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Experimental and statistical assessments of the mechanical strength reliability of gamma alumina catalyst supports

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ABSTRACT

The mechanical strength of solid catalysts is considered an important factor in terms of ensuring the reliable performance of industrial reactors. In this work, a pelletizing method was used to form gamma alumina support for catalysts. Response surface methodology (RSM) was employed to analyze and model the effects of various manufacturing parameters on the crushing strength of the supports. These parameters were binder concentration, compaction pressure, calcination temperature, and drying mode. The suggested model was verified by applying an analysis of variance to assess its validity with regard to crushing strength. The mechanical reliability of various supports was also determined by calculating their Weibull modulus values through linear regression of the Weibull equation. The material with the highest mechanical strength reliability will have both a high mean crushing strength and a high Weibull modulus, and the best values obtained for a support in this work were 70.7 MPa and 6.63, respectively. The conditions used to form this sample were: 20 mass% binder concentration, 861 MPa compaction pressure, 466 °C calcination temperature, and gentle drying.

Introduction

When employing a metal catalyst, it is generally necessary to prepare it such that its surface area is optimized, and this can only be accomplished by dispersing the metal on a refractory support. For this reason, almost all industrial catalysts are supported (Auer, Freund, Pietsch, & Tacke, 1998; Farrauto, 2007; Twigg, 1989). The physical characteristics of a supported catalyst are largely determined by the physical properties of its support (Jawad, Richeh, & Saleh, 2010b), and gamma alumina is commonly employed as a catalyst support in the oil and chemical industries (Couroyer et al., 1999; Lambert & Gonzalez, 1999; Williams, 2001). Support forming plays an important role in the catalyst preparation process, and will be modified depending on the type of reactor and the specific application for which the catalyst is intended. In the case of a fixed bed reactor, a low-pressure drop over the bed is important and this is usually achieved by employing catalyst particles in pelletized or extrudate forms (Jawad, Richeh, & Saleh, 2010a).

Appropriate mechanical strength is considered an important property of formed industrial catalysts since, during transport to and from the reactor as well as during the reaction, the catalyst particles experience various mechanical and thermal stresses that can lead to mechanical failure. Associated attrition and fragmentation of catalyst particles may increase the pressure drop in the fixed bed reactor because of plugging of the inter-particle voids by small fragments and fines. This can also lead to catalyst losses, thereby decreasing the performance efficiency of the catalyst, as well as environmental problems due to the release of fines to the atmosphere (Bukur, 2005; Subero-Couroyer, Ghadiri, Brunard, & Kolenda, 2005; Zakeri, Samimi, Khorrama, Atashi, & Mirzaei, 2010). For these reasons, in recent years, the mechanical strength of industrial catalysts has been studied by many researchers.

One of the main methods for analyzing the mechanical strength of catalysts is the standard single-particle crushing strength test (Couroyer, Ghadiri, Laval, Brunard, & Kolenda, 2000; Jawad et al., 2010b; Wu et al., 2002), since it has been shown that mechanical failures of mixed oxide catalysts and oxide-supported metal catalysts in both laboratory and industrial settings are due to brittle fracture. Solid catalysts are highly porous and contain numerous defects and discontinuations (Li et al., 1999, 2000), such that stresses are concentrated around the edges of existing

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micro-cracks, applying much higher localized tensions compared with distributed stresses in a catalyst bed. This concentrated stress is the primary cause of fracturing, leading to mechanical failure of the catalyst. Variations in the shape, size, and position of these flaws produce a wide range of strength data that more closely match a Weibull distribution than normal or lognormal distributions (Antonyuk, Tomas, Heinrich, & Mörl, 2005; Li, Wang, Yu, Zhang, & Chang, 1995; Li et al., 1999, 2000; Li, Wu, & Lin. 2004; Müller, Seeger, & Tomas, 2013). These scattered data are thus more fully explained based on statistical analysis. One technique suited to such analysis is response surface methodology (RSM), a powerful statistical technique in process optimization whereby the interactions and combined effects of parameters obtained from a set of experiments are characterized (Li, Wang, Zhang, & Chang, 1996; Zhang et al., 2009).

In the present work, a pelletizing method was employed to form a gamma alumina support and the effects of four variables were studied: the binder concentration, compaction pressure, calcination temperature, and method of drying. In the associated design of experiment and statistical assessments using RSM, the crushing strength was assessed as the response affected by these variables. The validity of the obtained model was then verified by an analysis of variance and the Weibull modulus values were obtained by linear regression of the Weibull equation for the crushing strength test results of all support samples.

Materials and methods

Forming of gamma alumina powder

Gamma alumina powder ($S_{\text{BET}} = 119.47\ \text{m}^2/\text{g}$, $V_p = 0.32\ \text{cm}^3/\text{g}$) was purchased from Nano Pars Spadana Co., Iran, and used to prepare the catalyst supports. In the forming step, varying amounts of aluminum silicate slurry (Nano Pars Spadana Co., Iran), serving as a binder (11.59, 15, 20, 25, and 28.41 mass%), were mixed with the gamma alumina powder. The resulting mixtures were held in sealed bottles for 24 h and then pressed to obtain pellets (6 mm diameter) under 379, 574, 861, 1148, or 1343 MPa pressure. After pelletizing, two different drying procedures were used to investigate the effect of the drying process on the mechanical strength of the catalyst supports. A number of pellets were dried at 30 °C for 24 h (termed gentle drying), while others were heated at 100 °C for 8 h (relatively fast drying). The pellets were subsequently calcined for 3 h at 466, 500, 550, 600, or 634 °C. Following calcination, the gamma alumina pellet samples were stored in sealed, dry containers to protect them from ambient humidity.

Mechanical strength measurement

Single-pellet crushing strength testing

A quasi static, single-particle compression test method was used to assess the failure strength of the support pellets (Ryu & Saito, 1991; Samimi, Hassanpour, & Ghadiri, 2005). Individual pellets, after measurement of their height and mass, were compressed between two rigid platens in the axial direction at a slow rate in the range of 0.1–0.5 mm/min, producing strain rates typically below $5 \times 10^{-3}\ \text{s}^{-1}$, using an Instron 4206 strength test apparatus (Instron, UK). Fracturing of the pellets was evident when a sudden drop in the load was observed and the crushing strength was defined as the maximum force measured prior to fracture divided by the cross-sectional area basis. The mean crushing strength was calculated as the arithmetical average of the obtained strength data for at least 15 pellets.

Applicability of Weibull analysis to data treatment

Griffith (1921) expressed the fracture strength of brittle materials as a function of surface energy, Young's modulus, and the size of micro-cracks inside the material (Wu et al., 2002). It is known that failure of supported metal catalysts occurs as a result of the growth of a critical flaw in response to stresses that develop in the bulk catalyst. The strength data scatter in such cases is well described by a two-parameter Weibull distribution (Eq. (1)) (Trustrum & Jayatilaka, 1983).

$$P(F) = 1 - \exp(-\beta F^m) \tag{1}$$

Here $P(F)$ is the probability of strength failure, F is the maximum load leading to fracture, m is the Weibull modulus (an empirical material constant that characterizes the distribution range of the strength data), and β is the size parameter of the Weibull distribution. There are several methods available in the literature for determining the Weibull parameters from a set of experimentally measured strength data, but the most widely used is the linear regression (LR) method because of its simplicity (Li et al., 2004; Wu, Zhou, & Li, 2006). In this method, the Weibull parameters can be obtained from regression, by twice calculating the logarithm of the value obtained from Eq. (1), as shown in Eq. (2).

$$\ln\left(\ln\frac{1}{1-P(F)}\right) = m\ln F + \ln\beta \tag{2}$$

The failure probability at various loadings may be evaluated using a probability estimator (Eq. (3)):

$$P_i(F) = \frac{i-0.5}{n}, \tag{3}$$

where i is the rank of the crushing strength data when the data are listed in ascending order and n is the total number of pellets tested. This estimator is recommended by Bergman (1984), Khalili and Kromp (1991), Li et al. (1999), Trustrum and Jayatilaka (1979), and Wu et al. (2001, 2002, 2006).

The Weibull modulus can thus be obtained directly from the slope term, m, in Eq. (2) and the Weibull size parameter can be determined from the intercept term $\ln\beta$ (Li et al., 2004).

Experimental design

RSM is a collection of mathematical and statistical techniques, and is applied in cases in which a response of interest is influenced by several variables and the objective is to optimize this response (Montgomery, 2001). RSM was thus employed in this study to optimize the catalyst support forming process to gain the highest possible crushing strength. A central composite rotatable design (CCRD) was used to design the experiments. This method requires fewer tests than a full factorial design and therefore allows optimization of the effective variables and analysis of the interactions between these variables and the response with a minimum number of experiments (Zhang et al., 2009). The effects of three numeric factors were investigated at five levels: Z_1 (binder concentration), Z_2 (compaction pressure), and Z_3 (calcination temperature). In addition, a categorical factor Z_4 (method of drying) was assessed at two levels (gentle and fast). The crushing strength was taken as the response of the designed experiments. The natural variable levels, X_i, were coded as Z_i according to the following equation in such a way that X_0 corresponded to the central value.

$$z_i = \frac{x_i - x_0}{\Delta x_i}, \quad i = 1, 2, 3, \ldots, k \tag{4}$$

where Z_i is the dimensionless value of an independent variable, X_i is the natural value of an independent variable, X_0 is the natural value of an independent variable at the center point and ΔX_i is the step change (Tanyildizi, Ozer, & Elibol, 2005).

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