Catalysis Today 140 (2009) 179–186

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Deactivation of ZSM-5 additives in laboratory for realistic testing

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ARTICLE INFO

Article history:
Available online 20 November 2008

Keywords:
ZSM-5
Y zeolite
Dealumination
Catalyst testing

ABSTRACT

ZSM-5 deactivates differently from Y zeolite. Dealumination of Y zeolite during deactivation causes UCS shrinkage and thereby decline in activity and changes in selectivity. For ZSM-5 instead deactivation removes alumina from the zeolite structure, but in spite of that the zeolite structure does not collapse. Therefore, deactivation causes activity decline due to loss of active alumina sites, but no significant changes in the strength and separation between acid sites. Unlike with FCC catalyst, physical properties of ZSM-5 additive do not change significantly with deactivation and surface area and pore volume measurements cannot be used as indications of additive performance. Yet, since both Y and ZSM-5 are used simultaneously in practice, the information on the relative rates of deactivation between the two zeolites is very important. Therefore, the question remains, what is the best way to deactivate and test ZSM-5 additives in the laboratory to obtain realistic performance, e.g. propylene yield and to obtain proper ranking of various additives. This paper discusses the effect of deactivation conditions as well as performance testing aspects of ZSM-5 additives. It is shown that choice of deactivation conditions has an effect on additive ranking and performance. By choosing the deactivation conditions properly ranking can be made clearer and more realistic additive performance is obtained.

1. Introduction

ZSM-5 containing additives were introduced to the Fluid Catalytic Cracking process (FCC) early in the 1980s to increase octane properties of gasoline [1]. This is achieved with the shape-selective structure of ZSM-5 zeolite which selectively cracks linear low octane compounds in the gasoline boiling range to mostly C3–C5 olefins [2–3]. Compared to Y zeolites, ZSM-5 has a higher selectivity towards C3 than C4 olefins. C4 and C5 hydrocarbons can be used as building blocks for high octane gasoline components in alkylation process as well as for octane boosters such as MTBE, ETBE and TAME. Moreover, by cracking linear low octane compounds, aromatics are concentrated in the gasoline fraction, resulting in an increase in its octane numbers.

Since the early 1990s the production of light olefins (C3–C4) has grown in importance relative to the octane gain in FCC application due to the worldwide development of a robust market for propylene. Propylene yield demand from FCC has increased from the usual level of 3–4 wt% to the new challenging target of 10–15 wt%. Therefore, more and more refineries/oil companies tend to evaluate the ZSM-5 additives in laboratory before making the final choice. To get an adequate picture of the additive performance, suitable test protocols need to be used. No general agreement exists in the literature on the most appropriate testing protocols that best mimic commercial performance.

Based on fundamentals of the behavior of pure zeolites and practical experience on real ZSM-5-based FCC additives, the present work aims to point out the general rules that must be followed to define an appropriate procedure to mimic the real working state of the additive in a commercial unit, commonly referred as deactivation in the field of FCC. This is important in view of realistic evaluation of these additives in laboratory.

2. Deactivation methods of ZSM-5-based additives

The choice of deactivation methodology and performance testing protocol for ZSM-5-based additives has two main objectives:

(1) to obtain realistic performance ranking and
(2) to reproduce realistic propylene (or light olefins) yields.

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doi:10.1016/j.cattod.2008.10.010

Table 1
ZSM-5 additive steaming conditions from various laboratories.

Laboratory	Deactivation conditions		
	Temperature (°C)	Time (h)	Steam (% vol.)
A	780	5	100
B	788	9 or 20	100
C	815	16	100
D	788	15	100
E	760	5	80
F[a]	816	18	80
G	788	3	100
H	815	4	100
I	760	16	100

[a] Conditions are equal to those applied to fresh catalyst to match equilibrium catalyst surface area.

Table 1 shows a list of ZSM-5 additive deactivation protocols applied by different laboratories as a result of a survey including oil refining companies and catalysts vendors. The list covers a wide range of steaming conditions and it seems to be almost a general agreement that contamination of metals is not applied in the laboratory. Only in one case the additive was deactivated with metals together with the FCC catalyst. In most cases laboratory deactivated additive is blended with equilibrium catalyst (working state of the FCC catalyst in an FCC unit, also called E-cat) prior to performance testing.

Systematic studies in literature on the effects of deactivation severity on the performance of commercial ZSM-5 additives and effect of deactivation severity on additive ranking, with respect to propylene make, are scarce. Increasing steaming severity reduces the activity of ZSM-5 additives, but the slope of the deactivation curve may differ, resulting in better or worse discrimination of additives. It is known from the literature that in the presence of P species in ZSM-5 the retention of active sites is greatly improved [1,4], although the real mechanism of the stabilization is still a subject of intense research. In a typical additive in addition to ZSM-5 and phosphate species, other materials such as silica–aluminas and clays are present, making the stabilization even more complex. In general it is expected that different additive compositions and preparation technologies will result in different stabilities under equal deactivation conditions. Consequently performance ranking of the additives may be influenced by the conditions chosen for deactivation. It has also been suggested [5] that an optimum deactivation temperature exists for ZSM-5, showing a maximum in acid site retention at a certain temperature. Minor structural destruction of ZSM-5 due to steam deactivation was confirmed but the effects on performance were not very clear.

3. Fundamentals on ZSM-5 and Y zeolite deactivation

The requirements for laboratory deactivation of ZSM-5-based additives are different from that of main FCC catalyst, which is based on Y zeolite. Effects of hydrothermal deactivation and contaminant metals are different on Y and ZSM-5 zeolites. Both in Y and ZSM-5 zeolites hydrothermal treatment causes removal of aluminium sites from the framework. However, since ZSM-5 zeolite has significantly higher initial silica to alumina mole ratio (SAR) than Y zeolite, the consequences of deactivation are different. Since the aluminium sites in ZSM-5 are already rather isolated in the original non-deactivated zeolite, dealumination will only cause decrease in the number of acid sites but will not have a large impact on the acid strength. Hence, the selectivity towards the cracking reactions will remain similar. Y zeolite behaves differently since the acid sites are not isolated like in ZSM-5, due to which removal of aluminium from the zeolite framework will cause change in the acid strength. The acid sites become more isolated during this process which reduces bimolecular reactions, like hydrogen transfer. Overall this is good for gasoline quality and when ZSM-5 additives are used. Also the quantitative amount of aluminium that leaves the zeolite framework is much smaller with ZSM-5 than with Y. Therefore, with ZSM-5 no important changes are observed with unit cell size, mesoporosity or structural collapse.

Extensive literature exists on the effects of contaminant metals such as nickel and vanadium on FCC catalysts [6–9]. While nickel is a strong dehydrogenating agent in the FCC conditions leading to an increase in coke and dry-gas (hydrogen) yields, vanadium is known to form highly destructive species onto zeolite surface which severely damage its structure (crystallinity). Destruction of the Y zeolite framework leads to changes in the acid strength distribution which in turn are reflected as activity drop and worse selectivity pattern. Moreover, vanadium itself has some dehydrogenation activity which introduces an extra detrimental effect by increased coke and dry-gas formation.

While dealumination caused by steam treatment on ZSM-5 zeolites has been studied quite often in the literature [10–15], the contamination of ZSM-5 by metals and their effects on textural and morphological transformations has not been sufficiently investigated, probably because ZSM-5 zeolite already has an aluminum depleted structure and therefore the effects of vanadium on the activity and selectivity for cracking reactions are expected to be less intense. Wallenstein et al. [16] have investigated the effect of Ni and V on coke yields in catalytic systems where both zeolite types Y and ZSM-5 were present, but their approach was only focused on the reversible deactivation by coke formation. However, since both types of zeolites can be present in an FCC inventory the comparison between their deactivation rates at the same severity conditions is of relevant importance. With this respect the literature is still quite limited.

4. Effect of steam treatment and vanadium contamination on pure H-ZSM-5 and USY zeolites

In spite of the general consensus that contaminant metals need not to be applied to rank ZSM-5 additives and although contaminant metal activities are difficult to simulate, for realistic evaluation of additives this effect cannot totally be ignored. This may be particularly important when high metal containing feeds are used.

To investigate the metals effect an ultrastabilized Y zeolite (USY) and an H-ZSM-5 zeolite with silica to alumina mol ratios (SAR) of 5.5 and 26, respectively, were impregnated with vanadium in laboratory using vanadium naphtenates to the contents of 1000, 3000 and 5000 ppmwt, following the procedure described by Mitchell [17]. The samples were steam deactivated in a laboratory furnace at 800 °C for 5 h in a 100% steam environment.

The results of textural properties of Y and ZSM-5 zeolites confirmed their different behaviors (Fig. 1). For Y zeolite the steaming treatment without metals had a significant impact on surface area and the contamination of vanadium resulted in an additional surface area drop, decreasing in an almost constant rate (around 10% area loss/1000 ppmwt V). For H-ZSM-5 zeolite the greatest impact was produced by the steaming treatment, while the effect of vanadium contamination was of secondary importance and much lower than that observed for Y zeolite. This can be explained by the fact that ZSM-5 zeolite has an already aluminum depleted framework (higher SAR) which is not as sensitive to the presence of vanadium species.

A second set of samples was composed only by H-ZSM-5 zeolites to which the same procedure as mentioned above was applied. The levels of vanadium impregnation in this second case

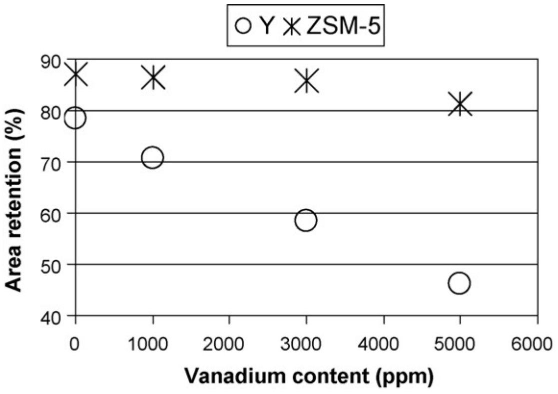

Fig. 1. Impact of vanadium contamination on Y and H-ZSM-5 zeolites, surface area retention.

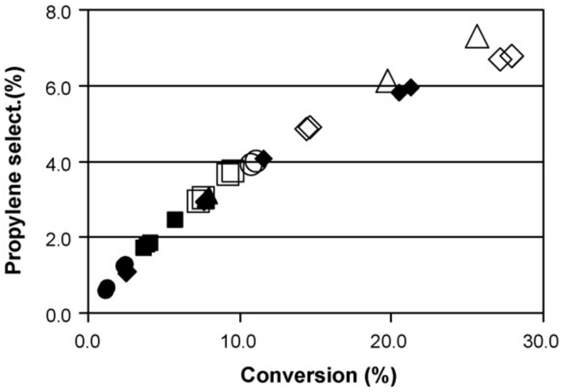

Fig. 2. Selectivity to propylene of impregnated and steamed samples of H-ZSM-5 under n-hexane cracking test.

were lower, e.g. 550 and 3000 ppmwt V. The impregnated samples were characterized before and after the hydrothermal treatment with respect to their textural and chemical properties. Samples submitted to hydrothermal treatment were labeled with "HT" as a suffix. Catalytic test with n-hexane was applied as a strong acidity measurement for H-ZSM-5 samples before and after hydrothermal treatment. The results are summarized in Table 2.

Interestingly, vanadium caused a significant drop in activity even before steaming, showing that the sparse aluminum sites in the framework (acid sites) are being poisoned by vanadium atoms. However, the largest activity drop was observed after the hydrothermal treatment. Without vanadium the hydrothermal treatment was responsible for 75% conversion drop while in the presence of 3000 ppmwt vanadium on the zeolite the activity decrease reached 96%. Activity ratio between hydrothermally treated and impregnated samples shows that vanadium enhanced dealumination due to steaming, leading to more activity decrease after steaming by V containing samples than the with the non-metallated sample. It should be noted that 3000 ppmwt on the zeolite is an extremely exaggerated approximation of what happens in commercial units. Considering that ZSM-5 content in additives range from 10 to 40%, this contamination corresponds to 7500 to 30,000 ppmwt vanadium in the inventory which is definitely in the high side of the industry experience even for resid FCC applications.

It is also worthwhile to notice that the hydrothermal treatment and vanadium contamination on pure H-ZSM-5 zeolite did not significantly change the selectivity to the main product (propylene) in the cracking of n-hexane as depicted in Fig. 2, although clear changes were observed in textural properties and activity.

It seems that the effect of vanadium cannot completely be ignored. Since contaminant metals interact also with other components of the additive and not only with ZSM-5, more investigation is necessary to quantify the effects on real additives.

5. Effect of steaming conditions on ZSM-5 additives and their performance

The effect of steaming conditions on the properties and catalytic performance of ZSM-5 *additives* was investigated using four commercial additives. Fresh and deactivated samples were analyzed for surface area by nitrogen adsorption (BET method) and the micropore volumes were estimated by the *t*-plot method [18–20]. Chemical composition was determined by X-ray fluorescence. Fresh additive properties are shown in Table 3. Note that additive C has the highest alumina content and the highest surface area in the mesopore range (MSA). This indicates a low zeolite-to-matrix ratio. Additive D has the highest ZSM-5 zeolite content as indicated by its high micropore volume. The additives were deactivated in a fluidized bed steamer using five different severities. The deactivation severity was increased by increasing steam partial pressure, temperature and time-on-stream. The deactivation conditions are shown in Table 4. The properties of deactivated additives were compared with those of calcined-only (2 h, 600 °C) samples (Fig. 3).

For the performance test, deactivated additives were blended with an equilibrium catalyst to the level of 2.5% ZSM-5 crystal in the total blend and tested in the FST Fluid-bed Simulation Test [21] using a light paraffinic vacuum gasoil (VGO), multiple cat/oil ratios and reaction temperature of 538 °C.

The BET surface area (Fig. 3) of the deactivated additives remains rather constant with the milder deactivations, but decreases slightly with the Long (788 °C/20 h) and High (810 °C/5 h) methods. The deactivated surface area compared to the calcined sample decreases for the high alumina additive C, but increases or remains constant for the other additives. The surface area change with the high alumina additive C is most probably due to the deactivation of the alumina matrix as it is evident from the reduction in meso-surface area (Fig. 4).

Meso-surface area (MSA) shows a decreasing trend with increasing deactivation severity for high alumina additive C but a (slight) increasing trend for the other additives. The MSA decrease in high alumina additive is caused by the deactivation of the alumina phase, while with the other additives, which contain less alumina, the contribution of created mesopores during steaming becomes more relevant.

Micropore volume (MiPV, Fig. 5) shows a decreasing trend with all additives with increasing deactivation severity. It seems however, that long deactivation (788 °C/20 h) affects MiPV more

Table 2
Impact of vanadium contamination on H-ZSM-5 zeolites measured in n-hexane cracking test.

Before HT	Relative activity (%)	After HT	Relative activity (%)	Activity ratio HT/non-HT
Fresh	100	0 V-HT	25	0.25
550 V	81	550 V-HT	14	0.17
3000 V	30	3000 V-HT	4	0.13

Table 3
Fresh additive properties.

Fresh additive properties	A	B	C	D
Al_2O_3 (wt%)	29.5	30.9	52.0	24.2
SiO_2 (wt%)	58.1	49.8	44.1	65.6
Na_2O (wt%)	0.04	0.22	0.12	0.00
Fe_2O_3 (wt%)	0.64	0.68	0.35	0.49
TiO_2 (wt%)	1.43	1.02	0.87	1.16
P_2O_5 (wt%)	10.0	16.2	2.5	9.3
BET surface area (m^2/g)	99	81	178	148
Meso-surface area (m^2/g)	38	17	134	47
Micropore volume (ml/g)	0.028	0.030	0.019	0.046

Table 4
Deactivation methods used.

Method	Base	Intermediate	Mild	Long	High
Deactivation time (h)	5.0	5.0	5.0	20.0	5.0
Deactivation temp (°C)	760	760	788	788	810
Steam (vol%)	80	100	100	100	100

than the high temperature, indicated by higher MiPV of the samples in the latter condition.

The deactivated additives are compared at constant conversion of 72%. The average yields at 72% conversion are summarized in Table 5. The activities (total conversion) of the catalytic systems (base catalyst + additive) were the same within test accuracy after different deactivation protocols, which makes the comparison adequate. Exception is the non-deactivated high alumina additive C, which presented a higher conversion compared to all other systems, possibly due to the high activity of the matrix alumina.

Propylene weight percent yields from performance test are shown in Fig. 6. Highest propylene yield is obtained with non-deactivated additives, e.g. maximum of about 11%. Even with the mildest deactivation the propylene yield decreases by 1–1.5% compared to the calcined, e.g. non-deactivated additives. Also the difference between additives becomes slightly larger. Increasing the steam partial pressure from 80 to 100% or the temperature from 760 to 788 °C does not cause any significant change in performance. However, this severity (788 °C/100%/5 h) seems to be a "turning" point where the ranking between additives becomes clearer. Increasing deactivation time from 5 to 20 h causes a clear reduction in propylene make for all additives. The ranking does not change, but the maximum difference between additives increases, being 1% between the highest and lowest propylene yield. Increasing temperature from 788 to 810 °C (100% steam/5 h) causes propylene yields to decrease compared to 788 °C, but increase compared to the 20 h protocol at 788 °C. Ranking remains the same, but individual deltas between additives change somewhat.

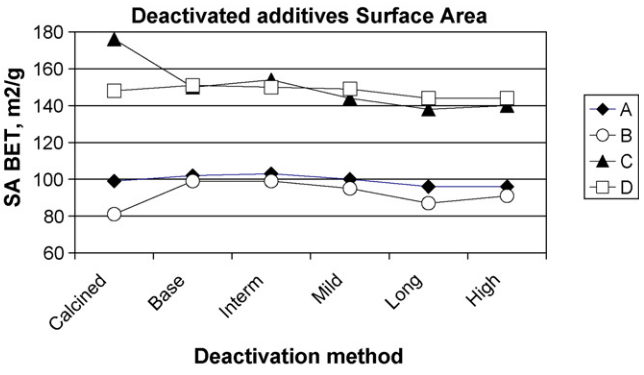

Fig. 3. Effect of deactivation severity on additive surface area.

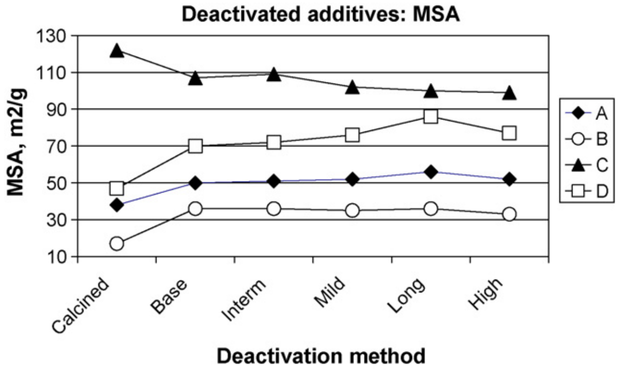

Fig. 4. Effect of deactivation severity on additive meso-surface area.

Propylene weight percent yields were plotted against the *t*-plot data (MSA and MiPV) of deactivated additives to see whether these parameters could characterize propylene yields. Since each additive has its own characteristic *t*-plot, it is not possible to use the *t*-plot data to compare additives with each other. Fig. 7 shows that for each individual additive increasing MiPV correlates with increasing propylene yield, indicating higher activity of the ZSM-5.

Interestingly, increasing MSA shows decreasing propylene yields, except for the high alumina-containing additive C. This difference is due to the fact that with low alumina additives mesopores are created due to steam deactivation, while additive performance with respect to propylene yields declines (due to dealumination of the ZSM-5). In the high alumina additive C, alumina matrix provides mesopores, which are disappearing due to the steam deactivation. This data indicates that the micropores (ZSM-5) rather than the mesopores are responsible for the propylene make. On the other hand with very different MSA or MiPV levels the maximum propylene make with each additive reaches about the same level. This suggests that other characteristics than the porosity of the additive are responsible for the propylene make, so additive performance cannot be predicted based on surface area or porosity before or after deactivation.

The differences in C4 olefins yields between deactivations were smaller than with propylene. Especially the differences from non-deactivated additive (calcined only) to deactivated additives were less obvious. Additive D with highest ZSM-5 crystal intake gave the lowest C4 olefins yield at all deactivations (Fig. 8). On the other hand at constant LPG comparison this additive showed higher propylene/C4olefins ratio than the other additives. This shift is possibly due to the ability of this additive to crack more C5 and C6 olefins, causing the slight increase in propylene/C4olefins ratio (Fig. 9).

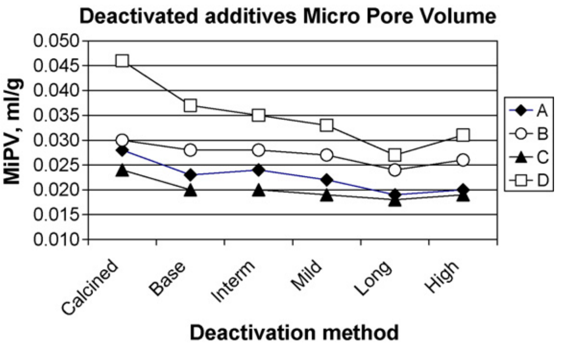

Fig. 5. Effect of deactivation severity on additive micropore volume.

Table 5
Average yields, %wt at 72% conversion for E-cat + additive blends.

Deactivation method		Calcined	Base	Intermediate	Mild	Long	High
Condition (temp °C/steam, % time, h)		600/0/2	760/80/5	760/100/5	788/100/5	788/100/20	810/100/5
Additive	E-cat only	A	A	A	A	A	A
Coke	2.7	2.8	2.8	2.9	2.8	2.9	2.9
Dry gas	2.0	4.7	2.7	2.7	2.8	2.4	2.5
Ethylene	0.7	3.1	1.3	1.4	1.4	1.0	1.2
LPG	17.4	30.4	26.5	26.3	26.8	24.5	25.2
Propylene	4.9	10.7	9.3	9.2	9.5	8.4	8.6
Isobutane	4.5	7.3	6.3	6.4	6.3	5.7	6.1
Total C4 olefins	5.6	7.8	7.6	7.4	7.7	7.4	7.2
Isobutylene	1.4	2.8	2.4	2.3	2.5	2.3	2.2
Gasoline	50.0	34.0	40.0	40.1	39.7	42.2	41.4
LCO	17.7	17.0	17.5	17.5	17.5	17.4	17.4
Bottoms	10.3	11.0	10.5	10.5	10.5	10.6	10.6
Additive		B	B	B	B	B	B
Coke		2.9	2.7	3.0	3.1	3.0	3.0
Dry gas		3.5	2.8	2.7	2.7	2.5	2.6
Ethylene		2.0	1.4	1.2	1.3	1.1	1.2
LPG		29.9	27.8	26.7	26.7	25.2	26.4
Propylene		11.1	9.9	9.4	9.4	8.5	9.1
Isobutane		6.9	6.5	6.3	6.3	6.0	6.2
Total C4 olefins		8.4	7.9	7.8	7.6	7.4	7.7
Isobutylene		3.0	2.6	2.9	2.5	2.3	2.4
Gasoline		35.7	38.6	39.4	39.5	41.4	40.0
LCO		17.1	17.5	17.6	17.5	17.6	17.5
Bottoms		10.9	10.5	10.5	10.5	10.4	10.5
Additive		C	C	C	C	C	C
Coke		2.8	3.2	3.0	3.2	2.9	3.0
Dry gas		5.5	2.7	2.6	2.6	2.3	2.5
Ethylene		3.8	1.3	1.3	1.1	0.9	1.1
LPG		31.7	26.8	26.7	25.3	23.5	25.3
Propylene		11.2	9.4	9.5	8.8	7.7	8.6
Isobutane		6.7	6.4	6.2	5.9	5.6	6.1
Total C4 olefins		8.2	7.6	7.8	7.5	7.2	7.4
Isobutylene		3.1	2.4	2.5	2.4	2.1	2.2
Gasoline		32.0	39.3	39.6	40.9	43.3	41.1
LCO		17.2	17.4	17.7	17.7	17.6	17.8
Bottoms		10.8	10.6	10.3	10.3	10.4	10.2
Additive		D	D	D	D	D	D
Coke		2.8	3.2	2.9	3.0	2.8	3.0
Dry gas		5.0	2.6	2.7	2.6	2.3	2.5
Ethylene		3.3	1.3	1.3	1.2	0.9	1.1
LPG		29.7	25.6	25.8	25.4	23.0	24.6
Propylene		10.4	9.0	9.0	8.8	7.5	8.3
Isobutane		6.9	6.0	6.2	6.0	5.6	6.0
Total C4 olefins		7.4	7.3	7.3	7.4	6.8	7.1
Isobutylene		2.8	2.3	2.3	2.3	2.0	2.1
Gasoline		34.5	40.7	40.6	41.1	43.9	42.0
LCO		17.1	17.4	17.5	17.7	17.6	17.4
Bottoms		10.9	10.6	10.5	10.3	10.4	10.6

A slight decreasing trend in hydrogen transfer index (HTI, defined as i-C4/total C4) was observed when the additives were deactivated more severely (Fig. 10). Consequently C4 olefinicity (defined as total C4olefins/total C4) showed a slight increasing trend with deactivation severity, although the differences were small.

Ethylene yield shows a slight decreasing trend with increasing deactivation severity (Fig. 11). This could be due to the fact that the light gasoline olefins, e.g. C5 and C6 olefins, which are the main source of ethylene via carbonium ion cracking, crack less with more deactivated additive. This is supported by the fact that even after a very mild deactivation ethylene yield drops drastically, compared to the calcined-only (e.g. non-deactivated) additive. It should be noted that from the non-deactivated additives the high alumina additive C gives the highest ethylene yield.

Depending on the additive, difference between highest and lowest propylene make due to deactivation severity is 2–3% abs. This is significant in view of projecting laboratory results into real FCC units.

From the deactivation parameters steaming time has more influence than temperature on the deactivation of the additives and consequent propylene yields. Differences between additives become clearer at more severe deactivation (788 °C or higher and 5 h or more). The more severe deactivation conditions seem to affect most the high ZSM-5 content additive D and additive C with high alumina content. For the latter this could be due to the fact that the deactivation of the alumina matrix was not complete at the milder deactivation conditions. It is known that only after 20 h deactivation alumina stabilizes to a constant level [22].

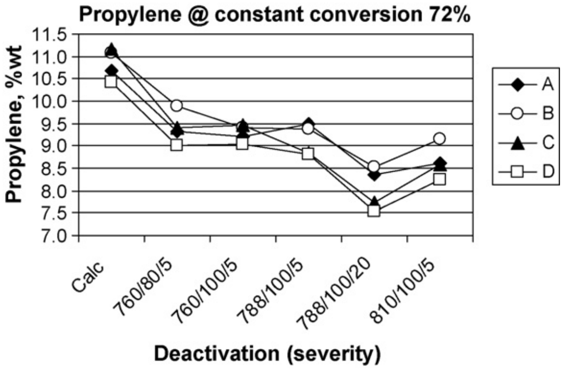

Fig. 6. Propylene at constant conversion of 72%, *x*-axis labels are deactivation conditions: temperature °C/steam%/time hours.

This data shows that the choice of deactivation method can affect *catalyst ranking*: in this additive set at deactivation severity of 788 °C or higher and 5 h or longer the ranking of additives for propylene make changes compared to milder deactivations (Fig. 6). Especially with additives with high alumina matrix content this could be important, since as mentioned above, alumina deactivation is known to stabilize only after 20 h deactivation.

6. Choice of performance test protocol

Fixed fluidized bed testing tools such as ACE units [23] are being used by refiners and catalysts vendors as standard tools to evaluate catalysts and additives for FCC applications. A comparison between propylene yields from ACE testing of some equilibrium catalysts with their respective commercial propylene yields (same period of commercial operation) shows that ACE results perfectly match commercial yields for equilibrium catalysts when ZSM-5 additives are not used. Fig. 12a and b presents such comparison for a Petrobras's FCC unit which processes a blend of vacuum gasoil and atmospheric distillation tower bottoms (Ramsbottom Carbon Residue = 1.1–1.5%) and has never used ZSM-5-based additives. The values of conversion for commercial data were all corrected to the same cut-points used in laboratory evaluation.

However, when ZSM-5 additive is present in the FCC inventory, ACE results of E-cats containing equilibrated ZSM-5 additive tend to show higher propylene yields than obtained in the commercial unit. Fig. 13a and b illustrates such comparison for a Petrobras's unit which processes a blend of vacuum and coker gasoil and applied an average amount of 4% of a ZSM-5 additive.

It is known that small scale testing tends to exaggerate the effects of ZSM-5 additives due to the intrinsic differences in the fluid dynamics, contact times and pressure between laboratory and industrial reactors. That was also shown in the above example

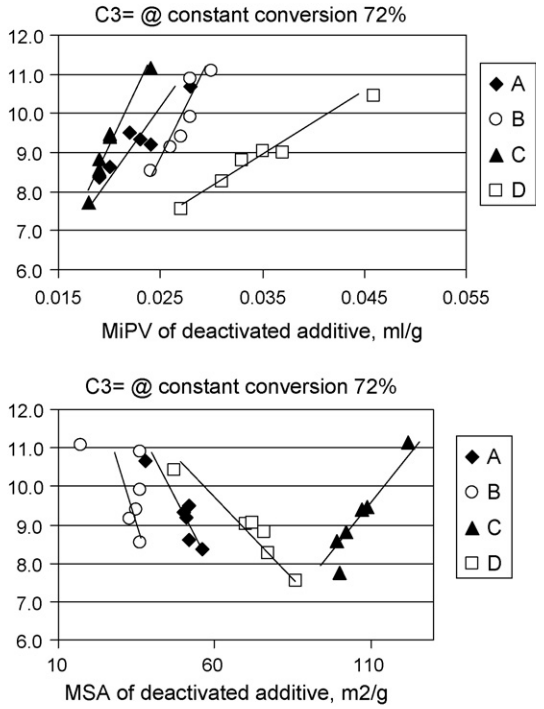

Fig. 7. Propylene yield at constant conversion of 72%, as function of the deactivated *additive t*-plot.

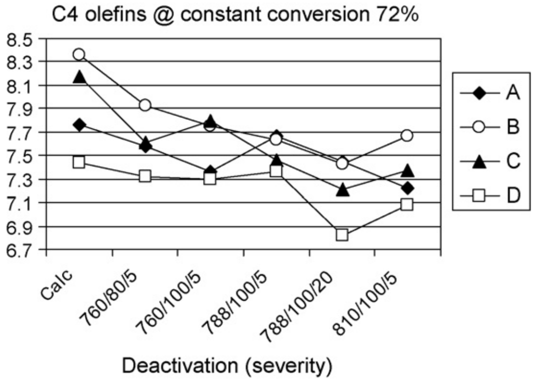

Fig. 8. C4 olefins yield at constant conversion of 72%, *x*-axis labels are deactivation conditions: temperature °C/steam%/time hours.

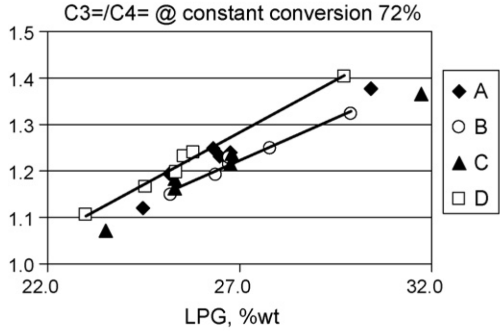

Fig. 9. Propylene/C4 olefins ratio as function of the LPG yield at constant conversion of 72%.

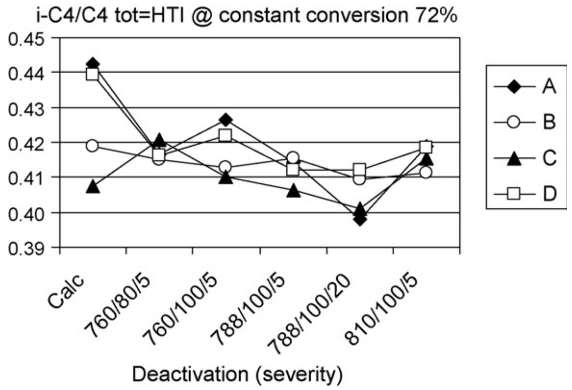

Fig. 10. Hydrogen transfer index (i-C4/total C4) at constant conversion of 72%, *x*-axis labels are deactivation conditions: temperature °C/steam%/time in hours.

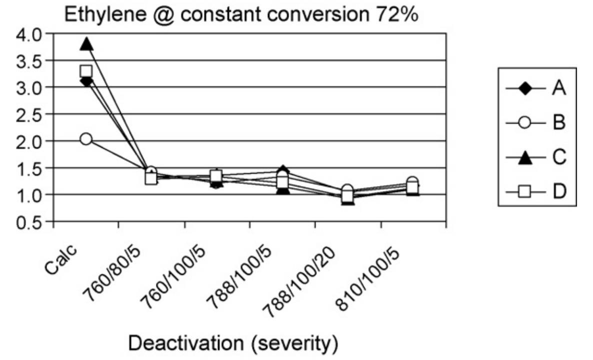

Fig. 11. Ethylene yield at constant conversion of 72%, *x*-axis labels are deactivation conditions: temperature °C/steam%/time hours.

comparing ACE and actual FCC unit propylene yields of an E-cat containing ZSM-5. Though the lab simulation does not match the exact propylene level of the FCC unit, it is still possible to mimic the delta propylene yield obtained with ZSM-5 equilibrated in the FCC unit. This is illustrated in an example in Fig. 14. A laboratory deactivated FCC catalyst and an equilibrium catalyst with the same catalyst formulation were blended with 2.5% of a commercial ZSM-5 additive previously steam deactivated in laboratory. The objective was to verify which system would be able to better simulate the performance of an E-cat containing the same amount of commercially equilibrated additive. It was observed that when deactivation conditions are chosen properly, it is possible to approach the equilibrium catalyst performance both with a laboratory deactivated base catalyst and with an equilibrated sample of the same catalyst. However, a closer match can be obtained when an equilibrated sample is applied. This was rather expected since, like it was already demonstrated in the previous section, a proper simulation of zeolite and matrix deactivation plays an important role in the final ZSM-5 additive performance.

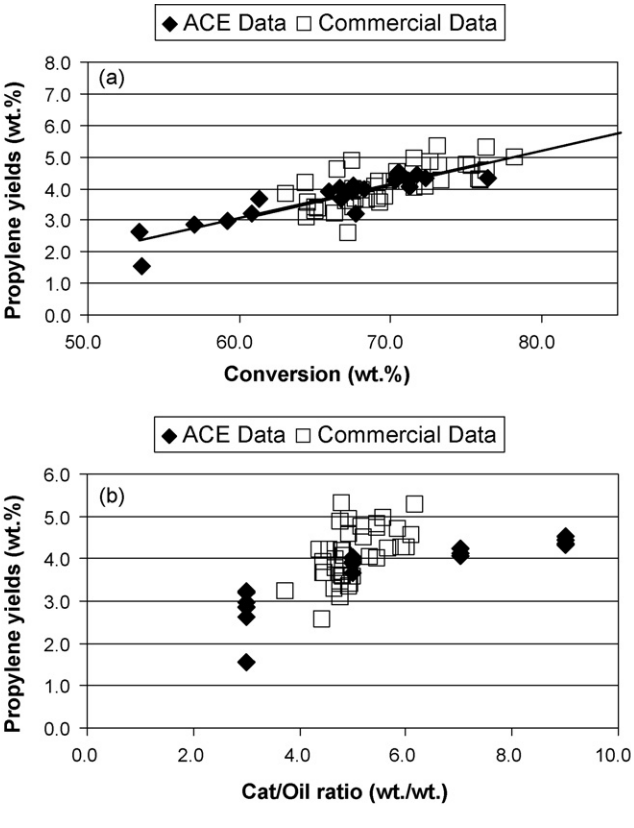

Fig. 12. (a) and (b) Comparison between ACE and commercial propylene yields for the same equilibrium catalyst without ZSM-5 additives.

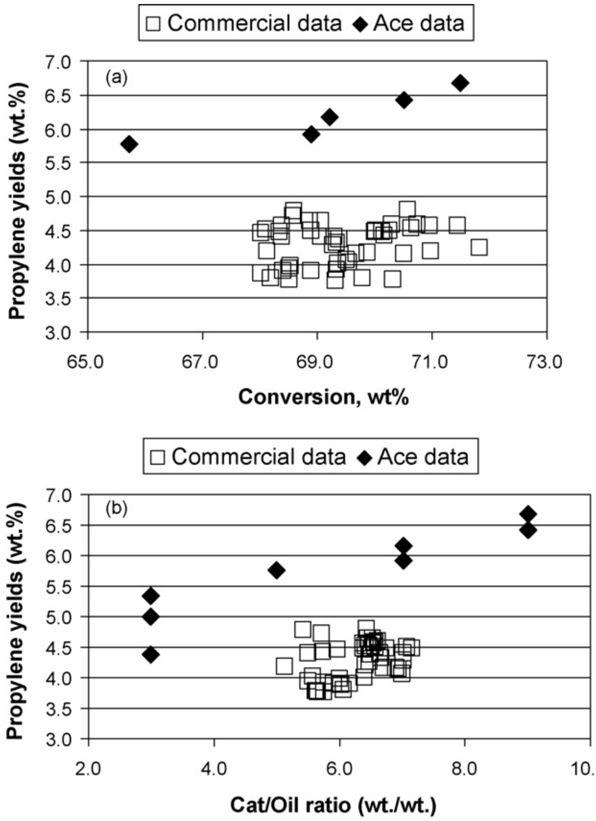

Fig. 13. (a) and (b) Comparison between ACE and commercial propylene yields for the same equilibrium catalyst which contains 4% ZSM-5 additive, commercially equilibrated.

As shown above, combination of equilibrium catalyst and laboratory deactivated (steamed) additive gives propylene yields close to commercial performance. However, not always a suitable or representative equilibrium catalyst is available for testing. In that case deactivation of the total system of the FCC catalyst and additive becomes important.

In the following example laboratory deactivated blends (shown in Table 6) of FCC catalyst and additive were compared to the

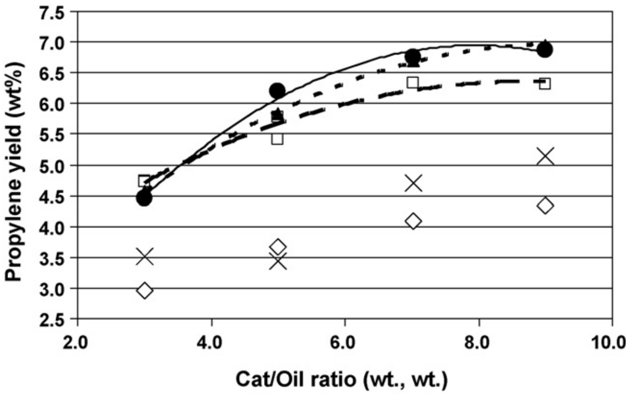

Fig. 14. Propylene yields vs. cat/oil ratio. Performance simulation of an E-cat with ZSM-5 additive. (◇) Lab deactivated base catalyst (B); (×) E-cat without additive (E); (□) B + 2.5% lab deactivated ZSM-5 additive; (▲) E + 2.5% lab deactivated ZSM-5 additive; (●) E-cat with 2.5% ZSM-5 additive.

Table 6
Catalyst blends, A and B refer to steaming severities, B being more severe condition. CD refers to metal deactivation (conditions to match E-cat metal and surface area).

FCC catalyst	Additive	Blend for performance testing
E-cat		E-cat
E-cat	Additive steamed A	E-cat + Add St A
Cat steamed B		Cat St B
Cat steamed B	Additive steamed A	Cat St B + Add St A
Cat steamed B	Additive steamed B	Cat St B + Add St B
Cat CD		Cat CD
Cat CD	Additive steamed A	Cat CD + Add St A
Cat CD	Additive CD with Cat	Cat CD + Add CD

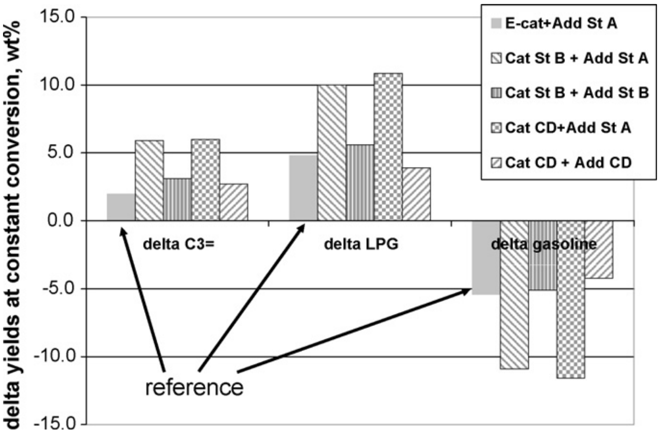

Fig. 15. Effect of deactivation method on delta propylene yield (see Table 6 for nomenclature).

system of E-cat + lab deactivated additive (E-cat + Add St A), which was shown above to be the best method to approach FCC unit delta propylene yields [24]. Deactivation methods varied from mild (A) to severe (B) steaming of catalyst and additive to cyclic deactivation (CD) [25–26] of catalyst or catalyst and additive blend. Catalyst and additive were deactivated together in cases where the deactivation conditions were the same for both. Note that the E-cat and laboratory deactivated FCC catalyst have the same composition. The catalyst blends were performance tested in a laboratory unit using vacuum gasoil feed. As was shown above, small scale testing can exaggerate the propylene yields compared to the real FCC unit. Therefore, it is better to compare the delta propylene in case of laboratory data.

Test results are shown in Fig. 15. Compared to the reference case, e.g. E-cat + steamed additive [E-Cat + Add St A], Catalyst + additive blend with severe steaming (B) [Cat St B + Add St B] or CD deactivated (CD) catalyst and additive blend [Cat CD + Add CD] give the closest match with respect to delta propylene and delta LPG. Using mild steaming of additive in combination with severely steamed or CD deactivated catalyst ([Cat St B + Add St A] or [Cat CD + Add St A]) gives almost twice the delta propylene compared to the reference. This shows that care should be taken when choosing the laboratory deactivation conditions and especially making sure that the conditions are not too mild, in which case (delta) propylene yields are clearly exaggerated. It should be noted that the most realistic delta propylene are obtained in cases were catalyst and additive are deactivated together as a blend.

7. Conclusions and recommendations

Generally the propylene levels obtained in laboratory testing are higher than those obtained in commercial units when ZSM5 is applied. This is primarily due to the choice of performance testing unit. The differences in fluid dynamics, contact times and pressure between different reactors can affect propylene yields considerably. Severity of laboratory deactivation can also play a role in this discrepancy. Laboratory deactivations can be too mild compared to industrial deactivation.

Below a few recommendations are made for selecting a proper deactivation method. The judgments are made based on (delta) propylene yields. However, the final choice of deactivation method will always depend on the target setting.

(1) General recommendation is not to use non-deactivated additives.
(2) To see the stability effects, temperatures from 788 °C and higher are recommended. Additives with high alumina content should be deactivated longer (more than 5 h), to reach the stable condition of alumina deactivation.
(3) To obtain a clearer ranking, severe deactivation conditions should be used, e.g. 788 °C or higher and 5 h or longer.
(4) Performance testing for realistic (delta) propylene yields:
    - Blending laboratory deactivated additive with E-cat is preferred to obtain realistic delta propylene in laboratory testing, since E-cats present proper zeolite and matrix properties decay.
    - If no E-cat is available, it is recommended to make a blend of fresh FCC catalyst with the additive and deactivated this blend either by severe steaming (minimum temperature 788 °C and preferably 20 h) or by Cyclic Deactivation with metals.
(5) As far as the current knowledge goes, metals effects are less important than steaming for the deactivation of ZSM-5 zeolite. Besides, activities of the contaminant metals are difficult to simulate in laboratory and can introduce a large source of errors. Therefore, steam deactivation is preferred for ZSM-5 additives. However, in high metal applications deactivation with metals might be necessary to get also the overall yield pattern more realistic.

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