Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Mesostructured Y Zeolite as Superior FCC Catalyst -- From Lab to Refinery

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Zeolite Preparation:

A slurry of NH_4Y in water was treated with a citric acid solution for 1 hour at room temperature. The acid treated material is then treated with a CTAB solution in NH_4OH to introduce mesoporosity. In order to convert the mesostructured NH_4Y to a typical USY, the mesostructured zeolite was calcined at 550-600 °C in a "deep-bed" fashion in a rotary kiln, followed by ammonium exchange. The zeolite was then mixed with rare earth salt (mainly lanthanum chloride), clay and binder, spray-dried, and calcined to produce the final FCC catalyst. The details of the manufacturing process of the mesostructured zeolite and the catalyst are proprietary.

Characterization:

Gas (argon and nitrogen) adsorption–desorption isotherms were measured on Quadrasorb-SI surface area/pore size analyzers from Quantachrome Instruments. Samples were activated at 400 °C under vacuum overnight before measurements. A NLDFT model was used to obtain pore size distribution from the adsorption branches of the argon isotherms. Surface areas were determined by nitrogen adsorption following ASTM D4365. X-Ray diffraction patterns were collected on a PANalytical Cubix Pro (PW3800) industrial X-ray diffractometer with a 1.8 kW Cu-target X-ray tube and the %XRD and UCS of the samples were determined following ASTM D 3906 and D3942. Samples were hydrated inside a closed chamber with saturated $CaCl_2$ aqueous solution overnight before analysis. Silicon powder was added as an internal standard. For TEM analysis, the samples (5–10 mg) were sonicated in ethanol solution and the resulting suspensions were dispersed on carbon film supported 200 mesh copper grids. The digital analysis of the TEM micrographs was done using DigitalMicrograph TM 3.6.1 by Gatan.

ACE® Testing:

The FCC catalysts were tested at the Technical Center of W. R. Grace & Company, Columbia, MD, using an ACE unit from Xytel and Kayser Technologies. The ACE unit was an automated fluidized bed widely accepted in the FCC industry. The reactor was fluidized with a stream of nitrogen. In these studies, the feed is flown over the catalyst at a rate of 3.2 g min^{-1} over 30 s. Different amounts of catalyst were fluidized and stabilized at a reaction temperature of 980 °F to achieve different catalyst/oil ratios. After the reaction, the catalyst was stripped by nitrogen to remove the adsorbed products. Coke on the catalyst was determined by a off-line carbon analyzer. Simulated distillation and on-line gas chromatography were used to determine the liquid and gaseous products, respectively.

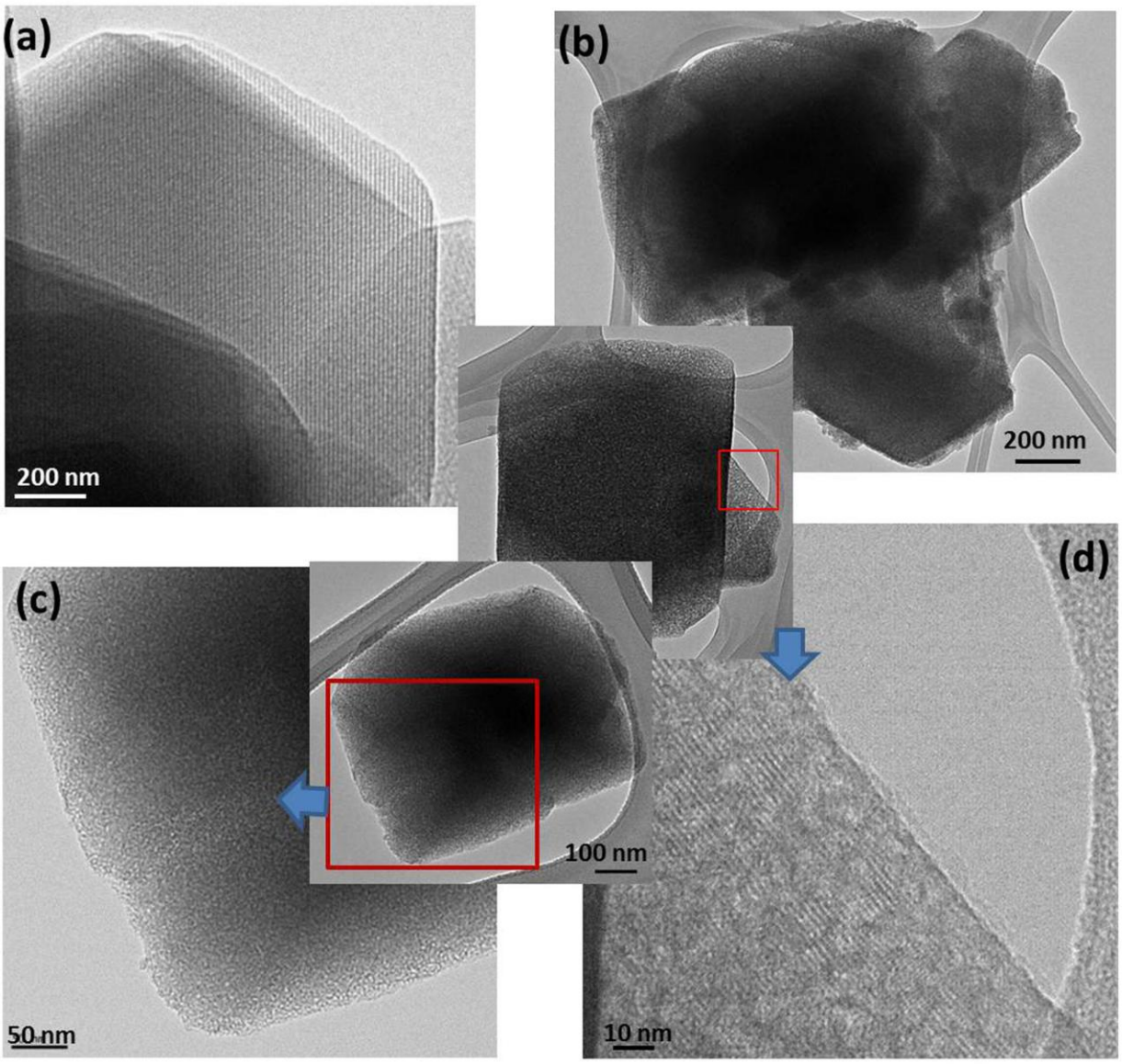

Figure S1 TEM images of (a) the starting NaY, (b, c & d) mesostructured Y zeolites at various magnifications (c & d are the close-up images of the red-boxed regions of the corresponding crystals, which clearly show the co-existence of the mesopores and the crystal lattice fringe lines).

Table S1 Physicochemical properties of mesostructured ultra-stabilized Y (USY) zeolites, the incumbent catalyst and the experimental catalyst GRX-3 before and after being steamed at 1450 °F (788 °C) in 100% steam for 8 hours.

	%XRD*	UCS (Å)	SAR	ZSA (m^2/g)	MSA (m^2/g)	Pore Volume 0-20 Å (cc/g))	Pore Volume 20-300 Å (cc/g)
Meso USY	59	24.48	6.7	489	172	0.29	0.13
Steamed Meso USY	41	24.27	6.7	364	105	0.17	0.15
Fresh Incumbent Catalyst	23	24.53	2.1	235	50	n/a	n/a
Fresh GRX-3	28	24.43	2.1	250	100	n/a	n/a
Steamed Incumbent Catalyst	18	24.27	2.1	133	47	n/a	n/a
Steamed GRX-3	17	24.26	2.1	121	60	n/a	n/a
Incumbent Equilibrium Catalyst	n/a	n/a	n/a	112	31	n/a	n/a
Trial Equilibrium Catalyst#	n/a	n/a	n/a	121	50	n/a	n/a

* A Zeolyst USY (CBV500) was used as crystallinity standard. The meso USY contains ~3% rare earth oxide, which diminishes the "apparent"crystallinity due to strong X-ray absorption.

At the end of the trial, there was ~66% change-out, i.e. ~66% of the equilibrium catalyst is GRX-3 and the rest is incumbent.

Table S2 Physicochemical properties of the CountryMark feed to the FCC Unit.

API	24.7	**Initial Boiling Point (°F)**	527
Specific Gravity	0.906	**5%**	651
Total Nitrogen, %	0.14	**10%**	691
Basic Nitrogen, %	0.046	**20%**	734
Ca	17.6	**30%**	773
Cn	20.3	**40%**	810
Cp	62.1	**50%**	848
Conradson Carbon (CCR)	0.32	**60%**	886
K Factor	12.01	**70%**	928
Refractive Index	1.504	**80%**	976
Sulfur, %	0.35	**90%**	1045
		95%	1108
		Final Boiling Point (°F)	1259

Table S3 Profitmatics® predicted yields comparison based on ACE testing results of lab deactivated CountryMark incumbent catalyst and GRX-3 catalyst (compared at constant coke of 4.5 wt%).

	Incumbent	Rive GRX-3	Delta
Conversion	77.5	78.4	0.9
Catalyst to Oil Ratio	6.3	6.6	0.3
Dry Gas, wt%	1.8	1.8	0
LPG, wt%	12.9	14.1	1.2
Gasoline, wt%	58.3	58.0	-0.3*
LCO, wt%	17.6	17.4	-0.2*
Bottoms, wt%	4.9	4.2	-0.7
Coke, wt%	4.5	4.5	0
Riser Top Temperature, °F	935	935	0
Feed Temperature to Riser, °F	546	546	0
Regenerator Bed Temperature, °F	1242	1231	-11

*The deficit in gasoline and LCO is attributed to the ZSM-5 in the formulation of GRX-3.

Table S4 DCR® testing results of the equilibrium catalyst samples withdrawn from CountryMark FCCU right before and at the end of the trial (compared at constant coke yield).

	Incumbent	GRX-3	Delta
Catalyst Change-Out	0%	66%	
Conversion	76.2	76.3	0.1
Yields, wt%:			
Dry Gas	1.7	1.7	0
LPG	16.0	16.7	0.7
Gasoline	54.6	54.0	-0.6
LCO	18.1	18.4	0.3
Bottoms	5.7	5.3	-0.4
Coke	3.9	3.9	0

Table S5 Brief information about CountryMark Refinery and FCCU and the trial of Rive GRX-3 catalyst.

Refinery Throughput	27,000 BPSD
Refinery Crude	Illinois Basin
FCC Feed Type	VGO
FCC Unit Feed Rate	7,400 BPSD
Catalyst Addition Rate	0.7 tons/day
Unit Inventory	45 tons
Objective	LCO Maximization
Trial Duration	~70 days