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Experimental Investigation of Attrition Resistance of Zeolite Catalysts in Two Particle Gas-Solid-Solid Fluidization System

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Abstract. In the study of mechanical degradation of 34 ZSM-5 and SAPO catalysts, using the gas jet attrition - ASTM standard fluidized bed test (D-5757), the effect of particle size and its quantitative analysis in co-fluidization environment was investigated on the air jet index (AJI) basis. In gas-solid-solid fluidized bed reactors (GSS-FBR), two different sized particles were fluidized under isothermal conditions. In case of ZSM-5 and SAPO-34, significant attrition resistance was observed, which was attributed to small pore size and specific structural strength of the mobile framework image (MFI) and chabasite (CHA) structures, respectively. The optimum AJI for SAPO-34 and ZSM-5 (of particle size 0.2 mm) in GSS-fluidization system was observed to be 0.0118 and 0.0062, respectively. In co-fluidization, deviations from Gwyn relationship were observed due to change in impact of collision. Therefore, zeolites are recommended as suitable catalysts or catalytic supports (for doping of expensive metals) and for commercial use in GSS-FBR.

Keywords: attrition; zeolite catalyst, two particle system, gas-solid-solid fluidized bed reactor

Introduction

Attrition in general terms can be defined as the fractionation of solid particles or generation of fine particles from an initial unique solid piece (Weeks and Dumbill, 1990). This unwanted breakdown of solid particles is a frequently encountered problem in the suitable use of catalytic processes. The common problems related to catalyst attrition may be loss of catalyst as a consequence of fines generation, change of bulk properties of the catalyst, loss of active surface coating, and decrease in the final quality of the product due to separation problems.

In general, attrition resistance is affected by several intrinsic properties of the particles (like size distribution, shape, porosity, surface, cracks and hardness of the particles) and the operation environment such as time of exposure, shear, velocity, pressure and temperature (Bemrose and Bridgwater, 1987). Thus the attrition resistance is an important parameter design and development of catalysts. A number of attrition test methods have been developed to evaluate attrition resistance of catalyst for fluidized bed reactors (Bemrose and Bridgwater, 1987). Catalyst attrition occurs in fluidized bed reactors owing to continuous catalyst movement and collision (Bemrose and Bridgwater, 1987). The ASTM standard fluidized-bed test (also known as air-jet test) is the most popular and reliable method of measuring attrition resistance of catalysts (Forsythe and Hertwig, 1949). Air-jet attrition apparatus configuration, test procedures and conditions were standardized in the ASTM fluidized-bed method (ASTM, 1995).

The present research was focused especially on zeolite catalysts used in the fluidized environment. Major disadvantages of fluidized beds relative to fixed beds are the generation of fines, loss of catalyst and separation problems (Johnsen and Grace, 2007). The attrition intensity depends on the flow regimes, superficial gas velocity, baffles and internals of the reactor as shown in Fig. 1. This may lead to change in fluidization properties and air pollution.

Even though there have been several studies on particle attrition, it is clear that attrition is a quite complex phenomenon. Each system has to be specifically studied in order to adequately explain its attrition behaviour and quantify it. Single particle attrition was extensively studied and well known empirical relationship, "Gwyn relationship", was drawn (Gwyn, 1969). The attrition rate is directly proportional to the difference between the superficial

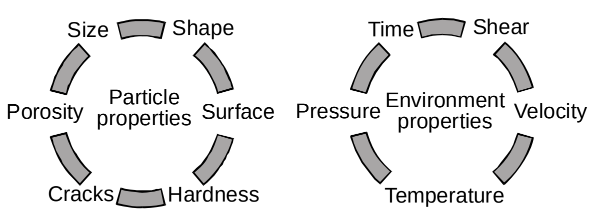

Fig. 1. Factors affecting attrition resistance.

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velocity, minimum fluidization velocity and catalyst's physical properties such as surface area, bulk density and size distribution changes. Recently, the idea of bi-modal particle fluidization (in which both particles are in fluidization state) has been floated by Nawaz *et al*. (2010). This sophisticated concept is applied to handle extremely exothermic and endothermic reactions in a fluidized bed technology. But hydrodynamics of the proposed design is complicated in comparison to the single particle fluidization. In single particle system, the attrition originates particularly from bubbling, grid jets and baffles and splashing of ejected particles in fluidized beds, while in co-fluidization system, it is attained due to internal collision of large particles which crush small catalyst particles. No information is available to date in open literature about attrition resistance of zeolite catalysts used in GSS-FBR. In the present work, attrition resistance of the commercially employed zeolite catalysts, which are extensively used in cracking and dehydrogenation reactions, has been investigated. The influence of small particle size on attrition that co-fluidized with large particles of the same material was also studied.

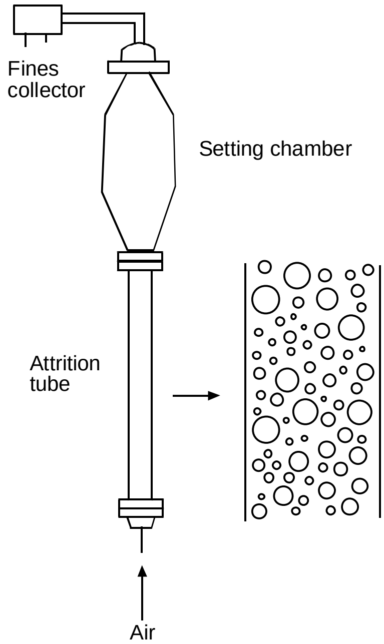

Fig. 2. Gas jet attrition apparatus.

Materials and Methods

Catalyst preparation. SAPO-34 catalyst was prepared by mixing of pure SAPO-34 zeolite, kaolin and silicon solution in the ratio of 30%, 40% and 30%, by weight, respectively. Powder ZSM-5 catalyst of different sizes was provided by Nankai Catalyst Company, Tianjin, China. Particle morphology was obtained for each catalyst (as prepared and after the jet-cup attrition testing) using a JEOL JSM 7401-F scanning electron microscope (SEM). The size distribution of small particles was characterized using a Malvern Mastersizer (MICRO-PLUS). The average size of large ZSM-5 particles, measured using a vernier calliper, was approx. 2.7 mm.

Gas jet attrition test (ASTM standard fluidized method). The attrition effect of big sizes ZSM-5 catalyst and self attrition were investigated here using a gas jet attrition apparatus (Fig. 2) at FLOTU, Tsinghua University, Beijing, China. This unit was designed on standard ASTM D-5757 test method for determining the attrition resistance of powdered catalysts (ASTM, 1995). The gas jet attrition apparatus is shown in Fig. 2 and its design features are as fallows:

(a) a stainless 70 cm long attrition tube of OD 12 cm,
(b) 3 nozzles of diameter 0.38 mm, equidistant from each other, 10 mm from the centre,
(c) settling chamber, 62 cm long cylinder of inner diameter 34 cm with conical ends and
(d) fines collection assembly, filtering the fines from the gas.

Attrition behavior for fluidized bed test is dependent upon parameters such as time, particle size, gas velocity, bed length and temperature. Therefore, attrition rate ($r_{attrition}$) can be expressed as a function of all the parameters listed above in single particle fluidization system (Carreto, 2003):

$$r_{attrition} = \alpha\,(H^m \rho_f \rho_s U_o^n \Delta T_f)\,(t^e D_p^g)^{-1}$$

where:

H^m = bed height in meters,
ρ_f = density of fluid,
ρ_s = density of solid,
U_o^n = fluidization of velocity (over distributer plate),
T_f = temperature of fluid,
t^e = time and
D_p^g = diameter of particles (granular).

Induced particle breakage mechanisms in air-jet test are believed to be fracture (in the grid region of the apparatus) and abrasion (in the bubble zone of the apparatus) (Bemrose and Bridgwater, 1987). Previous studies on spray-dried iron catalysts confirmed the time dependency of attrition, suggesting that air-jet tests are related to abrasion mechanisms (Zhao *et al*., 2000; Gwyn *et al*., 1969). In a properly constructed air jet apparatus, the interaction between catalyst particles is dominant. All tests were conducted with nitrogen at room temperature. Catalyst attrition is determined by means of gas jets to provide information about the ability of catalyst to resist particle size reduction in a fluidized bed environment.

With the increase in gas velocity from terminal velocity, fine particles were transported to fine collection chamber.

Before operation, the fines collection assembly (filter) was weighed and fixed properly to ensure no loss through the assembly fittings. Then standard mass of 50 g catalyst was loaded in attrition tube according to the ASTM standard D-5757 and fixed with flanges. The gas supply was opened at 2 bars and the gas flow rate was adjusted slowly at 0.6 m^3/hr. The attrition mass was measured every hour from the start up to 5 h. The attrition tube was disassembled and the catalyst remaining inside was weighed. Overall weight loss was calculated by subtracting it from the total loading. AJI is then calculated using the following expression:

Air jet index after 5 h = $(m_5 - m_0) / m_s$

where:

m_0 = mass of the first empty fines collection assembly at the start of the test (g),

m_5 = mass of the fines collection assembly after 5 h operation (g) and

m_s = mass of the sample charged to apparatus (nominally 50 g).

Results and Discussion

The air jet index (AJI) of all samples was calculated from the elutriated fines collected during the experimentation. This empirical index gives information about relative attrition mass generated, under different operating conditions. The experimental results of single particle fluidized system and double particle (GSS) fluidization system are tabulated in Table 1 and 2, respectively. Negligible loss of catalysts, associated with disassembly of the attrition tube, was observed and the recoveries were approx. 99% in all experiments. The experimental data of single particle system (Table 1) follow linear function of time and their plot is shown in Fig. 3. Then different sizes and types of zeolite materials of similar densities were co-fluidized and their attrition response was analyzed for the commercial use of the individual as GSS cracking or dehydrogenation catalyst or catalyst support. Attrition relationship was still observed to be linear with time in two particle fluidization system, but the attrition derbies largely increased and deviation from Gwyn formulation was noted (Fig. 3).

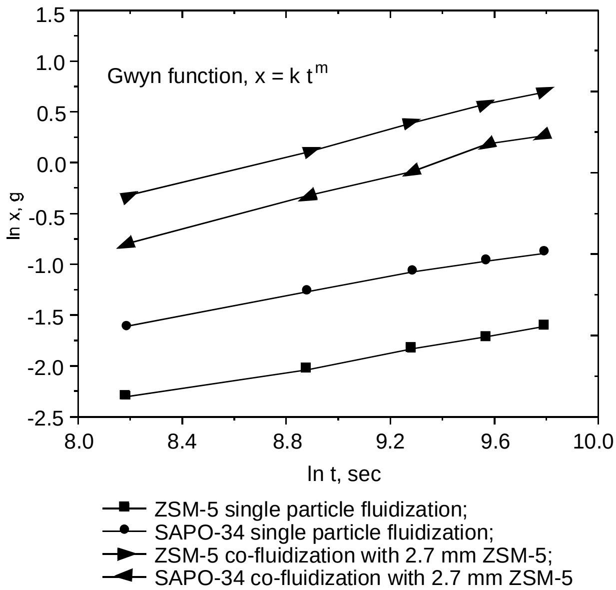

Fig. 3. Gwyn plot of 0.1 mm zeolite catalyst under fluidization and co-fluidization (GSS) environment.

Table 1. Attrition results of single zeolite particle fluidization in gas jet attrition test

Exp. no.	No. of runs	Zeolite material type	Size (mm)	Fines after 1 h (g)	Fines after 2 h (g)	Fines after 3 h (g)	Fines after 4 h (g)	Fines after 5 h (g)	Overall weight loss (%)	A J I after 5 h
1	I	ZSM-5	0.1	0.1	0.11	0.12	0.13	0.14	0.4	0.0028
	II	ZSM-5	0.1	0.1	0.13	0.16	0.18	0.2	0.6	0.004
2	I	ZSM-5	0.15	0.05	0.07	0.09	0.11	0.13	0.4	0.0026
	II	ZSM-5	0.15	0.06	0.07	0.08	0.11	0.13	0.4	0.0026
3	I	ZSM-5	0.2	0.03	0.05	0.07	0.08	0.09	0.4	0.0018
	II	ZSM-5	0.2	0.04	0.05	0.06	0.07	0.08	0.5	0.0016
4	I	SAPO-34	0.1	0.2	0.28	0.34	0.38	0.41	1.2	0.0082
	II	SAPO-34	0.1	0.19	0.25	0.31	0.36	0.4	0.8	0.008
5	I	SAPO-34	0.15	0.13	0.16	0.2	0.23	0.26	1	0.0052
	II	SAPO-34	0.15	0.12	0.16	0.19	0.23	0.26	0.8	0.0052
6	I	SAPO-34	0.2	0.07	0.09	0.11	0.13	0.16	0.61	0.0032
	II	SAPO-34	0.2	0.06	0.09	0.11	0.13	0.15	0.7	0.003
7	I	ZSM-5	2.7	0	0	0	0	0	0	0
	II	ZSM-5	2.7	0	0	0	0	0	0	0

Table 2. Attrition results of GSS co-fluidization of zeolite catalysts in gas jet attrition test

Exp. no.	No. of runs	Zeolite type	Small particle size (mm)	Elutriated fines after 1 h (g)	Elutriated fines after 2 h (g)	Elutriated fines after 3 h (g)	Elutriated fines after 4 h (g)	Elutriated fines after 5 h (g)	A J I after 5 h
1	I	ZSM-5	0.1	0.45	0.72	0.92	1.2	1.31	0.0262
	II		0.1	0.46	0.71	0.91	1.18	1.29	0.0258
2	I		0.15	0.23	0.33	0.42	0.51	0.61	0.0122
	II		0.15	0.25	0.34	0.41	0.51	0.6	0.012
3	I		0.2	0.13	0.18	0.23	0.27	0.31	0.0062
	II		0.2	0.15	0.2	0.24	0.29	0.33	0.0066
4	I	SAPO-34	0.1	0.72	1.11	1.48	1.79	2	0.04
	II		0.1	0.71	1.15	1.47	1.76	1.94	0.0388
5	I		0.15	0.4	0.65	0.8	0.96	1.11	0.0222
	II		0.15	0.41	0.66	0.81	0.91	1.07	0.0214
6	I		0.2	0.22	0.34	0.42	0.51	0.6	0.012
	II		0.2	0.21	0.32	0.41	0.5	0.59	0.0118

Large particles are ZSM-5 catalyst of size 2.7 mm and mass mixture is 1:1.

The self attrition of small zeolite catalysts (ZSM-5 and SAPO-34) of particle size 0.1, 0.15 and 0.2 mm were tested for standard testing time of 5 h and maximum AJI value of 0.0082 was noted; it meant that 0.82% of the initial sample was lost. While the self attrition of big ZSM-5 catalyst of average particle size 2.7 mm showed excellent resistance to attrition. The AJI value of zero or no loss meant that 100% sample was recovered after 5 h. It was further observed that the attrition resistance of zeolite catalysts largely improved with the increase in catalyst particle size.

As it is desired to develop GSS-FBR for commercial application (or process requirement) the attrition in co-fluidized bed of the same material was focused. This unique piece of equipment has superior features in operation, while at the same time catalysts responsibilities increased towards physical stability of operation. AJI of SAPO-34 is comparatively higher than ZSM-5 in co-fluidized system (GSS-FBR). Similar trend of particle size influence on attrition was noted (Fig. 4). Using particle size of 0.2 mm and operation time 5 h, remarkable attrition resistance of ZSM-5 and SAPO-34 were observed with AJI of 0.0066 and 0.012, respectively. The attrition rate is time dependent phenomenon as reported in various studies (Carreto, 2003; Zhao *et al*., 2000; 1999), while zeolite catalysts clearly demonstrates its remarkable robustness to withstand co-fluidized bed severe operating conditions over 5 h operation. The particle size distribution before and after fluidization tests was observed to be almost the same (Fig. 5).

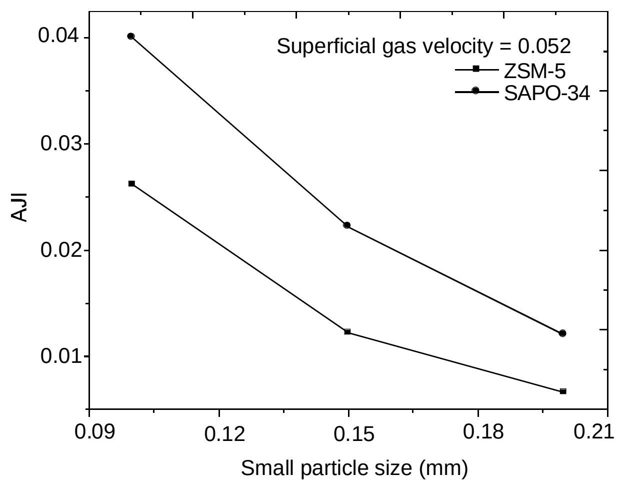

Fig. 4. Influence of particle size on AJI under GSS fluidization environment with 2.7 mm ZSM-5.

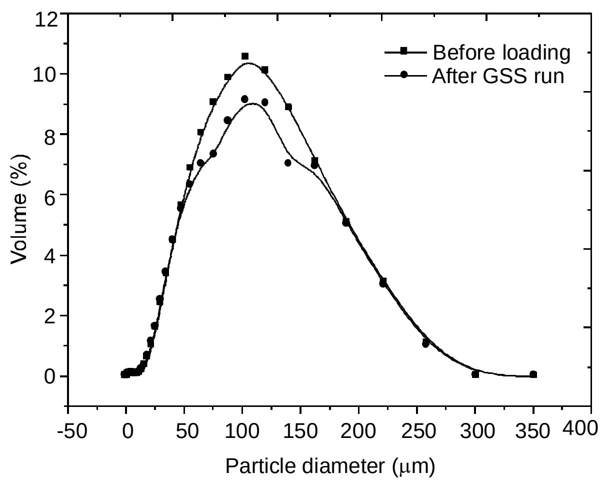

Fig. 5. Particle size distribution before and after attrition test of 0.1 mm SAPO-34 zeolite sample at 5 h.

It can be seen, that the catalyst particle sizes did not decrease much in both single particle fluidization and co-fluidization tests, but still attrition mass was recovered. The ZSM-5 catalyst particles of 0.1 mm were selected for explaining this degradation phenomenon using micro-graphs. Fig. 6(a) shows ZSM-5 catalyst topology before the fluidization tests. In single particle attrition test the particles recovered had slight cracks on their external surface as demonstrated in Fig. 6(b), but no major abrasion and fragmentation were noted. On the other hand catalyst recovered after mixed bed (both big and small particles co-fluidized) had large cracks (fractures) and abrasions on their surfaces, and these fragmented from fines of less than 20 µm size over surface, as shown in Fig. 6(c). In order to develop mechanistic understanding of attrition during co-fluidization, all samples were analyzed using SEM, before and after each test. It may be observed from the SEM images that both abrasion and fracture mechanisms are in effect, but in the case of co-fluidization, fracture process plays major role. This may be due to stronger collision impact (Fig. 6). High fracture resistance is also observed in the case of larger zeolite particles in comparison with the small particles.

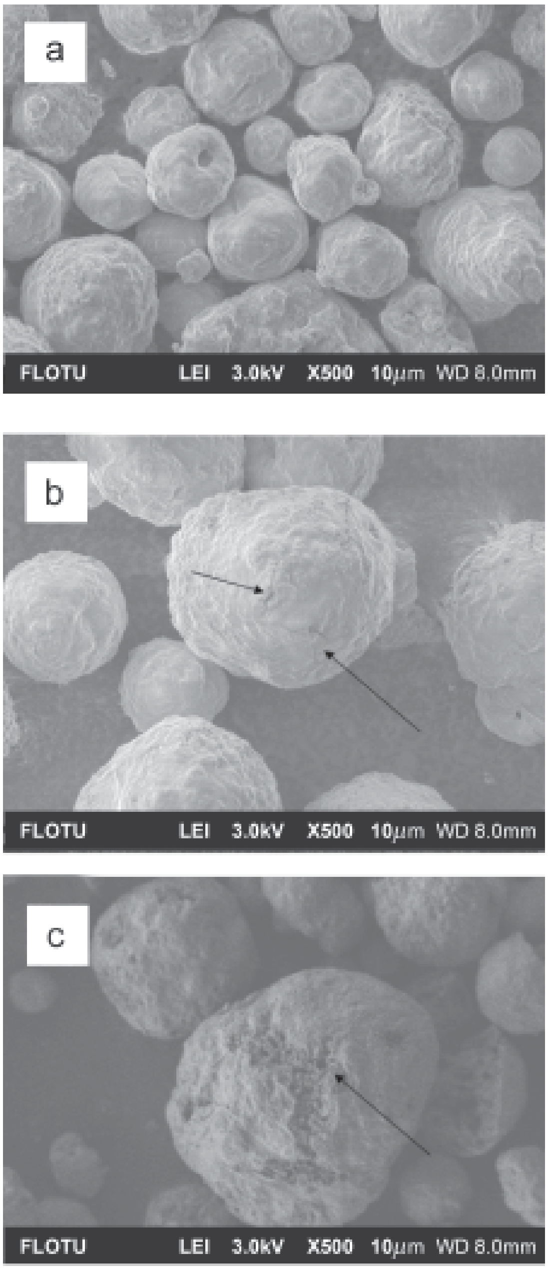

Fig. 6. SEM micrograph of 0.1 mm ZSM-5 catalyst; (a) before attrition, (b) after single particle fluidization system after 5h run and (c) after co-fluidized system after 5h run.

Conclusion

Several attrition debris were observed in case of co-fluidization environment under identical conditions and their deviations from Gwyn formulation was noted. The attrition resistance continuously increased with the increase in small zeolite particle size during co-fluidization. Thus particle size of zeolite catalysts is the critical parameter. From this extensive experimental study, it was confirmed that the zeolite material is comprehensive opportunity for its use as catalyst in a GSS-FBR due to its excellent attrition resistance. Furthermore, its stability provides room for its use as a base for expensive metal doping to develop bi-, tri-metallic zeolite supported catalysts.

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