The choice of the fraction of iron-chromium catalyst powder providing the correct fluidization process

Jerzy Baron
Gabriela Berkowicz
Stanisław Kandefer
Witold Zukowski
Stefan Szarlik, et al.
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JERZY BARON*, GABRIELA BERKOWICZ*, STANISŁAW KANDEFER**, WITOLD ŻUKOWSKI*, STEFAN SZARLIK***, MARIA ZIELECKA***, ZBIGNIEW WIELGOSZ***, DARIUSZ JAMANEK***,

reviewed by dr hab. inż. Włodzimierz Ciesielczyk, prof. PK, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Poland

ABSTRACT

Keywords
iron-chromium catalyst, SEM images, gas fluidization

Introduction

The synthesis in the fluid-bed catalytic reactor provides high efficiency by maximum use of surface of the catalyst. Iron-chromium catalyst is characterized by high activity and selectivity, that make it such an attractive bed for fluidized-bed reactor. The choice of the appropriate fraction of the catalyst is necessary to ensure a proper organization of fluid flow.

EXPERIMENTAL PART

The study involved three types of iron-chromium catalyst: catalysts DJ/6 and DJ/7 (are synthetized by Industrial Chemistry Research Institute in Warsaw) and TZC-3/1 catalyst (are produced in Zakłady Azotowe in Tarnowie -Mościcach S.A.). The studies also involved different fractions, which were obtained after grinding and mechanical separations of the TZC-3/1 catalyst. The bulk densities of tested powders were determined in acording to the standard PN-EN 1097-3:200, and pycnometric densities were also established. X-ray density

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* Faculty of Chemical Engineering and Technology, Cracow University of Technology, Poland, gberkowicz@chemia.pk.edu.pl

** Faculty of Environmental Engineering, Cracow University of Technology, Poland

*** Industrial Chemistry Research Institute, Warsaw, Poland
was determined on the basis of the composition of the TZC-3/1 catalyst, which were significantly deviated from the apparent density obtained from the mass and volume of catalyst pellets. The images of grains of tested powders were taken by using scanning electron microscopy. The fluidization process at different temperatures: 22°C, 55°C, 120°C, 200°C and 300°C were examined for the isolated fraction giving correct bed.

**RESULTS AND DISCUSSION**

The information about the size and the shape of grains, allow to classify the tested material to the appropriate group of Geldart’s classification. The results indicate that receiving the proper fluid states from DJ/6 and DJ/7 catalysts and the fractions of the catalyst TZC-3/1 containing grains less than 75µm will be extremely difficult and possible only with the use of additional devices. It was decided that to further design the synthesis in fluid-bed reactor the fraction with size of grains of 75-150 µm obtained from TZC-3/1 catalyst will be used. The process of fluidization of fraction 75-150 µm of TZC-3/1 catalyst were examined at different temperatures: 22°C, 55°C, 120°C, 200°C and 300°C.

**CONCLUSIONS**

The fraction of iron-chromium catalyst which gives the correct process of fluidization has been separated. The minimum fluidization velocities of fraction 75-150 µm of TZC-3/1 catalyst, which allow for future design the synthesis in catalytic fluidized bed reactor with using iron-chromium catalyst have been designated.

1. **INTRODUCTION**

   The synthesis in a fluid-bed reactor is an efficient method for carrying out the reaction which requires high temperatures (300-1200°C). In this way: acrylonitrile (INEOS acrylonitrile technology [1], Lenntech BV [2]), polypropylene (UNIPOL PP process) [3], polyethylene (UNIPOL PE process) [4], maleic anhydride (ALMA process/Lummus Technology a CB&I company [5], INEOS maleic anhydride technology [6]), phthalic anhydride are obtained on an industrial scale. These are just some from a huge range of compounds that we can obtain through the process of fluidization. The scale of production of these products is really huge. Only UNIPO process has more than 100 reactors for the production of PE and over 50 reactors for PP manufacturing, which operate or are being built all over the world.

   Fluidization is a process in which solid particles are introduced into a pseudo-liquid state by a stream of gas or liquid. [7] In a certain speed range of the flowing medium, the solid bed is in a quasi-stable state. When the reaction proceeds in the fluidized-bed reactor with a catalytic bed, the process must be carried out above the minimum fluidization velocity. The minimum fluidization velocity, sometimes called the critical velocity can be estimated using empirical equations, such as proposed by Wen and Yu [8] or determined experimentally.

   Solid particles, which are close to each other, are introduced in the fluid state. Therefore the fluidization process depends on the forces between liquid(gas)-particle, and also on the forces coming from the interaction among particles of the fluidized bed. When Geldart was studying the fluidization of various types and sizes of grains, he identified four categories of solid particles. He took as a criterion for the division: difference in density \(\rho_{\text{solid}} - \rho_{\text{fluid}}\) and the average grain size \(d_{\text{particle}}\) [9]. In this study we are going to take a closer look at an iron-chromium catalyst as a potential bed for the reaction in the fluidized bed reactor.
2. EXPERIMENTAL PART

2.1. TESTED MATERIAL

Three types of an iron-chromium catalyst were studied: catalysts DJ/6 and DJ/7, which were synthesized by the Industrial Chemistry Research Institute in Warsaw and TZC-3/1 catalyst, which was produced in Zakłady Azotowe in Tarnowie-Mościcach S.A.. The powder catalyst marked TZC-3/1 was taken from the production line before tableting. Other fractions of the TZC-3/1 catalyst were derived from crushing of ready pills of the catalyst, sold by Zakłady Azotowe. The composition and the densities of the catalyst components, which are declared by the manufacturer are shown in Table 1.

Tab. 1. The composition of TZC-3/1 catalyst

<table>
<thead>
<tr>
<th>No.</th>
<th>Substance</th>
<th>CAS</th>
<th>content, %</th>
<th>Density, kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe₂O₃</td>
<td>1309-37-1</td>
<td>72 ÷ 90</td>
<td>5 240</td>
</tr>
<tr>
<td>2</td>
<td>Cr₂O₃</td>
<td>1308-38-9</td>
<td>7 ÷ 11,5</td>
<td>5 220</td>
</tr>
<tr>
<td>3</td>
<td>CrO₃</td>
<td>1333-82-0</td>
<td>0 ÷ 0,95</td>
<td>2 700</td>
</tr>
<tr>
<td>4</td>
<td>CuO</td>
<td>1317-38-0</td>
<td>1.5 ÷ 4.0</td>
<td>6 320</td>
</tr>
</tbody>
</table>

2.2. MICROSCOPIC ANALYSIS OF IRON-CHROMIUM CATALYST SAMPLES

For the tested materials microscopy images were taken using a SEM microscope Tabletop Microscope TM3000. The samples of the crushed catalyst were placed on a graphite plate without metallization. Accelerating voltage was set at 5 kV.

Fig. 1. SEM images of DJ/6 catalyst
Fig. 2. SEM images of DJ/7 catalyst

Fig. 3. SEM images of powdery TZC-3/1 catalyst

Fig. 4. SEM images of 0-120 μm fraction of TZC-3/1 catalyst obtained by the process of crushing and mechanical segregation
Each type of a catalyst sample was photographed at a magnification of x40, x120, x500 and x2500 to show respectively: the geometric character and grain size, the grain shape of about 100 microns, the surface condition of individual grains as well as the presence and morphology of ultrafine particles located in the largest grains.

The microscopic analysis of DJ/6 catalyst grains whose images are shown in Fig. 1, reveals that the grains of 50-100 µm size constitute only a part of the catalyst. Most of them have the shape of flat trapezoidal plates. At magnifications of x500 and x2500 particles whose size is less than 1 µm are visible on the surfaces of larger crystals. Powders with that kind of fragmentation may belong to the group C of Geldart’s classification (cohesive powders). They significantly disrupt the fluidization of larger particles. At a magnification of x2500 the surface of larger crystals is smooth, although covered with tiny grains. The photos show that the analyzed samples are polydisperse, with a very wide range of grain sizes.

Figure 2 shows the microscopic picture of particles of the DJ/7 catalyst. Only a few grains of the catalyst are of more than 100 microns. The finer grains with a diameter of 5-15 microns are surrounded by a filiform grains with a thickness of about 1 micron and a length of 10 µm. As in the case of DJ/6 catalyst, the pictures of DJ/7 catalyst indicates on considerable variation in size of grains and - additionally - a significant morphological variation.

Microscopic observations of samples of the TZC-3/1 catalyst reveal its heterogeneous composition. Already at a magnification of x40 (Fig. 3), we can see single dark crystals on
a bright background of other grains. On SEM images, illustrating the sample at a magnification of x500 and x2500 we can see significant difference between the light and dark grains. The first ones (the same as in the optical image of the DJ/6 and DJ/7 catalysts samples) do not reveal a crystalline structure, because they have a different shape and sizes of granules. The largest grains have a diameter of about 30 microns. Darker grains have a clearly defined edges and flat surfaces, and are arranged in many layers.

The fraction of 0-120 microns was separated from powder obtained by crushing pills produced in ZA Tarnów. The microscopic images for such obtained samples are shown in Fig. 4. The number of the smallest particles is significant. The surface of larger grains is partially covered with finest grains, like in previously samples. It can cause difficulties in fluidization, so the attempt of fluidization was made. Negative disturbances of fluidization such as: piston flow and channeling with agglomeration was observed for this fraction. In such a situation a fraction of 75 - 150 microns was isolated for further tests.

Fragmented catalyst pellets TZC-3/1 were sieved through a system of sieve. In Fig. 5 the fraction of 75 - 150 µm is shown. The sieving process with the use of vibrations does not work. The finest fraction of grains adheres to the surface of larger grains. The use of such a material as a bed in the fluidized bed reactor can lead to disturbances of fluidization like the formation of agglomerates. The sieving attempt was failed because of the large cohesive interactions between the smallest grains. The pneumatic method, in which the separation is made on the sieve with a mesh size of 75 microns, and the driving force behind the process (instead of gravitational forces in conjunction with the transverse vibration sieve,) is vacuum produced on a small area under the sieve was designed. The SEM images of 75-150 µm fraction of TZC-3/1, obtained after pneumatic purification are shown in Fig. 6. The negligible share of grains smaller than 75 microns is visible even at small magnifications (x40 and x120), especially, the grains smaller than 30 microns. Very small grains of size less than 1 micron are visible at high magnifications (x500, above all, X2500). Significant reduction of the finest particles in the fraction of 75-150 microns leads to the correct fluidization process of iron-chromium catalyst.

2.3. DENSITIES OF TESTED CATALYSTS SAMPLES

Several series of measurements of bulk density of the tested powders were made. The density of the powders was also evaluated by pycnometric method. Technical conditions for the determination of bulk density are determined by the standards: PN-EN 1097-3:2000 and PN-EN ISO 3953:2011. The measurements were made with the PN-EN 1097-3:2000 method, because of the amount of samples and the fact that the measurement is used only to establish the category in Geldart classification. The pycnometer with a thermometer was used in the pycnometric method, and distilled water was used as a reference liquid. The results of density measurements are shown in Table 2.

Bulk densities of the tested powders ranged from about 290 kg/m³ to about 1020 kg/m³. The lowest value of bulk density was determined for the powder marked DJ/7. During the measurement, this catalyst showed the most typical symptoms for cohesive powders (no free pouring in, agglomerates formation). The highest value of bulk density was determined for TZC-3/1 C1-PK catalyst, with grain sizes of 75-150 µm. This powder showed no signs of agglomeration, and its bulk density was similar to the bulk density of TZC-3/1 pellets, reported by the manufacturer (1250 kg/m³).

Based on the data referring to density of individual components of the TZC-3/1 catalyst, the X-ray density was determined. It equals 5250±40 kg/m³. The apparent density of the tested material which equals 2171±79 kg/m³ was determined on the basis of masses and the
volumes of TZC-3/1 pills. Such a serious difference in density may indicate on defects in the structure of crystal oxides and indicate on a large volume of pores on the surface and within TZC-3/1 pills. The main reason for this defect may come from the method of catalyst preparation. The pycnometric density of the examined powders are changes from about 1900 kg/m$^3$ (DJ/6 catalyst) to about 3600 kg/m$^3$ (75-150 µm fraction of the catalyst TZC-3/1 after pneumatic purification). This is caused by the presence of large volume of closed pores within the grains and micropores on the surface of the grains in to which water - because of their size - could not pour.

2.4. THE SUMMARY OF RESULTS FROM MICROSCOPIC ANALYSIS AND DENSITIES OF THE SAMPLES OF CATALYSTS

The obtained information about various densities of tested catalysts and about the size and shape of grains indicate that achieving a stable state of a fluid layer of powder marked DJ/6, and DJ/7 can be extremely difficult. However, that it is not impossible. Methods which involve mechanical mixing devices or mechanical/ acoustic vibrations can be used to introduce shallow beds into a fluidized state, even for Geldard’s C category of powders [10,11]. In order to determine the conditions under which it will be possible to carry out further synthesis in the fluidized bed, the 75-150 microns fraction, obtained by the fragmentation and pneumatic purification of the TZC-3/1 catalyst was chosen and, the process of fluidization will not have to be supported.

2.5. THE FLUIDIZATION PROCESS FOR THE ISOLATED FRACTION AND THE MINIMUM FLUIDIZATION VELOCITY

The fluidization process of iron-chromium catalyst was performed in a U-tube reactor with an internal diameter of 3 cm and a height of 25 cm. The bed of catalyst was placed at the bottom of the sieve of sintered glass with a thickness of about 0.2 cm. The fluidization medium was nitrogen. In the experiments the TZC-3/1 C1-PK fraction with a grain size of 75-150 microns, and purified from small grains by pneumatic method was used. The catalyst was not previously dried at elevated temperature. The experiments were preformed for three masses of the catalyst: 50g, 100g and 150g. The fluidization was examined at temperatures: 22°C, 55°C, 120°C, 200°C and 300°C for each mass of bed. For each experiment two trials was performed. The trials had a different initial state of packing of a the bed. In the first test, the packing of the bed was looser, and in the second test the packing of the bed was more compact. The pressure drop was measured by a differential pressure sensor which is a part of gas analyzer ECOM SG+. The results of these experiments are presented as a graphs of pressure drop vs. velocity of the gas.

That kind of plots of fluidization process and the parameters of grains of the tested material match to group A of Geldart’s classification [9]. The minimum fluidization velocities which were obtained from the curves, are presented in table 3. The $U_{mf}$ needed to
achieve the fluid-state decreases with an increase of the temperature. The minimum fluidization velocities which are determined from a selected fraction of the catalyst at different temperatures allow for future design of synthesis in the catalytic fluidized bed reactor with an iron-chromium catalyst as a bed.

Tab.3. The minimum fluidization velocity of the fraction of TZC-3/1 catalyst with a particle size of 75-150 µm at different temperatures

<table>
<thead>
<tr>
<th>process temperature [°C]</th>
<th>22</th>
<th>55</th>
<th>120</th>
<th>200</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimum fluidization velocity [cm/s]</td>
<td>1.5</td>
<td>1.25</td>
<td>1.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Fig. 7. The plots of fluidization of TZC-3/1 C1-PK catalysts at different temperatures
3. CONCLUSIONS

− The fraction of the iron-chromium catalyst, ensuring the correct fluidization process was selected from the tested samples of catalysts.
− The fraction of TZC-3/1 catalyst with grain sizes of 75-150 µm was classified to group A of Geldart’s classification.
− The determined minimum fluidization velocities of the selected fraction allow for a future design of synthesis in a fluidized bed reactor at specified temperatures using the iron-chromium catalyst as a bed.

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