminate solution which corresponds to the supersaturation state. Chemical reaction of precipitation is described by the equation:

$$Na[Al(OH)_4] \rightarrow Al(OH)_3 \downarrow + NaOH \quad (2)$$

Pieces of the mesh of desired size were immersed in the solution in suspended state to provide a free space for aluminum foil beneath the meshes. Typically, the distance between the bottom of the beaker and low edges of the meshes was about 30 mm. The total volume of the solution was determined on the basis of general conditions to minimize it and to provide the submerged state of the meshes in the solution for the whole process taking into account the gradual evaporation of the solution during the process. Usually the upper edge of the solution was 20–30 mm above the highest edges of the meshes immersed in the solution.

There is a connection between the total volume of the solution, initial concentration of sodium hydroxide, amount of aluminum and the meshes. The optimal content of alumina is 3–8% relative to the mesh. So, the total weigh of meshes influences the amount of the used aluminum. Besides, it is necessary to bear in mind that precipitation of aluminum hydroxide occurs not only on the mesh, but also on the walls of the beaker. Usually the portion of precipitated aluminum hydroxide on the meshes is 50–70%. On the other hand, the meshes affect the solution volume, as shown above. And, last but not least, the total amount of aluminum should be in more than stoichiometric amount in accordance with the Eq. (1) taking into account the total weigh of sodium hydroxide in the solution.

Therefore, it is necessary to meet a number of the requirements simultaneously. We used a flexible approach with respect to the initial concentration of the solution. The initial concentration of sodium hydroxide was chosen within a relatively wide range of 10–20 g/l. Other parameters were chosen (for instance, beaker shape, volume solution), first of all, considering the shape and dimensions of meshes.

For example, we prepared plane sheets of the meshes with dimensions of 50 by 50 mm with the total weight of 550 g. Then we immersed them in the solution in vertical position with a distance between neighboring pieces of 3–8 mm. In this case we used the solution with sodium hydroxide of 10 g/l. The total volume of the solution was 5.8 l. Then the pieces of aluminum foil were immersed in the solution. The total weight of aluminum was 63 g.

Precipitation of aluminum hydroxide occurred both on the mesh and on the walls of the beaker. A larger portion of aluminum hydroxide was precipitated on the mesh. In total, the whole process of precipitation took 25–30 h. At the end of the process the meshes were removed from the solution, washed from alkali with hot water, dried at 110 °C during 5 h and calcined in air at 600 °C