Catalyst Characterization: From Fresh to Spent

Relevant for: powder rheology, zeolites, FCC catalysts, metal catalysts, active metal area, dispersion, acid sites, particle size analyzer, BET surface area, pore size distribution, hierarchical materials

Characterization of catalysts, both prior to reaction and in their spent form, can provide valuable information about the efficiency of the catalytic process and guide future design of new catalysts. Through determination of the pore size, pore volume, active surface area, particle size, surface acidity, fluidization behavior, cohesion strength and elutriation rate with Anton Paar instruments, insights can be derived that contribute to catalyst development and quality control.

1   Introduction

Catalysts, particularly heterogeneous catalysts, are used in many different industries to enhance efficiency and quality in material production. Structural, particle, and powder flow information of both fresh and spent catalysts can aid researchers and manufacturers in optimizing catalyst design for the desired application. While this report uses examples of catalysts from the oil and gas industry, specifically Fluidized Catalytic Cracking (FCC) zeolites, the techniques outlined here are of benefit to all catalyst researchers.

FCC is an important part of the world's energy production and responsible for half of gas and kerosene output [1]. Developed to rapidly scale up fuel production in the beginning of World War II, to this day it remains one of the most intensively used chemical engineering processes in the world. FCC is a fluidized bed process which uses hot, gaseous heavy fractions left over after initial distillation in a fuel refinery and breaks them down further into useful portions for subsequent distillation steps.

Characterization plays a crucial role in the development process of all new catalysts and is of great importance for FCC catalysts in the oil and gas industry. Pore size and connectivity within FCC zeolite catalysts can affect the transport of molecules to the catalytic sites. Gas sorption (physisorption) is used to determine the micro- and mesoporous structure of the pores within the zeolite. Advanced techniques such as interpretation of the hysteresis loop and hysteresis scanning can also be used to determine pore connectivity, which drives transport and diffusion to the active catalytic sites. Flow chemisorption experiments such as ammonia temperature programmed desorption (TPD) are used to determine the acid site quantity and strength within the zeolite and to differentiate between Lewis and Brønsted acid sites.

In addition to the characterization of fresh catalysts, the continuous running of an FCC reactor is a challenging environment for the catalysts themselves, therefore it is a logical conclusion that characterization of spent catalysts is equally important. High temperature, oxidative reaction of fuel leads to coking in seconds, which makes a regeneration step necessary. Coking effects on catalysts are studied via surface area and pore size changes in the material. Furthermore, high shear rates and many collisions (due to the fluidized bed) provide an environment where physical degradation of the zeolite catalysts becomes an issue.

A large part of degradation of catalysts in an FCC process is due to attrition. Attrition is one of the two mechanisms by which a granular medium in a fluidized bed process is broken apart. In contrast to breakage, in an attritive process, the bulk solid is not broken into parts that are of roughly the same dimension, but rather pieces are shorn off, which results in a fine fraction one or multiple orders of magnitude smaller than the original particle. Because these new fractions are all but invisible to most traditional methods such as sieving or visual inspection, it is challenging to quantify the amount of

lost material. An insight into these processes becomes possible with the broad portfolio of Anton Paar instruments. Gas sorption instruments such as the NovaTouch (for surface area and mesopore analysis), autosorb iQ-C (for complete surface area, micro- and mesopore analysis, as well as static and flow chemisorption) or the ChemBET Pulsar (for flow chemisorption) provide an efficient catalyst structural characterization. On the other hand, particle size analysis with the PSA series and powder rheological methods (cohesion strength, fluidization by oscillation, elutriation rate, and fluidized bed rheology) are both useful tools for understanding and controlling attrition.

In addition to the FCC zeolite catalysts discussed above, supported metal catalysts are also extensively used in many industries: in the chemical industry, from production of bulk and fine chemicals, in the petrochemical industry in reactions such as hydrogenation, dehydrogenation, and cracking, among others. For these types of catalysts, it is important to determine the active metal surface area and metal dispersion. Chemical adsorption (chemisorption) with the ChemBET Pulsar (flow) or autosorb iQ-C (static and flow) allows one to determine these parameters.

This report provides examples of catalyst characterization for structural, particle, and flow properties using a wide range of Anton Paar instrumentation on fresh, spent, and metal-supported catalysts.

2 Fresh FCC Catalysts

2.1 Gas Sorption – Surface Area, Pore Size and Volume

Gas sorption (physisorption) can be used to determine the BET surface area and pore size distribution of zeolite FCC catalysts. Ar (87 K) is recommended as the adsorptive for the analysis due to specific interactions of N_2 (77 K) with the polar sites in the zeolite [2]. Because zeolites are microporous, the linear BET range shifts to lower relative pressures. The Micropore BET Assistant feature in the Anton Paar software can be used to quickly determine the correct linear range [3]. Ar (87 K) adsorption, coupled with state-of-the-art density functional theory (DFT) methods for pore size analysis can be used to give accurate micro- and mesopore size distributions [4]. DFT methods for both cage and channel zeolite structures are available. In addition, hierarchical zeolites are easily characterized using a single DFT method. An example of a series of micro-mesoporous (hierarchical) Y zeolites characterized using Ar (87 K) adsorption and non-local DFT (NLDFT) measured on an autosorb iQ XR is shown in Figure 1 [5]. These

methods are sensitive enough to detect small differences in pore size as illustrated in Figure 1d, which shows the tailored mesopore sizes and constant micropore size in a series of Y zeolites.
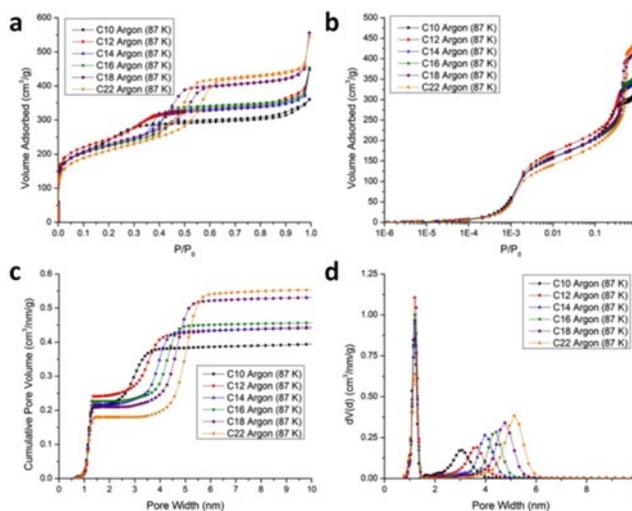
Figure 1: Argon (87 K) adsorption isotherms (a) linear and (b) semi-logarithmic and NLDFT cumulative pore volume (c) and pore size distribution (d) on a series of hierarchical Y zeolites. Reproduced from [5] with permission from Wiley.

2.2 Gas Sorption – Hysteresis Scanning

Advanced gas sorption techniques such as hysteresis scanning can be used to determine additional structural characteristics of the pore system of hierarchical materials. Scanning of the hysteresis loop gives information regarding desorption mechanism (equilibrium, cavitation, pore blocking) and pore connectivity [6]. Pore connectivity is crucial for transport and diffusion into zeolite pores, where, ideally, added mesopores in the zeolite funnel into the inherent microporosity. Figure 2 shows an example of hysteresis scanning applied to hierarchical zeolite Y measured using the Anton Paar autosorb iQ, which contains a special hysteresis scanning mode to easily program and measure all scans in one experiment [5]. Hysteresis scanning was used to confirm equilibrium desorption for the majority of the pores and cavitation for the remaining.
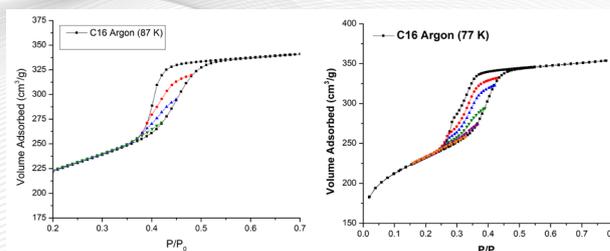
Figure 2: Hysteresis scanning of the Ar (87 K) (left) and Ar (77 K) (right) in a hierarchical zeolite Y [5] indicating the majority of

2.3 Chemisorption – Ammonia TPD

Important catalytic information about zeolites can be determined using chemical gas adsorption (chemisorption). Acid sites (both quantity and strength) are analyzed using ammonia TPD. In addition, Lewis and Brønsted acid sites can be determined [7]. Figure 3 shows an ammonia TPD of ZSM-5 and NaY zeolites. The TPD of ZSM-5 shows two peaks for two different strengths of acid sites present in the sample with the stronger sites represented by the peak at higher temperature, while the NaY TPD only shows the presence of a single type and strength of acid site.
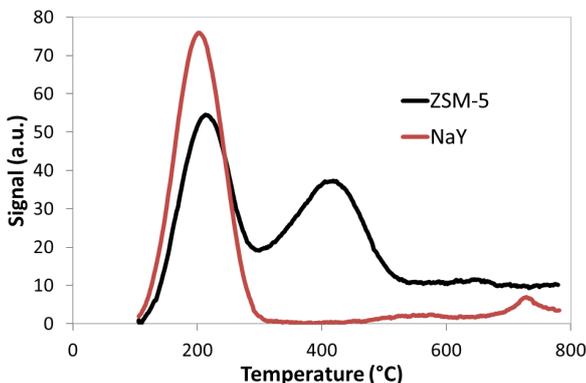
Figure 3: Ammonia TPD of ZSM-5 and NaY zeolites. Each peak represents different types/strengths of acid sites in the zeolite.

3 Spent FCC Catalysts

Two batches of platinum coated FCC catalysts were obtained, with identical initial particle size distributions (measured by the provider of the samples, not shown here), but used in two different reactor designs for the same amount of time. The aim of the following investigation is to analyze how the difference in reactor design affects the expected length of the catalysts life cycle, and therefore the cost efficiency of the process.

3.1 Gas Sorption – Surface Area and Pore Size

3.1.1 Challenges

In order to determine the changes a catalyst has undergone during the catalytic process, physical properties such as surface area, pore volume, and pore size, which can be determined via gas adsorption, assist researchers in elucidating these changes.

3.1.2 Material and Experimental Setup

Two different production batches of spent FCC zeolites (Batch 1 and 2) were analyzed using an Anton Paar autosorb iQ with Ar (87 K). Non-local density functional theory (NLDFT) was used to calculate micro-mesopore size distributions. N_2 (77 K) was also measured in the mesopore range to determine micropore volume and area via the t-method.

3.1.3 Measurement and Results

Figure 4 shows the Ar (87 K) isotherms on the two catalysts. Table 1 summarizes the BET surface area, micropore size, micropore area, and micropore volume calculated from the Ar (87 K) and N_2 (77 K) measurements. In this particular case, gas sorption gives BET areas and micropore size, volume, and area information that is nearly identical. Additionally, an overlay of the DFT pore size distributions from the Ar (87 K) isotherms is shown in Figure 4. The micro- and mesopore regions of the distributions are identical for Batch 1 and 2. The porosity of these two samples was affected in the same way (or unaffected) by the catalytic process and they are indistinguishable by gas sorption.

Sample	BET Area $(m^2/g)^a$	Micro-pore Size $(nm)^b$	Micro-pore Volume $(cm^3/g)^c$	Micro-pore Area $(m^2/g)^c$	External Area (m^2/g)
Batch 1	112	1.2	0.03	70	42
Batch 2	113	1.2	0.03	69	44

Table 1: Physical properties calculated from gas sorption isotherms. [a] Calculated from the Ar (87 K) isotherms [b] Calculated from the Ar (87 K) isotherms using a spherical/cylindrical NLDFT model [c] Calculated from the N_2 (77 K) mesopore isotherms (not pictured) using the t-method.
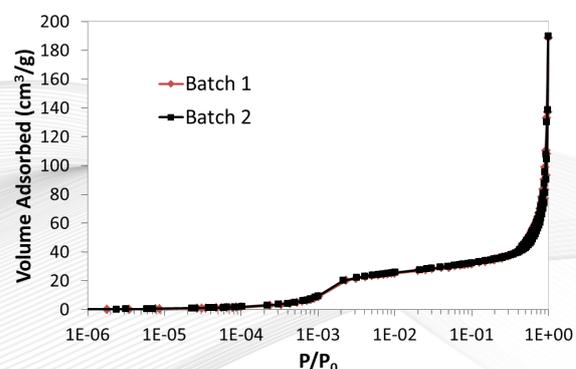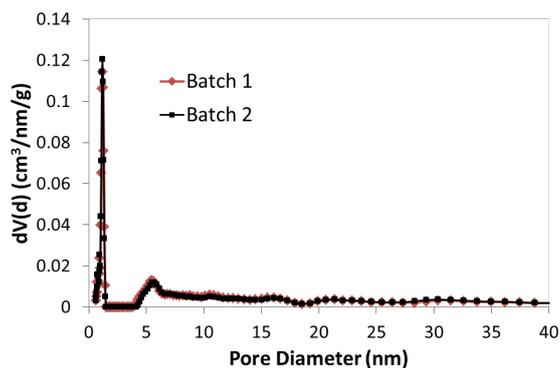
Figure 4. Ar (87 K) isotherms (top, logarithmic x-axis to highlight the micropore filling region) and corresponding NLDFT pore size distributions (bottom).

Although in this particular example gas sorption cannot differentiate between the two samples, gas sorption is regularly measured on spent catalysts, particularly in situations where coking occurs, as coking can cause drastic changes in surface area, pore volume, and even pore size distributions.

3.2 Particle Size Analysis

3.2.1 Monitoring the Particle Size

Particle size analysis by laser diffraction offers an easy and quick method for the characterization of physical degradation of catalyst powders, through the evaluation of the fine fraction development. Continuous monitoring is useful during catalyst and reactor development in deciding which reactor puts a higher wear on the zeolite and helps to determine the current state of the catalyst bed during everyday operation of the FCC plant.

3.2.2 Materials and Experimental Setup

The two batches of platinum-coated FCC catalysts were investigated also by particle size analysis. (Batch 1, Batch 2). Two further samples of the same material were taken from a third reactor after different times spent in the reactor (Batch 3, Batch 4). The spent catalysts were analyzed with the PSA 1190 L/D (Figure 5) in liquid mode. Because the optical properties of the zeolites were unknown, the Fraunhofer reconstruction model was chosen. The powder sediments quickly in the water tank, therefore the stirrer speed was set to its maximum. Input parameters are summarized in Table 2.
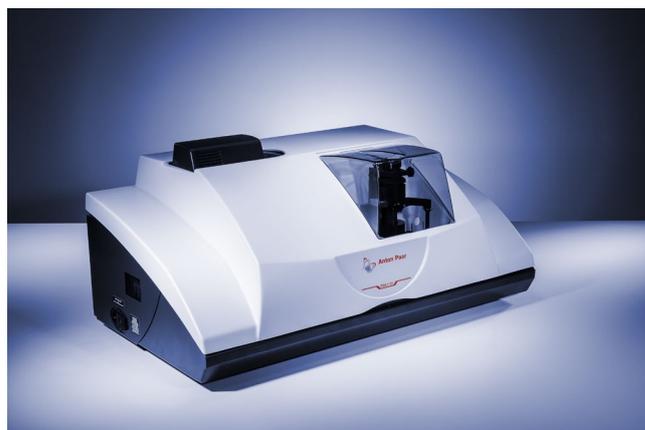
Figure 5: PSA 1190 L/D.

Parameter	Value
Measurement time	30 sec
Ultrasound	No
Stirrer	450 rpm (Fastest)
Pump speed	120 rpm (Medium)
Reconstruction model	Fraunhofer
Repetition	3
Dispersant	Water

Table 2: Input parameters for the PSA measurement liquid mode

3.2.3 Measurement and Results: Catalyst Powders from Different Reactors

Figure 6 shows a representative particle size distribution of the two batches of catalyst powder from two different reactors (Batch 1, Batch 2). D_{10}, D_{50} and D_{90} values summarized in Table 3 vary less than 0.5% reflecting excellent reproducibility. Both powders show a similar particle size distribution with a main peak at 90 µm, and a small side peak in the 20 µm range.
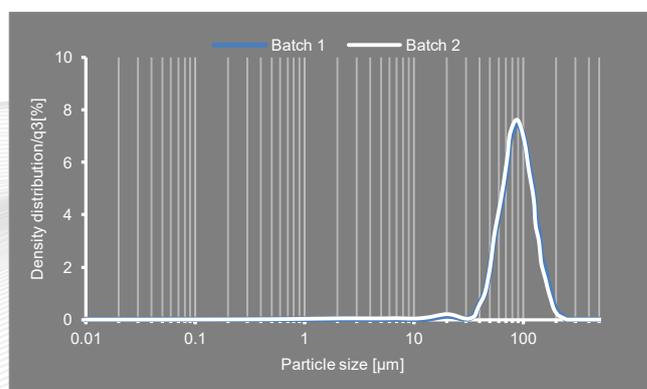
Figure 6. Volume weighted particle size distribution.

Sample	D_{10} [µm]	D_{50} [µm]	D_{90} [µm]
Batch 1	52.8 ± 0.1	84.9 ± 0.1	133.3 ± 0.5
Batch 2	50.6 ± 0.2	82.7 ± 0.3	128.6 ± 0.5

Table 3: Volume based undersize D-values of catalyst powders. Mean ± SD; n = 3

At first glance, the two batches look identical. However, the particle size distribution (PSD) delivered by laser diffraction is volume weighted, which is known to emphasize larger particles, while being insensitive to the fine fraction. In order to increase the representation of the fines in the distribution, it is advised to switch from volume to surface weighted results (Figure 7).
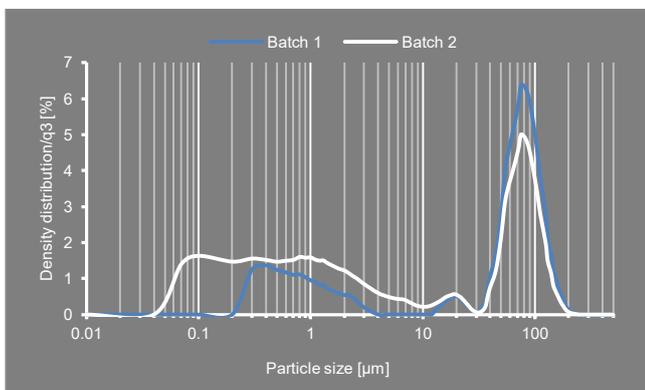
Figure 7: Surface weighted particle size distribution.

Sample	D_{10} [µm]	D_{50} [µm]	D_{90} [µm]
Batch 1	0.39 ± 0.01	59.6 ± 0.3	108.9 ± 0.3
Batch 2	0.38 ± 0.01	18.9 ± 1.9	99.2 ± 0.2

Table 1: Surface-weighted undersize D-values

The surface weighting reveals the significant difference between the fine content of the two batches. While the range of the distribution - reflected in the D_{10} and D_{90} values - are almost identical, a largely different D_{50} value highlights the shift in average size (Table 4).

The amount of fine fraction present in the sample reflects the extent of attrition the catalyst went through in the reactor. As the two catalysts have spent the same amount of time in the reactors, based on these results we can conclude that the second reactor design inflicts higher wear on the catalyst. This leads to faster degradation and higher elutriation rates (see Section 3.3.5), and ultimately to decreased cost efficiency of the plant.

3.2.4 Measurement and Results: Continuous Monitoring of FCC Catalysts

Figure 8 shows the surface weighted particle size distribution of the two batches of catalysts taken as part of continuous monitoring of an FCC reactor. Batch 4 has spent longer time in the reactor.
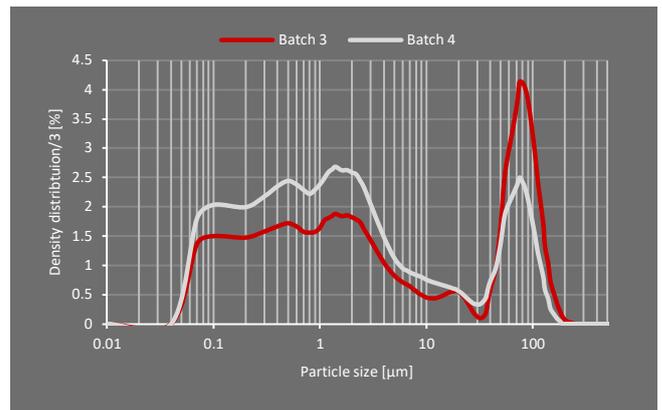
Figure 8: Surface weighted particle size distribution of catalysts taken after different reactor times.

It can be observed how the attrition creates a fingerprint-like broad fine fraction ranging over two orders of magnitude, which more or less evenly increases over prolonged time spent in the reactor. The longer reactor time is reflected in a significantly increased fraction of fines in case of Batch 4. The physical degradation is also revealed by the drastically decreased surface weighted undersize D_{90} value, seen in Table 5.

Sample	D_{10} [µm]	D_{50} [µm]	D_{90} [µm]
Batch 3	0.084 ± 0.005	1.26 ± 0.06	85.1 ± 0.6
Batch 4	0.084 ± 0.001	1.03 ± 0.02	63.2 ± 0.4

Table 5: Surface weighted undersize D-values of catalysts taken after different reactor times

In conclusion, it was shown that laser diffraction is not only a useful tool during development of catalysts and reactors, but also during everyday operation, guaranteeing smooth operation by delivering reliable information about the current state of the catalyst bed.

3.3 Powder Rheology

3.3.1 Challenges

Figure 9: MCR equipped with a **powder flow cell** (left side) and a **powder shear cell** (right side).

The physical characterization of FCC catalysts through a variety of powder rheological methods offers a plethora of properties and results useful to the applied chemical engineer both in a developmental capacity and in the day-to-day plant operation. To this end, we propose a two-step process consisting of a quick and easy cornerstone analysis (Cohesion Strength), which can be done on a daily basis that segues into a more complicated analysis further down the line.

The cornerstone analysis is Cohesion Strength, a quick and completely automated method that can be performed in as little as a few minutes and offers a highly selective and highly repeatable method (usually in the 0.1 percentile in fluidizable powders such as FFC catalysts) that serves as a daily or frequent desktop measurement to determine the continuing suitability of the catalyst batch. When prompted by an abnormality in the cohesion strength, deeper analysis can be undertaken. Examples in this work are fluidization measurement by oscillation, elutriation rate measurements and fluidized bed rheology; however, this can be expanded to include several further tests (see Figure 10).
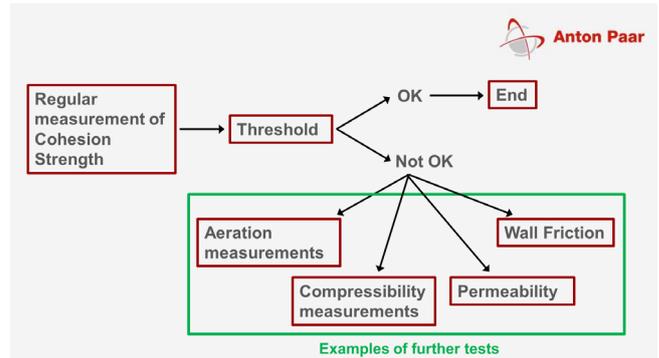
Figure 10: Quality control scheme.

3.3.2 Materials and Experimental Setup

Two batches of FCC catalysts, introduced in Section 3 (Batch 1, Batch 2) were further analyzed with an Anton Paar Powder Flow cell.

3.3.3 Measurement and Results: Powder Flow Cell – Cohesion Strength

Cohesion strength describes the internal resistance of the powder to flow. As it is quick and reproducible, it serves as a screening tool to know when to apply more time consuming methods. For a detailed description of the method refer to [8].
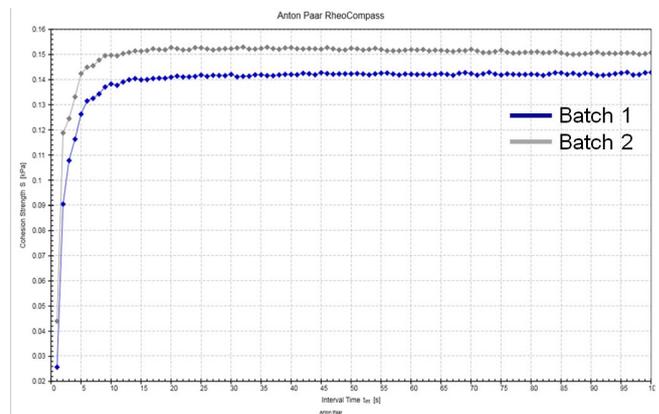
Figure 11: Cohesion strength curves of two FCC catalysts.

Unexpectedly, the batch with the higher attrition based fine content (Batch 2) has a lower cohesion. The fine content of Batch 2 is more than two orders of magnitude smaller than the primary peak at ~100 μm (see Figure 7). The hard to distinguish fine content is acting not as a hindrance to flow but as a flow aid; similar to flow aids used in various industrial powders that share a similar gap in grain size to facilitate the "spacing" effect that is at the core of flow aids [9].

3.3.4 Measurement and Results: Powder Flow Cell – Fluidization Measurement by Oscillation

Fluidization measurement by oscillation is a patented method available with the powder flow cell. It allows a more fine-grained determination of minimum fluidization velocity than the usual pressure drop method. Also, it has the benefit of being substantially faster because no baseline measurement to calibrate is necessary. It works by oscillating a graduated cylinder within the flow cell with a frequency of 7 Hz and amplitude of 2°. For more details, refer to [8].

A distinct difference was observed between the two batches of spent catalysts, showing that a larger amount of very fine content due to attrition will influence the fluidization behavior and therefore the throughput of gaseous reactants into the reactor (Figure 12). The arrow in Figure 12 denotes the shared point of incipient fluidization (the overshoot) and the bar indicates the area where it is unclear from the pressure drop data when full fluidization has occurred. The oscillogram reaches a phase shift angle of 90°, therefore showing the loss of the pseudoelastic part of the fluidized bed by completely overcoming the influence of gravity, producing the effect.
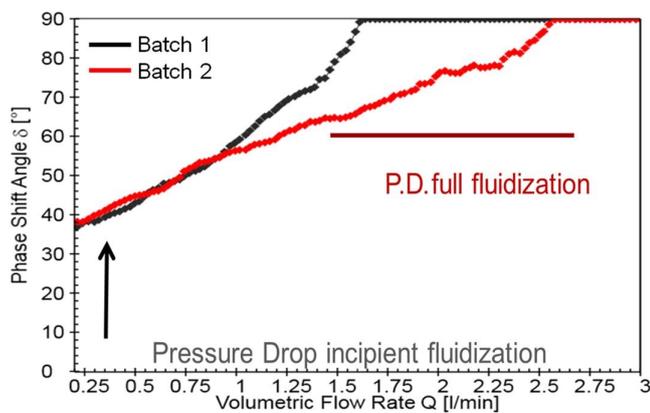
Figure 12: Fluidization measurement through oscillation.

3.3.5 Measurement and Results: Powder Flow Cell – Elutriation Rate

The elutriation rate of a catalyst is a core design problem of an FCC process. Cyclonic separators take the dust phase out of the top part of the column; however, it needs to be determined how much of the powder is elutriated (moved to the top of the fluidization column) per unit of time. To this end we fixed a vacuum device to the dust protection filter of the Powder Flow Cell that retains the elutriated powder at the filter and measured the mass loss in the fluidization column itself. The results (Table 6) show that the fine containing batch has a much larger

(nearly double) elutriation rate than the low attrition batch. This must be addressed in the reactor's design.

Sample	Filling [g]	Loss after 1 h [g]	Elutriation Rate [%]
Batch 1	87.05	1.05	1.21
Batch 2	86.95	2.10	2.42

Table 6: Elutriation Rate after 1 hour

4 Supported Metal Catalysts

4.1 Active Metal Area and Metal Dispersion

Chemisorption can be used to determine properties such as active metal area, metal dispersion, and oxidation/reduction properties of supported metal catalysts. Static (vacuum-volumetric) chemisorption performed using H_2 or CO gas allows one to calculate active metal area and dispersion on samples containing metals such as Pt and Pd, among others. H_2 and CO chemisorption isotherms on a Pt/alumina catalyst measured on an autosorb iQ C are shown in Figure 13. Combined and weak isotherms were measured, which allows the chemisorbed (strong) isotherm to be accurately determined via subtraction of the weak from the combined. From the volume in the plateau region of the strong isotherm, active metal area, metal dispersion, and crystallite size are calculated. For example, for the CO analysis in Figure 13, the active metal area was found to be 1.75 m^2/g with 35% dispersion and an average crystallite size of 32 Å.
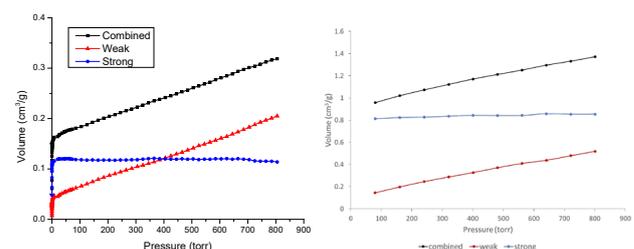
Figure 13: H_2 (left) and CO (right) chemisorption isotherms on Pt/alumina catalysts.

5 Conclusion

In this report it was demonstrated, how Anton Paar instrumentation can be used as powerful tools to characterize fresh and spent catalysts during research and development, as well as during everyday operation. Information such as surface area, pore size and volume, acid site strength, particle size, cohesion strength, and flow properties allow researchers to study and optimize their materials for the desired use and plant operators to screen their materials in quality control applications.

6   References

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Contact Anton Paar GmbH

Tel: +43 316 257-0

rheo-application@anton-paar.com

application-sp@anton-paar.com

pc-application@anton-paar.com

www.anton-paar.com