Supporting information to manuscript entitled "Photo-spectroscopy of Mixtures of Catalyst Particles Reveals their Age and Type"

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1. FCC laboratory deactivation methods

Two sets of FCC catalysts from different manufacturing technologies, both containing zeolite Y (further denoted as FCC1 and FCC2, respectively), were deactivated by either steam treatment (ST), Mitchell impregnation (MI), or cyclic deactivation (CD), as described in detail by Buurmans *et al.* [1]. In short, samples were sieved, making use of the particle sizes between 38 and 125 μm, and then deactivated by either ST, CD, or MI. ST-based FCC samples were preheated and dried in air (873 K) for 1 h after which they were steamed in 100% steam at 1061 K for 20 h. CD-based FCC samples were preheated and dried at 873 K for 1 h and loaded onto an Imtech Cyclic Deactivation unit where they received 20 cycles of alternating cracking-regeneration followed by 120 cycles of alternating oxidation-reduction steps. MI-based FCC samples were impregnated with metal naphthenates dissolved in hexane and after drying a multistep calcination was performed followed by the steam treatment of the ST-based FCC samples for 10 h. The differently deactivated FCC samples were used as received, except for the CD-based FCC samples, which were calcined for 2 h at 973 K.

2. N_2-physisorption measurements

Micropore volumes were reported by Buurmans *et al.* [1] and obtained as described below. Samples were heated in a calcination furnace at 773 K for 3 h (Ecats) or 1 h (all other samples) and vacuum treated at 573 K until a degas rate < 20 mTorr over 120 s was achieved before physisorption measurements. N_2-physisorption isotherms were recorded at 77 K using a Micromeritics ASAP 2405. BET surface areas were determined using five P/P_0 points between 0.06 and 0.22. To ensure inclusion of all five minimum required pressure points, micropore volumes were determined by t-plot analysis for t between 3.3 and 5.4 Å. The obtained data on micropore volumes are summarized in Table S1.

Table S1: Reported micropore volumes (ml g^{-1}) of the fresh, laboratory deactivated and density separated FCC catalyst samples.

Catalyst sample	FCC1	FCC2
Fresh	0.0552	0.0855
ST	0.0253	0.0478
CD	0.0234	0.0451
MI	1 X 10^{-4}	0.0068
BOL (beginning of life)	0.0243	
MOL (middle of life)	0.0163	
EOL (end of life)	0.0140	

3. Catalytic activity testing

Catalytic activity tests on the lab-based deactivated FCC samples were performed by Buurmans *et al*. [1] on a Fluid Simulation Test apparatus, which simulates the product yield of a commercial FCC reactor. Catalysts were dried in air at 473 K for 1 h and transferred into the reactor where they were fluidized with a flow of nitrogen. The average bed temperature of 811 K was monitored by a thermocouple embedded in the middle of the fluidized catalyst bed and controlled by an electrical clamshell furnace at pseudo-isothermal reactor conditions. A catalyst mass to feed mass ratio of 3 was used to compare the activity of the different catalysts. The feed consisted of Kuwait vacuum gas oil feed (20.8 API gravity, 2.8 wt% total sulphur, 1040 ppmwt total nitrogen, 250 ppmwt basic nitrogen, 0.26% Conradson carbon) which was injected down flow into the reactor to a fixed axial position of 3.175 mm from the bottom of the 1.6 cm internal diameter reactor at a constant feed rate of 0.2 g s^{-1} for 60 s. Afterwards, the catalyst was stripped for 100 s in N_2 to remove any remaining hydrocarbons before catalyst collection. Reaction products were cooled to 263 K in a glycol bath to condense heavier compounds before disengagement of gaseous products. Mass recovery was determined by volumetric water displacement and weighing for gaseous products and total liquid products, respectively. Product yield structure determination occurred by gas chromatography: gas products (H_2, C1-C6) were measured with an MTI Analytical Instruments QUAD and total liquid products via simulated distillation (ASTM D-2887) on an Agilent 6890. Carbon depositions on the spent catalysts were measured ex-situ by IR measurements (LECO CS-400) of CO_2 generated by combustion. The activity values are summarized in Table S2.

Table S2: Activity values found for laboratory deactivated and density separated

FCC catalyst samples, using a catalyst to oil ratio of 3.

Catalyst sample	FCC1	FCC2
ST	73.09	69.17
CD	67.29	66.97
MI	40.19	34.31
BOL (beginning of life)	65.12	
MOL (middle of life)	57.59	
EOL (end of life)	54.52	

4. Photo-spectroscopy data analysis

4.1 Laboratory deactivated FCC-Y

Table S3: The amount of foreground pixels analyzed for each laboratory deactivated or density separated FCC sample and the related average red, green, and blue values. Eight images taken after a applying the 4-methoxystyrene staining reaction were analyzed for each sample.

Sample	Foreground pixels analyzed	Average value normalized red	Average value normalized green	Average value normalized blue
FCC1 Fresh	4729527	0.3962	0.2854	0.3183
FCC2 Fresh	3804121	0.4088	0.2699	0.3213
FCC1 ST	3643306	0.3523	0.3160	0.3317
FCC2 ST	2452332	0.3499	0.3127	0.3374
FCC1 CD	2660880	0.3780	0.3156	0.3064
FCC2 CD	2795852	0.3572	0.3182	0.3246
FCC1 MI	2445677	0.3704	0.3444	0.2852
FCC2 MI	3004438	0.3619	0.3517	0.2864
BOL	2054116	0.3721	0.3307	0.2972
MOL	2027479	0.3689	0.3331	0.2980
EOL	1697512	0.3728	0.3341	0.2931

4.2 *FCC-ZSM-5 and FCC-Y mixture analysis*

Photographs of the mixtures were loaded into Photoshop and cropped to solely display the area of interest; the borosilicate on which the particles were dispersed.

The background was then removed using the magic wand tool with a tolerance setting of 25. (The tolerance setting in Photoshop determines the range of colour that the magic wand tool selects.) The same tool was then used, with the same tolerance, to remove the edge of the borosilicate window in the photograph. From this image both the FCC-ZSM-5 and FCC-Y images were prepared by selecting either orange (FCC-Y) or pink (FCC-ZSM-5) particles and using the magic wand tool with a tolerance of ten to remove particles with a similar color. Removal of the FCC-Y particles yields the FCC-ZSM-5 image and removal of the FCC-ZSM-5 particles yields the FCC-Y image. An overview of the workflow is shown in Figure S1.

The resulting FCC-Y and FCC-ZSM-5 images were loaded into Matlab, were they were converted into a black-white-image using the 'im2bw'-function with a level of 0.1 to ensure also slightly darker colored particles (especially the contrast orange/brown and black background can be low) are detected. The black-white (BW) images of the pink and orange image were multiplied to construct a mask indicating pixels, which were ascribed to both orange and pink. These were then subtracted from both BW images. The method could be further sophisticated by calculating the probability that a pixel is assigned to FCC-ZSM-5 or FCC-Y and using this value instead of removing pixels which are assigned to both FCC-ZSM-5 and FCC-Y due to the tolerance level used. This would reduce the amount of rejected ambiguous pixels significantly. Regions smaller than 10 pixels on the BW images were then removed to prevent salt and pepper noise to be detected as small particles, and the remaining regions were analyzed using the 'regionprops'-function. The results were used to establish a calibration curves based upon the amount of particles and the area of the particles, which was then used to analyze the amount of FCC-ZSM-5 in Ecat. The photographs of the unknown Ecat were treated as above with the

exception that the tolerance for background and edge removal was set to 10 because color differences between different features such as background versus particles are less distinct.

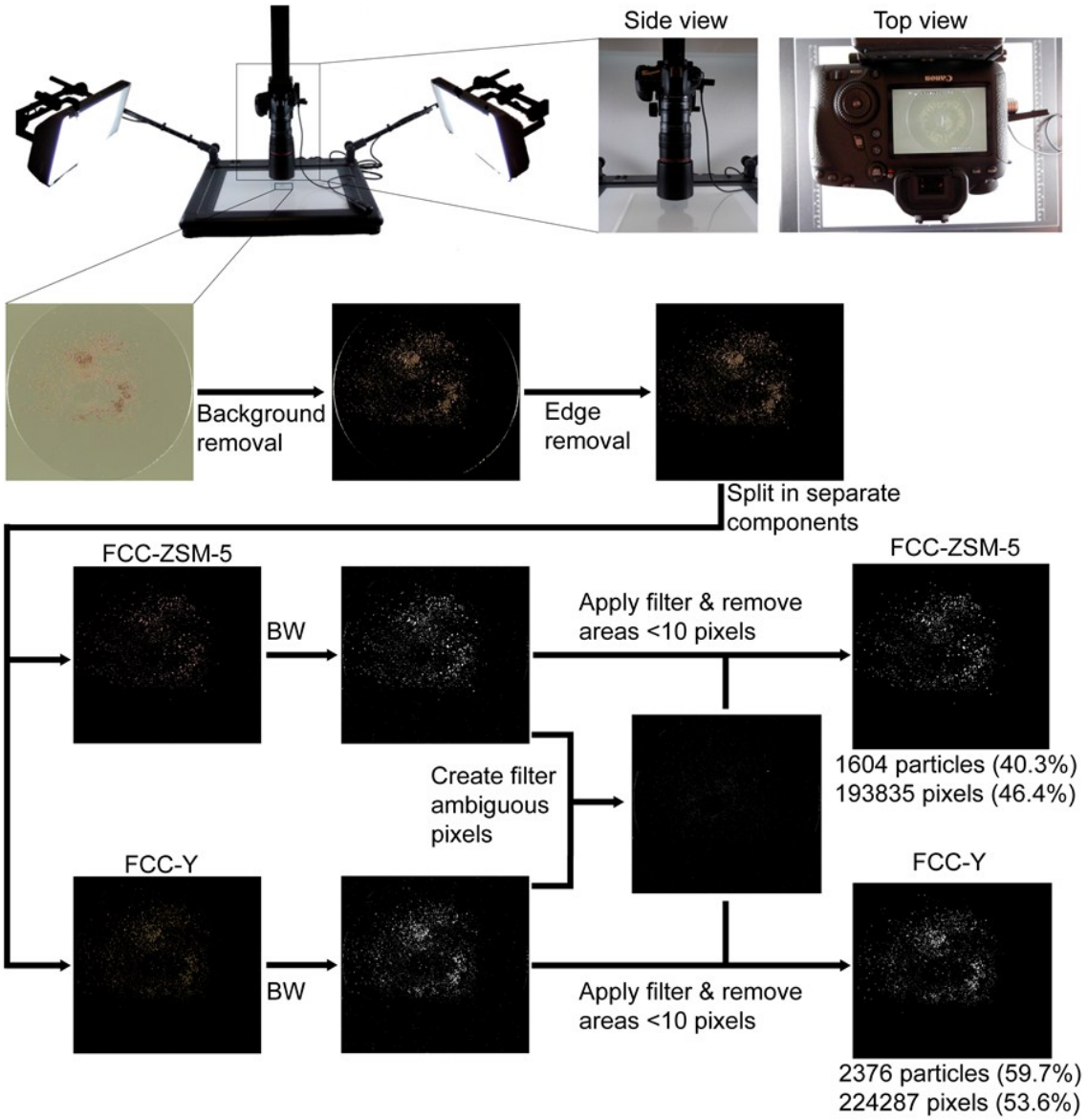

Figure S1: Overview of the data collection and analysis of mixtures of FCC-Y and FCC-ZSM-5. FCC mixtures are photographed after reaction with 4-fluorostyrene. As an example, the workflow for a 50 wt% FCC-ZSM-5 sample is shown. First, the image is cropped after which the background is removed with the magic wand tool set to a tolerance of 25 in Photoshop. The edge is then removed with the same tool

with a 25 tolerance setting (for the Ecat samples these steps are performed with a tolerance of 10). The FCC-Y or FCC-ZSM-5 particles are then removed with a tolerance setting of 10, sometimes in several steps due to color differences, to yield a FCC-ZSM-5 or FCC-Y image, respectively. Both images are transformed to a black white (BW) image using a threshold of 0.10. Both images are then multiplied to create a filter of ambiguous pixels, which are ascribed to both FCC-ZSM-5 and FCC-ZSM-5. This filter is then applied to both images and areas smaller than 10 pixels are filtered to remove salt and pepper noise. The resulting amount of particles and area of the particles in both images is then analyzed and fractions calculated.

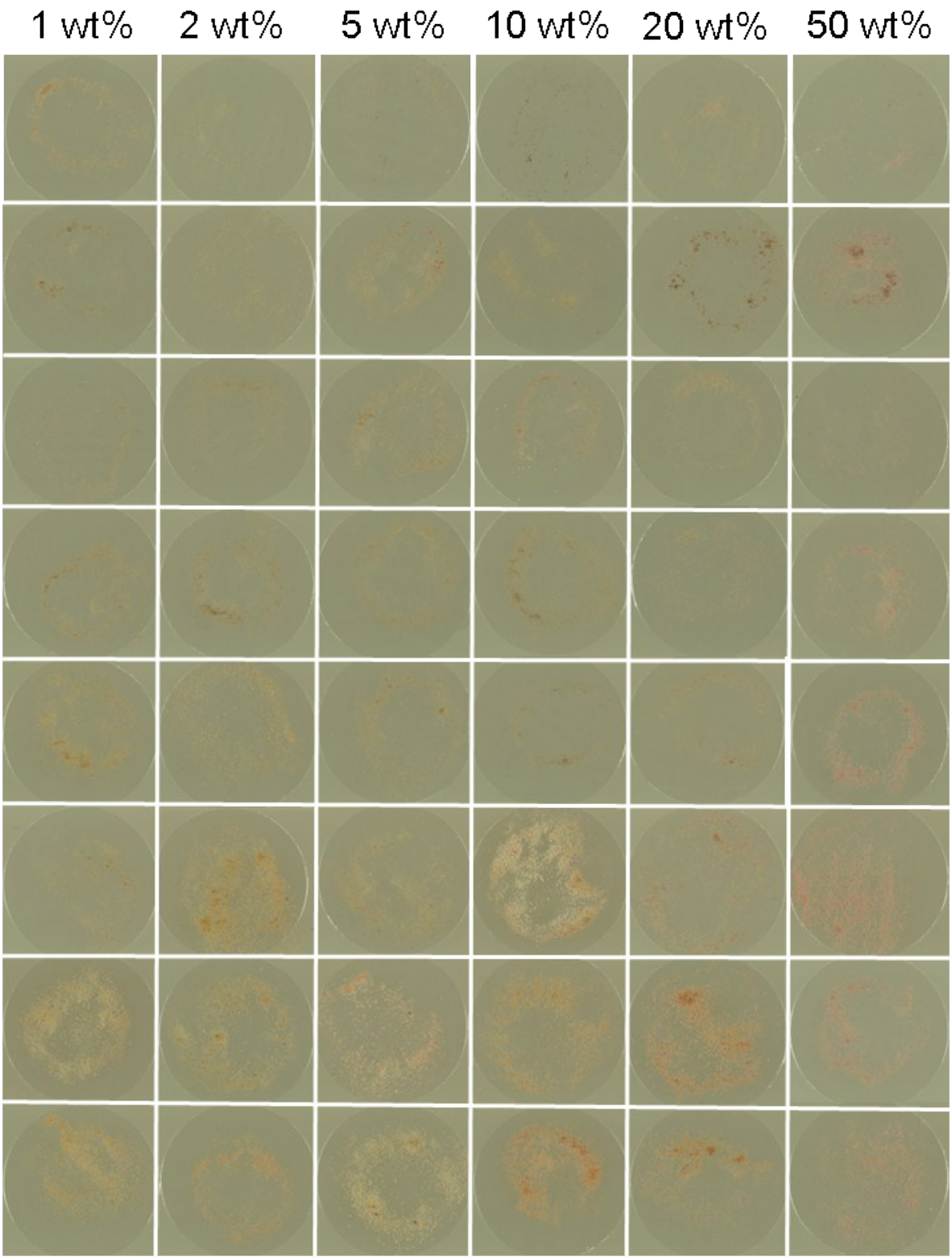

Figure S2: Cropped images (n = 8) of the mixtures of 1,2, 5, 10, 20, and 50 wt% FCC-ZSM-5 in FCC-Y after applying the 4-fluorostyrene staining reaction.

Table S4: Overview of the observed amount of FCC-ZSM-5 particles and total amount of particles for different mixtures of FCC-Y and FCC-ZSM-5 (n = 8 for each mixture). Between brackets the percentage of FCC-ZSM-5 particles in the white light image is given. In the last row the average values and standard deviations are given.

Observed amount of FCC-ZSM-5 particles in mixture					
1 wt%	2 wt%	5 wt%	10 wt%	20 wt%	50 wt%
37/1600 (2.3)	14/1075 (1.3)	46/1406 (3.3)	63/960 (6.6)	189/1337 (14.1)	247/711 (34.7)
17/1429 (1.2)	32/2322 (1.4)	86/2733 (3.1)	148/1963 (7.5)	509/2090 (24.4)	1604/3980 (40.3)
15/1940 (0.8)	34/2039 (1.7)	110/2333 (4.7)	162/1364 (11.9)	345/2134 (16.2)	316/716 (44.1)
18/1446 (1.2)	44/2474 (1.8)	95/2431 (3.9)	296/3790 (7.8)	177/1410 (12.6)	1238/3915 (31.6)
24/2814 (0.9)	61/3745 (1.6)	141/3267 (4.3)	138/1792 (7.7)	452/2400 (18.8)	1865/4704 (39.6)
19/2429 (0.8)	101/4058 (2.5)	181/4397 (4.18)	898/8201 (10.9)	681/3637 (18.7)	2725/6091 (44.7)
58/2924 (2.0)	115/3632 (3.2)	152/2412 (6.3)	355/4197 (8.5)	1165/4872 (23.9)	1516/4305 (35.2)
54/3733 (1.4)	41/1912 (2.1)	296/5345 (5.5)	419/3361 (12.5)	734/3210 (22.9)	1382/3249 (42.5)
1.3%±0.6	1.9%±0.6	4.4%±1.1	9.2%±2.2	18.9%±4.5	39.1%±4.8

Table S5: Overview of the area for FCC-ZSM-5 particles and total area of particles found in images of different mixtures of FCC-Y and FCC-ZSM-5 after applying the 4-fluorostyrene staining reaction (n = 8). Between brackets the percentage of the area FCC-ZSM-5 particles in the white light image is given. In the last row average findings and standard deviations are given.

Observed area of FCC-ZSM-5 particles in mixture					
1 wt%	2 wt%	5 wt%	10 wt%	20 wt%	50 wt%
2459/245836 (1.0)	791/67369 (1.2)	4161/120161 (3.5)	5212/79149 (6.6)	8675/84329 (10.3)	23145/60159 (38.5)
1537/167743 (0.9)	1875/184425 (1.0)	13808/318979 (4.3)	15450/197374 (7.8)	53229/302357 (17.6)	193835/418122 (46.4)
1024/166798 (0.6)	2159/179790 (1.2)	10502/312301 (3.4)	25197/229832 (11.0)	19254/157951 (12.2)	22053/501302 (44.0)
1239/248596 (0.5)	5534/371071 (1.5)	5933/239756 (2.5)	23043/342150 (6.7)	14621/117356 (12.5)	94007/321903 (29.2)
2582/445052 (0.6)	4329/446625 (1.0)	10225/314577 (3.3)	7300/132120 (5.5)	31998/201698 (15.9)	171009/431004 (39.7)
1082/241274 (0.4)	11803/84213 9 (1.4)	13754/430831 (3.2)	104216/122860 6 (8.5)	96800/488436 (19.8)	351919/849387 (41.4)
8986/870769 (1.0)	16596/744074 (2.2)	28004/766646 (3.7)	39242/761170 (5.2)	130148/115208 62 (11.3)	142458/456487 (31.2)
4217/745466 (0.6)	4045/343895 (1.1)	27357/796361 (3.4)	47122/841328 (5.6)	59781/641953 (9.3)	191316/460783 (41.5)
0.7%±0.2	1.3%±0.4	3.4%±0.5	7.1%±1.9	13.6%±3.7	39.0%±6.0

Table S6: Overview of the amount of pixels rejected from the total amount of pixels in the foreground for all images taken of the different wt% mixtures of FCC-ZSM-5 in the FCC-Y sample (n = 8 for each mixture) after applying the 4-fluorostyrene staining reaction. Percentages are given between brackets. In the last row average findings and standard deviations are given.

Rejected pixels					
1 wt%	2 wt%	5 wt%	10 wt%	20 wt%	50 wt%
18821/264657 (7.1)	18507/85876 (21.6)	27749/14791 (18.8)	16430/95579 (17.7)	7403/91732 (8.1)	24229/84388 (28.7)
12007/179750 (6.7)	23131/20756 (11.1)	23931/34291 (7.0)	15853/21327 (7.4)	30672/33302 (9.2)	50087/46820 (10.7)
20395/187193 (10.9)	4117/18390 7 (2.2)	36112/34841 3 (10.4)	28802/25863 4 (11.1)	3251/16120 2 (2.0)	26282/76412 (34.4)
1289/249885 (0.5)	12063/38313 4 (3.1)	5010/244766 (2.0)	33210/37536 0 (8.8)	1738/11909 4 (1.5)	10418/33232 1 (3.1)
8048/453100 (1.8)	15251/46187 6 (3.3)	40890/35546 7 (11.5)	20965/15308 5 (13.7)	14213/215911 (6.6)	53432/48443 36 (11.0)
7274/248548 (2.9)	218601/1072502 (20.4)	26081/45691 2 (5.7)	276089/1504695 (18.3)	18250/506686 (3.6)	93298/94268 5 (9.9)
201504/1072273 (18.8)	44536/78861 0 (5.6)	112444/879090 (12.8)	85051/846221 (10.1)	8389/1161251 (0.7)	5201/461688 (1.1)
11217/756683 (1.5)	44746/38864 1 (11.5)	76226/87258 7 (8.7)	17466/85879 4 (2.0)	3780/645733 (0.6)	21162/48194 5 (4.4)
6.3%±6.2	9.9%±7.7	9.6%±5.0	11.1%±5.3	4.0%±3.5	12.9%±12.2

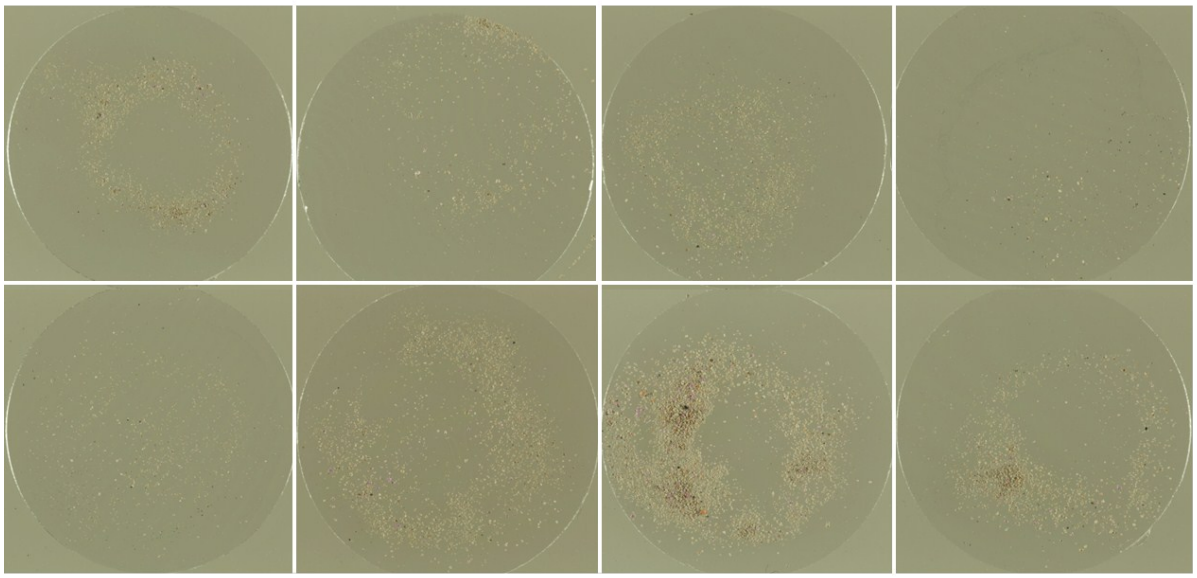

Figure S3: Cropped images (n=8) of the Ecat samples with an unknown amount of FCC-ZSM-5 after applying the 4-fluorostyrene staining reaction.

Table S7: Analysis of the amount of FCC-ZSM-5 in the Ecat sample based upon the amount of particles and the area in images taken after a 4-fluorostyrene probe reaction (n = 8). Percentages are converted in weight percentages using the calibration lines. Negative values found for the number of particles method were rounded to zero as they have no physical meaning. As mentioned before, the method based upon the number of particles is not sensitive to agglomerated particles and does not take different size distributions between the FCC-ZSM-5 and FCC-Y particles into account and the area method is thus thought to be more robust. Average findings and standard deviations are given in the bottom row.

FCC-ZSM-5 particles	Wt% FCC-ZSM-5	Area FCC-ZSM-5	Wt% FCC-ZSM-5
18/1962 (0.9)	0	2405/79340 (3.0)	4.6
38/2022 (1.9)	1.1	6318/227586 (2.8)	4.3
59/4285 (1.4)	0.4	8352/495018 (1.7)	2.9
117/697 (16.8)	20.2	9239/94048 (9.8)	13.3
16/4241 (0.4)	0	2058/318415 (0.6)	1.6
151/3519 (4.3)	4.1	27324/539951 (5.1)	7.2
302/19378 (1.6)	0.6	67215/1988509 (3.4)	5.1
84/3521 (2.4)	1.7	16853/520438 (3.2)	4.9
	3.5 wt% ± 6.9		5.5 wt% ± 3.6

Reference

[1] I.L.C. Buurmans, J. Ruiz-Martínez, W.V. Knowles, D. van der Beek, J.A. Bergwerff, E.T.C. Vogt, B.M. Weckhuysen, *Nat. Chem.* **2011**, *3*, 862-867.