



Webinar – FCC Chemistry Demystified (Q&A)

Q 01. Is the rate of hydrogen transfer reactions faster than cracking because it is exothermic rather than endothermic?

A 01. Thermodynamically they will be the same, because both require the same activation energy in order to form the carbenium ion intermediates. Heat of reaction (whether it is endothermic or exothermic) does not thermodynamically influence the reaction rate. Activation energy determines reaction rate.

From a kinetic standpoint, hydrogen transfer will in fact be a little bit slower than cracking, because it requires two molecules, of the correct types, to both meet each other in the Y zeolite at the same time. Whereas, cracking reactions are unimolecular, so the probability of them occurring is higher.

Q 02. I have seen increased RE on ECat, but the UCS is the same. Why is this?

A 02. Rare Earths measured in equilibrium catalysts (ECat) are the sum of Lanthanum, Cerium, Praseodymium and Neodymium in the sample because most catalyst suppliers use a mixed Rare Earth for zeolite stabilization to minimize cost (typically is ~85-90% La, 10-15% Ce and balance others at much low levels).

Rare Earths exchanged into Zeolite Y do stabilize against dealumination as mentioned during the Webinar (especially the Lanthanum). Higher levels of Rare Earth on Zeolite Y will increase the equilibrated framework alumina and therefore increase the equilibrated unit cell size (UCS).

In addition, Rare Earths can also be used in vanadium traps in the matrix (e.g. Lanthanum Oxide), where they are not directly stabilizing Zeolite Y against dealumination. However, such Rare Earths do help to protect Zeolite Y from vanadium attack, which in turn helps retard dealumination, but the impact this non-



Zeolite Rare Earth has on the UCS will not be in the same proportion as for Rare Earth directly exchanged into Zeolite Y.

A further source of Rare Earths that may also be included in the total measured Rare Earths on ECat, is the Cerium contained within SO_x control additives. Cerium is used to oxidize SO₂ to SO₃ in the regenerator which is a fundamental step in SO_x reduction.

Q 03. What property of ZSM5 helps in oligomerization of C4/C5 olefins? or this oligomerization is a function of Y zeolite?

A 03. Oligomerization is the dimerization, or recombination, of smaller olefins into larger olefins (i.e. the reverse of cracking). This reverse reaction competes with the forward cracking reaction, but occurs relatively slowly while light olefin concentrations are low. The main driver for the oligomerization is the amount of ZSM-5 that is used. ZSM-5 produces small olefins, which are at relatively high concentrations within ZSM-5 crystals, therefore oligomerization is faster when using ZSM-5 (reaction rate equations typically take the form, $\text{rate} = k [A]^a [B]^b$ – so higher concentrations of smaller olefins (A and B) increase the rate of oligomerization). At very high ZSM-5 usage levels (e.g. over 20%) oligomerization can get close to the thermodynamic equilibrium limit. Under typical FCC conditions this is normally around the point when the propylene yield has reached around 11-12 wt%.

Q 04. Which property in ECat helps in naphthene ring cracking?

A 04. Naphthene cracking reactions occur on the Lewis acid sites where a hydride ion is abstracted by the Lewis acid site which leaves a naphthenic carbenium ion. Beta-scission occurs and both electrons in the 'beta bond' pass over to the positive charge of the carbenium ion and form a double bond. This opens the ring and forms a new carbenium ion on the carbon that has lost its electrons, and the hydride ion on the



Lewis sites returns to satisfy the positive charge. So for cracking naphthenic rings you require Lewis acid sites.

Q 05. I want to maximize both LCO and LPG. What is the best way to do this?

A 05. Many refiners around the world have been following this operating strategy during the recent global pandemic and the impact it has had on the gasoline demand and market value. In order to maximize the LCO, refiners have been turning down the unit severity in order to reduce the conversion of LCO into gasoline. The main problem with this however, is that the slurry yields also increase and the LPG yields decrease.

Loss of LPG can easily be resolved by using ZSM-5 additives, and many refiners have been using ZSM-5 at increased concentrations in order to fill up their gas plants.

Increased slurry yields can be counteracted by increasing the Zeolite to Matrix ratio (Z/M) of the equilibrium catalyst. The quickest and easiest way to do this is to use a bottoms cracking additive (which can be quickly base-loaded into the unit) to increase "M", while decreasing catalyst additions to decrease "Z" and ECat activity. Bottoms cracking additives contain mesoporous Lewis sites (matrix) and are specifically designed to improve the conversion of HCO and bottoms into LCO.

It is possible to change the catalyst formulation to decrease the Z/M ratio, but this usually takes months before the change is seen in the FCC unit: it takes time for a supplier to manufacture a new catalyst, ship it to the refinery, for the refiner to consume any remaining catalyst stock they hold at site and to reach a suitable level of catalyst changeout. Additives offer a more flexible and faster way for refiners to respond to market prices change.

Q 06. Catalyst suppliers rate catalyst by coke selectivity, when they say this, what exactly does that mean?

A 06. In most cases, it is beneficial to have a catalyst that makes less coke, so when catalyst suppliers talk about a catalyst being 'more coke selective', they generally mean that the catalyst makes less coke for the same conversion.

Many refiners process heavier feeds in the FCC in order to maximize FCC margins, and as a result, the units are often constrained by high regenerator temperatures or maximum air blower rates. These refiners require a catalyst with good stability (to protect against contaminant metals and high regenerator temperatures) and especially minimum delta coke level to minimize regenerator constraints.

Contrary to the usual definition, in FCC parlance we consider a 'more coke selective catalyst' to be one that makes 'less coke'.

Q 07. Can you tell me a little bit more about antimony use?

A 07. Antimony (Sb) has been used to passivate nickel (Ni) since 1976 (over 40 years), and it does a really good job of minimizing the dehydrogenation reactions and decreasing the H₂/CH₄ ratio of the fuel gas resulting from contaminant feed nickel. It is generally most beneficial to use antimony if the nickel on the ECat is in the region of 1,000 ppm or higher.

For best results, the ratio of Sb to Ni on the ECat should be monitored. ECat Sb/Ni ratio depends on the effectiveness of any incorporated Ni trapping components in the catalyst. Because Sb only sticks to the active Ni, catalysts incorporating more effective Ni-traps will do some of the passivation and therefore the ECat will equilibrate with lower Sb/Ni ratios.

The main problems with antimony usage are:

(1) in most cases presence of Sb increases NO_x emissions. Therefore, it may not be possible to use it in units that are against a tight NO_x constraint;

(2) Sb injection is also notorious for having blockages in the injection quills, and there has also been cases where refiners have had fouling issues in the slurry circuit.

(3) toxic Stibene gas (SbH_3) may be liberated from antimony contaminated metallurgy when hot work is carried out in the regenerator during unit shutdowns. Therefore, appropriate PPE is required if antimony was used in the operation prior to S/D. Many refiners have guidelines that antimony usage should be halted for a minimum period prior to planned shutdowns (e.g. 30 days). Clearly this may not be possible in cases of emergency/unplanned shutdowns.

Nonetheless, as mentioned, antimony has been used for over 40 years to passivate nickel and is very effective at minimising dehydrogenation reactions. However, it should be used with care and where NO_x emissions are not a major concern.

Q 08. Is cracking on the catalyst particles liquid phase or vapor phase? In the riser the feed is injected in as liquid droplets. So it is preferable for feed to vaporize prior to contact the catalyst site or as droplet as liquid?

A 08. For selective cracking reactions to occur, the feed must be vaporized. FCC feed injectors are designed to atomize the feed into very small droplets which can vaporize very quickly upon contact with the hot catalyst. Vapours formed can then enter the catalyst pores and selectively crack. Full feed vaporization is normally considered to be complete a little above the feed injectors at the mix zone.

If the feed does not fully vaporize, the liquid droplets can only crack on the external surface of the catalyst which will result in a lot of coke and dry gas formation. Coke breeds coke, so any un-vaporized feed can result in excessive coking problems in the riser, reactor dome, cyclones, overhead transfer line and the main fractionator. In cases where feed is incompletely vaporized, much of the "un-vaporized" feed deposits on the catalyst where it is observed as an increase in delta coke – it is better here than forming coke on reactor internals!



FCC licensors design their feed injectors to optimize droplet size and penetration across the riser cross section. This is to maximize the rate of vaporization, which minimizes coke and gas make. We would recommend you speak to your FCC licensor about the most recent developments in FCC feed injector design.

It would not be easy to vaporize the FCC prior to injection / contact with the catalyst, because this would likely result in excessive non-selective thermal cracking reactions.

Q 09. What is the difference between the matrix being put into BCA and normal matrix in base catalyst?

A 09. Active Matrix is generally amorphous alumina which contains the relatively large mesopores and Lewis active sites required for cracking "large" feed molecules. The base catalyst comprises of both matrix activity and zeolite activity, whereas BCA contains matrix only.

Cracking on the Brønsted active sites of the zeolite has a higher initial rate of coking than the Lewis acid sites on the matrix. At long contact times however, the matrix will eventually make more coke than zeolite. Most FCC's today have advanced riser termination systems that decrease contact time resulting in the final delta coke levels being similar for both zeolite and matrix.

As the initial rate of coking on the zeolite is faster than the rate of coking on the matrix, it is possible for coke precursors to form on the zeolite and 'spill-over' onto the matrix. This ultimately leads to an early deactivation of matrix activity on the base catalyst in the lower section of the riser, where bottoms cracking is most important.

Separate particle Bottoms Cracking Additives do not contain any zeolite, which eliminates the 'coke spill-over' effect seen on the base catalyst. The resulting improved coke selectivity makes zeolite-free Bottoms Cracking Additives more effective at cracking bottoms.

Q 10. The zeolite and matrix cracking reactions that were shown didn't make any coke. So if that is the case, why does my regen temp increase when I increase conversion?

A 10. Although coke is not a direct product of beta scission or hydrogen transfer reactions, conversion does have a large impact on the coke make. Many coke precursors (olefins and aromatics) are formed within the catalyst during normal operation. Some of these do go on to condense and form coke via the polymerization mechanism mentioned in the webinar while cracking progresses.

Q 11. How does RE increase HT?

A 11. Rare Earth stabilization results in a higher acid site density in Zeolite Y. Hydrogen transfer is bimolecular and requires two molecules to be at the same place at the same time. Having a greater density of acid sites allows better stabilization of carbenium ions on the pair of molecules (as the charge migrates from one to the other) within the zeolite, which increases the amount of hydrogen transfer.

Q 12. We target an antimony to nickel ratio? What is the ideal ratio for that?

A 12. ECat Sb/Ni ratio depends on the effectiveness of any incorporated Ni trapping components in the catalyst. Because Sb only sticks to the active Ni, catalysts incorporating more effective Ni-traps will do some of the passivation and therefore the ECat will equilibrate with lower Sb/Ni ratios – see also Q 07.

Catalysts that contain highly effective nickel traps can have a Sb/Ni ratio as low as about 0.1, whereas catalysts that do not contain any nickel traps often have a Sb/Ni ratios in the region of 0.3-0.4.

The important thing about the Sb/Ni ratio is that, whatever your catalyst, you will eventually reach some limiting ratio. Addition of antimony beyond that ratio is much less effective and usually often leads to problems. Excess antimony usually ends up in the bottoms product.



Q 13. Do you have experience to crack the vegetable oil in FCC? What is the impact of vegetable oil to catalysts performance and yield pattern?

A 13. Vegetable based bio-oils have been tested in pilot plant FCC's and have shown to have little impact on the product yields or coke make when co-processed at about 10% or lower with a conventional feed.

One of the main problems that should be anticipated when processing bio-oils is that they contain much more oxygen than typical FCC feeds. This means that a lot of oxygenates will be formed in the FCC riser (e.g. aldehydes, ketones, CO₂ etc.) which cause problems with the downstream purification and separation units and are likely to end up as contaminants in propylene.

If you plan to run bio-oil to the FCC, a full study should be carried out to identify all the potential secondary effects.

Q 14. Do you have any plan to discuss about FCC process?

A 14. The next two FCC topics which will be covered in Webinar sessions in August are on controlling contaminant feed metals and on maximizing LPG olefins. A schedule of the up and coming Webinars can be seen on the ProcessWise website.

If a Webinar that covers an overview of the FCC process is of interest, then I would happily run a session.

We at JM would like to thank you for participating in this Webinar