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Role of shaping in the preparation of heterogeneous catalysts: Tableting and slip-casting of oxidation catalysts

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ABSTRACT

The process and impact of shaping mixed vanadium aluminum (hydr)oxides, VAlOH and VAlO, respectively, and BiMo catalysts by tableting and slip-casting were examined. Graphite (G) was employed as a shaping agent for tableting. Without it tableting was impracticable. Graphite was found to enhance the mechanical resistance of VAlOH-xG and BiMo-xG and changed the surface area by increasing it for the non-porous BiMo and by decreasing it for the mesoporous VAlOH. In addition, graphite modified the catalytic performance despite changing neither the chemical nor the structural state of the base VAlO(H) and BiMo catalysts. A positive effect on the performance of VAlO-xG in propane oxidative dehydrogenation was found. It was proposed that catalytic active sites are formed on graphite during calcination. Conversely, graphite was harmful for non-calcined VAlOH-xG and BiMo-xG. On the other hand, the preparation of chemically and physically stable VAlO(H) suspensions for slip-casting was accomplished. Chemical stability was achieved at pHs near the isoelectric point of these catalysts. For physical stability, the use of a dispersing agent, poly(acrylic acid), combined with a control of the solids concentration was necessary. A simple and reliable method for preparing VAlOH and BiMo pellets by slip-casting was thus developed with the use of colloidal silica as binding agent. The so prepared pellets were mechanically resistant and kept the surface area of the base materials. A decrease in the surface concentration of the active metals due to surface active site masking by silicon for VAlOH-xSi and BiMo-xSi led to an inferior catalytic performance.

1. Introduction

Simply put, catalyst shaping, or forming as it is often also called, is the process by which a catalytic powder is transformed into a structured body such as a tablet or pellet, an extrudate or *spaghetti*, a bead or a monolith (Fig. 1). Most academic researchers skip the subject and consider it a matter of practical interest but not a research topic per se. Conversely, shaping is often conducted in industry by mere trial and error. Furthermore, as an author admitted [1], secrecy is the rule: "The patent literature gives some information, but catalyst manufacturing technologies are often not patented but kept secret." Therefore, in most cases, there is a huge gap between the fundamentals of the process, the phenomena occurring during catalyst shaping, and the correlation of the latter with the performance of real life catalysts, the so-called technical catalysts. The literature for shaping is scarce despite several interesting contributions dating back to the 70s; all of them belonging to the first "International Symposium for Scientific Bases for the Preparation of Heterogeneous Catalysts" [2–5]. The two most popular methods for catalyst shaping are tableting and extrusion. For tableting, the few information available consists on a general description of the process; including lists of the most preferred tableting additives; binders, lubricants, and fillers, and their general role on the mechanical resistance, the porous structure, and, ironically, marginally the catalytic performance [6–8]. Among the different tableting additives, graphite (G) is often employed although with great caution. According to Stiles [9]: "to emphasize once more – graphite is harmful; the more graphite, the more harm."

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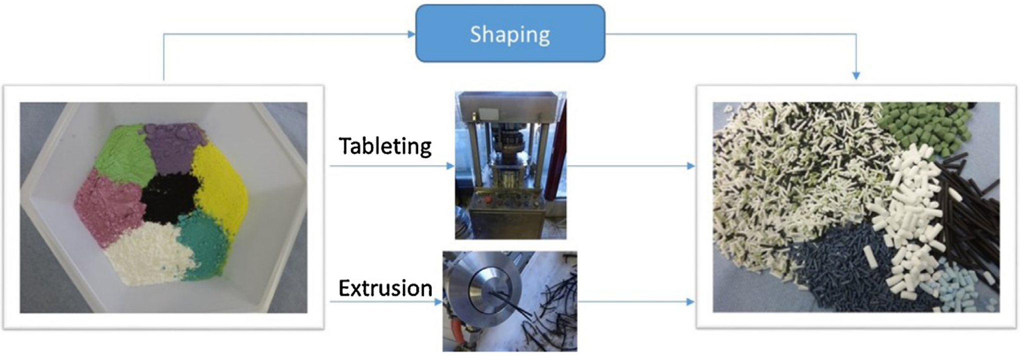

Fig. 1. Representation of the process of shaping of catalytic powders.

For extrusion, which is basically a wet plastic molding process for powder shaping, a very recent review by Mitchell et al. [10] addressed how important is controlling the physicochemical characteristics of catalyst extrudates for producing efficient and durable technical catalysts such as the zeolites employed in the FCC process. It must be said that, it is indeed FCC catalysts that have drawn most of the attention in this sense given the enormous economic stake of this process. Most studies concern the effect of the nature of extrusion additives; peptizers and binders, on the catalytic activity from a phenomenological approach disregarding the fundamentals of the phenomena therein involved. Although, a high volume of information on the wet processing shaping of ceramic powders is available in journals not normally consulted by the catalytic community, see for example Refs. [11,12] from the Journals of the American and European Ceramic Societies, respectively, and more recently, even in videos posted in youtube [13]. It is somehow amazing that the catalytic community has kept its look away from such knowledge.

This work was made within the frame of a project that aims establishing molecular basis for understanding the impact of shaping on the physicochemical and catalytic properties of materials as well the evolution of catalysts during the shaping process [14–16]. Herein, particular attention was paid to: first, the effect of the loading of the “objectionable” graphite on the properties of tableted bismuth molybdate (BiMo) and vanadium–aluminum mixed (hydr)oxides (VAlO(H)) catalysts. Second, the process of preparing pellets of BiMo and VAlO(H) by slip-casting and to the physicochemical and catalytic properties of the thus obtained materials. BiMo and VAlO(H) are catalysts employed in selective oxidation reactions [14,17–19]. In this case, the oxidative dehydrogenation of propane to propylene (ODHP) and the oxidation of propylene to acrolein were studied.

2. Experimental methods

2.1. Preparation of powdered catalysts

Both the hydroxides of bismuth molybdate [14] and of vanadium–aluminum [19] were prepared, at the 1 kg scale, by coprecipitation. For BiMo, the concentration of the metallic precursors was adjusted as to obtain a bulk Bi/Mo molar ratio of 1.3. A typical synthesis consisted in preparing a solution of 121.25 g of bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, Riedel-de Haën) in 0.0185 dm^3 of concentrated HNO_3 and 0.375 dm^3 of distilled and de-ionized H_2O. This solution was mixed with another of 33.95 g of ammonium heptamolydate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Merck) in 0.192 dm^3 of H_2O. This mixed solution was strongly agitated to prevent a premature precipitation of the bismuth molybdate hydroxide. Drying of the resulting slurry at 353 K was carried out until complete removal of excess water. The obtained powder was dried at 393 K and calcined at 823 K for 3 h. Under such conditions, the formation of the more catalytically active β- and γ-BiMo oxide crystalline phases is favored [20]. VAlOH was prepared from appropriate amounts of ammonium metavanadate (NH_4VO_3, Isochim, technical degree) and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Merck, 95%) considering a bulk V/Al molar ratio of 0.25. In a typical synthesis, 280.74 g of NH_4VO_3 were dissolved at $T = 333$ K in 56.1 dm^3 of water at a pH of 3 as adjusted by the addition of HNO_3 (Merck, 65%). The NH_4VO_3 solution was mixed with 24.01 dm^3 of an aqueous solution of 3601.05 g of $Al(NO_3)_3 \cdot 9H_2O$. The pH of the mixed solution was adjusted to 5.5 with NH_4OH (Merck, 25%). The formation of a yellow coprecipitate was observed under such conditions and the resulting suspension was stirred continuously during 30 min. The synthesis was performed in an 80 dm^3 stainless steel homemade reactor vessel provided with a boat-like propeller and an insulating double jacket. The synthesized slurry was filtered with a belt-filter and then washed overnight under stirring with hot water in the coprecipitation reactor vessel. After a second filtration step, the still wet VAlOH was dried in a static air stove at 333 K. Fig. 2 shows pictures of the basic equipment and steps involved in the process. Further details can be found elsewhere [15,16,19,21].

2.2. Shaping of powdered catalysts by tableting

The synthesized catalytic powders were grounded and sieved to a particle size below 100 μm before tableting. Sieved powders were mixed inside a bottle with the following loadings of graphite (Merck, commercial grade): $x = 0$, 1, 3, and 7 wt.%. The bottle was rolled over and shook in order to homogenize the mixed powders. Tablets of $L = 2.3$ mm × $Ø = 5.1$ mm were prepared using a hand-operated machine (Ateliers Ed. Courtoy, series 796), see Fig. 3. A certain number of VAlOH-xG tablets were calcined under static air at 773 K for 4 h in order to obtain VAlO-xG oxide shaped catalysts [15].

2.3. Physicochemical properties of tableted catalysts

The axial tensile strength of the tablets (σ_z [=] MPa) was measured at constant speed (5 mm/min) in an Instron 5566 machine by placing them in a vertical position and then applying a controlled constant force. Reported axial tensile strength values correspond to the average of at least five measurements. The accuracy and reproducibility of the measured force were within the range ±1 N.

The BET surface area (SA_{BET}), before and after tableting, was determined by measuring N_2 and Kr adsorption–desorption isotherms at 77 K in a Micromeritics TriStar 3000 apparatus and in a Micromeritics ASAP 2010 apparatus for VAlO(H)-xG and BiMo-xG, respectively. Samples for N_2 physisorption were outgassed overnight at 423 K under a vacuum pressure of 15 Pa, while samples for Kr physisorption were outgassed at the same temperature but