ELSEVIER

Catalysis Today 49 (1999) 211–220

CATALYSIS TODAY

Zeolite containing catalysts for the conversion of C_8-aromatics fractions

H.H. John*, H.D. Neubauer, P. Birke

KataLeuna GmbH, Am Hauptor, D-06236 Leuna, Germany

Abstract

C_8-aromatics processing catalysts on the basis of mordenite and pentasil zeolites have been developed and commercialized for several years. The mordenite-catalyst isomerizes EB into xylenes, the pentasil catalyst converts EB into benzene up to 80% with low xylene loss. Both catalysts can improve the operating results in *p*-xylene producing plants. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: C_8-aromatics; Xylene; Ethylbenzene

1. Introduction

Para- and *ortho*-xylenes are important raw materials in the petrochemical industry. Notwithstanding the continual, short-term fluctuations on the market, the consumption of xylenes, first of all *p*-xylene (PX), has been growing continuously and will continue to rise. During the last 10 years, PX-consumption increased by a rate of about 8% per annum up to a volume of about 10 million tons per annum. *p*-Xylene is being used almost exclusively for the manufacturing of polyester fibres, resins, and films.

Therefore, the improvement of all the processes connected with the manufacturing of xylenes will become more and more important. The creative use of existing BTX-resources will result in the identification of additional capacities. The available options allow to overcome the bottlenecks in existing plants, to reload them with new catalysts and to restart idle units.

The main feedstocks for *p*-xylene manufacturing are mixtures of C_8-aromatics, which also contain *o*-xylene (OX), *m*-xylene (MX) and ethylbenzene (EB) from catalytic reformate or pyrolysis gasoline. PX is recovered from the mixtures by crystallization or by a selective adsorption process like Parex®. The aromatics stream relieved from PX is recycled via an isomerization reactor in order to re-establish the equilibrium between the xylene isomers to the PX-recovery unit (Fig. 1).

EB is the key compound in this recycle scheme. It is essential that EB must be converted at least in part in the isomerization step, in order to avoid that EB builds up in the recycle stream.

There are two options for EB conversion:

- inclusion of EB in the isomerization reaction of the xylenes, or
- dealkylation of EB into benzene.

The commercial realization of both principles is possible, depending on the selected type of catalyst.

---

*Corresponding author.

PII: S0920-5861(98)00426-X

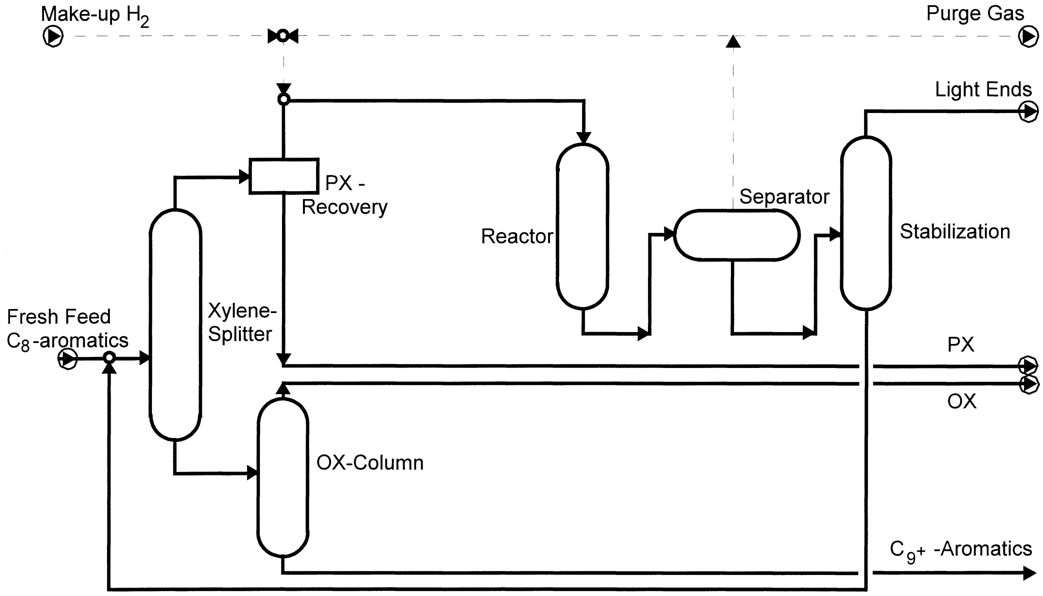


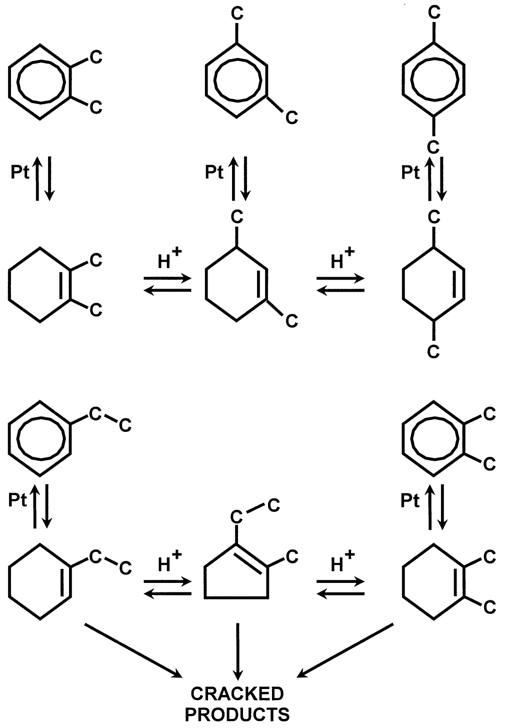
Fig. 1. Simplified scheme of C_8-aromatics process.

2. Reactions of C_8-aromatics

Xylene isomerization is a relatively simple reaction which can proceed as a purely acid-catalyzed reaction via a carbenium ion as intermediate or via a bifunctional catalyst (Scheme 1) [1].

Isomerization of EB into xylenes, however, is a more complicated reaction that requires a bifunctional catalyst [2]. At first, the aromatic ring is partially hydrogenated, and via a ring contraction and expansion mechanism we will obtain xylene isomers (Scheme 1). A complete hydrogenation of the aromatic ring would not necessarily be a disadvantage, as the cycloalkanes can be recycled. On the other hand, the irreversible ring opening and hydrocracking of the C_8-molecule result in losses of aromatics. Therefore, an appropriate ratio between acidic and hydrogenation qualities of the catalyst is required in order to obtain a good selectivity.

In addition, the proper choice of the reaction conditions will allow the minimization of aromatics loss [3]. An optimal temperature can be chosen depending on the reaction pressure, whilst lower and higher temperatures will bring about increased C_8-losses (Fig. 2).



Scheme 1. Simplified scheme of bifunctional isomerization reactions of C_8-aromatics.

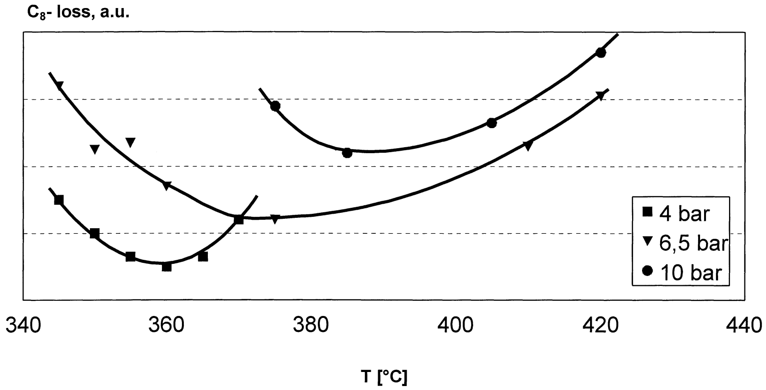
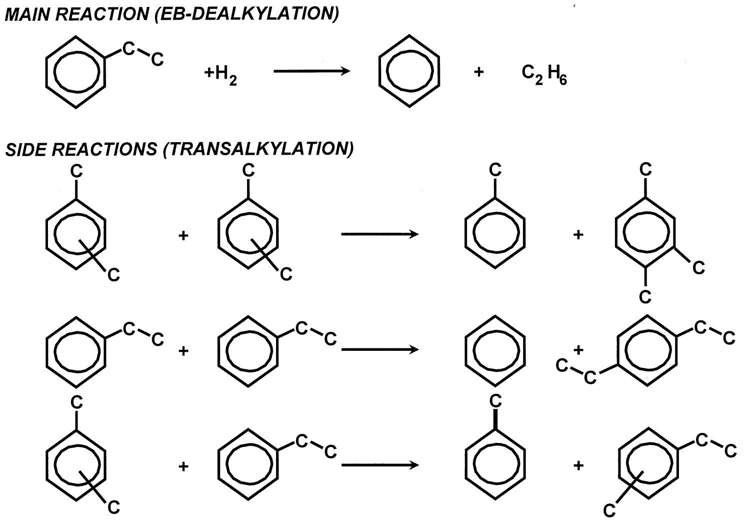


Fig. 2. Effect of temperature and pressure on loss of C_8-aromatics over a Pt/mordenite catalyst (source: S.T. Sie et al., 1996; permission of reprint granted by Erdöl Erdgas Kohle).



Scheme 2. Conversion reactions of C_8-aromatics.

Pure C_8-aromatics isomerization on acidic catalysts is accompanied by several other conversion reactions, e.g. dealkylation and transalkylation (Scheme 2). Assuming high selectivity, hydrodealkylation of ethylbenzene (EB conversion) could be an important reaction, whilst the transalkylation reactions are considered to be undesired side reactions. These reactions also explain the presence of toluene and C_9/C_{10}-aromatics in the reaction products of the C_8-aromatics conversion.

Dealkylation and transalkylation require relatively strong acidic centres. The rate of these reactions is not only influenced by the strength and the number of the acidic centres, but also by the pore size of the zeolites. It is known that there is a strong increase in the ratio between the rates of xylene isomerization and xylene disproportionation when zeolite pore sizes become smaller. For ZSM-5 zeolites, mordenite, and faujasite, this ratio amounts to 1000, 70, and 10–20, respectively [4]. These characteristics also explain the high selectivities of ZSM-5 type zeolites for xylene isomerization.

Similarly, the medium-pored ZSM-5 zeolites are not suitable for a conversion of EB via an associated transalkylation mechanism [5]. Conversion of EB takes place via dealkylation reaction which provides for very good selectivities.

3. Development of catalysts for C_8-aromatics processes

3.1. Objective, history

In consideration of the possible reactions within the C_8-aromatics, the following options have been identified for a possible optimization of the PX- and PX/OX-recovery processes with the help of tailor-made catalysts.

In the case of mordenite-based catalysts, include, as far as possible, the EB in the isomerization of the C_8-aromatics, however:

- the conversion rate of EB is limited by the thermodynamic equilibrium concentration, e.g. about 8% EB (between 400°C and 420°C) and
- there is a chance to gain xylene.

In the case of pentasil-based catalysts, conversion of EB by dealkylation into a marketable by-product, with the effects of:

- no limitations to the conversion rate because of thermodynamic equilibrium,
- high EB conversion with lowest xylene loss and
- formation of considerable quantities of high-purity benzene as desired by-product.

Both options have been successfully realized by commercial catalysts developed by KataLeuna GmbH [6–10].

There are no fundamental differences in the process conditions for both catalyst types, and the most evident differences apply to pressure as well as quality of the cycle gas (Table 1), i.e. the function of the catalyst allows to integrate both catalyst systems in existing plants.

A summary of the important phases of this development is given in Table 2. More than 20 years ago, we gathered our first experience with zeolite-containing catalysts for the conversion of C_8-aromatics fractions. In 1976, the first commercial application of a mordenite-containing catalyst was realized in the refinery PCK Schwedt (Germany). In an existing Octafining®-plant, a catalyst made of an amorphous alumina–silica was replaced by the mordenite-catalyst 8830. At the same time, the efficiency of the PX/OX-recovery process was considerably increased by using distilled concentrated aromatics as feedstock.

In 1983, a modified catalyst with higher performance was used, and on the basis of this experience a new OX-recovery unit was commissioned in a Hungarian refinery in 1986.

The development of a pentasil-based catalyst with a high EB conversion was completed by the commercial application of catalyst 8835 in the Schwedt-refinery in 1991. This catalyst has been used in two more plants in Hungary and Germany since 1992/1994.

Not all the refineries consider benzene from the EB conversion to be a desired by-product of PX-recovery. Therefore, the performance of the mordenite-catalyst has been further developed; in 1996, the new catalyst 8832 was commercially used in the refinery DEA Mineraloel AG Wesseling (Germany).

Table 1
Typical process conditions of C_8-aromatics conversion catalysts

	Mordenite-based catalyst		Pentasil-based catalyst
	8831	8832	8835
Pressure (bar)	10–15	7–18	5–12
Temperature (°C)	410–425	375–430	370–430
LHSV (v/v h)	1.0–2.5	1.5–4.5	1.5–6.0[a]
H_2/C_8-ratio (mol/mol)	4–8	4–5	2–4
Recycle gas (H_2-content) (vol%)	75–85	75–85	55–65

[a] 3.0 realized commercially.

Table 2
Experience with Leuna catalysts in the C_8-aromatics processing

1976	First commercial application of a mordenite-based catalyst – catalyst 8830 – at the PCK refinery Schwedt (Germany); development of a modified C_8-aromatics process on the basis of special catalyst properties with high flexibility
1983	Introduction of new mordenite-based catalyst with higher performance – catalyst 8831 – in an existing plant
1986	Start-up of a newly erected isomerization plant on the basis of catalyst 8831 in Hungary
1991	First commercial application of a pentasil-based catalyst – catalyst 8835 – at the PCK refinery Schwedt (Germany)
1992, 1994	Further commercial plants with catalyst 8835 in Hungary and Germany (refinery VEBA OEZ AG)
1996	Start-up with the new mordenite-based catalyst – catalyst 8832 – with better performance at the refinery DEA Mineraloel AG Wesseling (Germany)

3.2. *Mordenite-based catalyst*

Already two decades ago, a catalyst was developed on the basis of partially dealuminated H-mordenite and Pt/Al_2O_3 as hydrogenation component [6–9]. Experience with catalysts like 8830 and 8831 gathered over many years showed that PX-approaches of 90–95% and EB-approaches of 30–40% were attainable under the conditions of a stable operation (Table 3).

Besides the good isomerization activity, these catalysts had selective hydrocracking properties for paraffinic hydrocarbons with C-numbers of 6–8. This allowed to process feedstocks containing nonaromatics.

The increased losses of C_8-aromatics during the start-up phase proved to be a minor disadvantage of the aforementioned catalysts. Dosing of very small quantities of ammonia turned out to be a method to reduce the losses of C_8-aromatics without simultaneous, considerable decrease of the isomerization activity. This method was used successfully in several commercial units. With regard to the isomerization process, ammonia is a temporarily acting poison, and after about 300 h, the PX- and EB-approaches are nearly the same as in the case of the unpoisoned catalyst (Fig. 3). In contrast to this phenomenon, the C_8-aromatics loss remains below the level of the unpoisoned catalyst. The assumption was made that this change of selectivity would result from an irreversible adsorption of ammonia on centres which catalyze dealkylation and disproportionation.

Although catalyst 8831 cannot fulfil all the actual demands as to the conversion rates, the results obtained from its commercial application and the operational characteristics at stable selectivity are noteworthy, a summary is given in Table 4. Attention should be focused on the specifically processed quantities of EB and nonaromatics (NA), as both components mainly influence the stability of the catalyst.

The results and the experience gathered from the application of catalyst 8831 served as a basis for the further development of such a catalyst type in terms of conversion rate and space velocity. Selected commercially available mordenites have been modified by varying decationization and dealumination. The basic system – similar to that of catalyst 8831 – remained unchanged. A great many of pilot test runs served for

Table 3
Performance data of mordenite-based isomerization catalysts

	Catalyst 8831[a]	Catalyst 8832[b]
PX-approach (%)	90–95	94–97
OX-approach (%)	85–92	90–95
EB-approach (%)	30–40	50–60
Xylene gain (over reactor) (%)	1.5–2.0	2.0–3.0

[a] Activity adjustment by basic N-compound.
[b] No basic N-compound.

Table 4
Performance of mordenite catalyst 8831

	Until 1st reg.	Until 3rd reg.	Until 5th reg.
Time on stream (month)	26	55	79
Processed reactor feed			
EB (t/kg cat)	9.7	20.4	29.1
NA (t/kg cat)	2.4	5.1	7.3
Selectivity over reactor			
C_8-Ar.-loss (wt%)	4.0	3.0	3.5
X-gain (wt%)	1.5	2.0	1.5

PX-approach 90–95%, EB-approach 30–40%; cat inventory 20 mt.
EB – ethylbenzene, NA – nonaromatics.

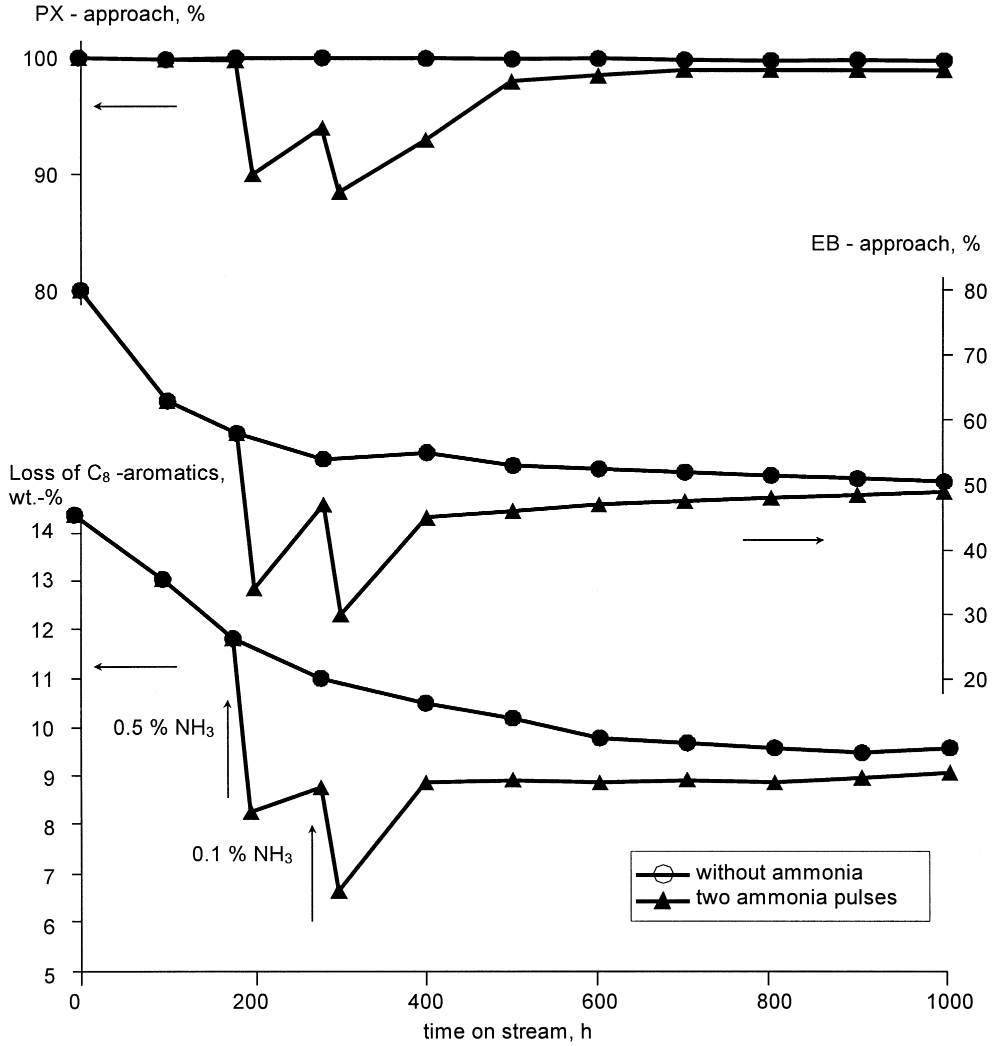


Fig. 3. Influence of ammonia on isomerization activity (PX, EB) and C_8-aromatics loss on catalyst 8830.

the development of a procedure for a commercial catalyst. As you can see from Table 3 the new catalyst has a higher approach of PX and EB and allows a higher space velocity (Table 1). Because of new mordenite properties, catalyst 8832 does not require an activity adjustment in order to obtain a good selectivity.

For several months, catalyst 8832 has been in commercial operation, and the better performance has been confirmed. The PX-output has been increased remarkably by changing the catalyst loading with 8832.

3.3. Pentasil-based catalyst

The interesting catalytic properties of ZSM-5 zeolites triggered development work for a commercial catalyst based on those zeolites.

Different commercially available pentasil zeolites with an SiO_2/Al_2O_3 ratio of about 30 were exchanged with ammonium ions. Together with alumina as binding material, the exchanged zeolites were shaped as extrudates and afterwards calcined at a temperature of 550°C. After impregnation with different hydrogenation metal compounds like iron, molybdenum, and platinum, another calcination was performed at 500°C. The following results were attained from catalytic testing in pilot plants using real feedstocks [10]:

- The addition of iron oxide or molybdenum oxide to the zeolite-binder extrudates results in an activity similar to that of the pure zeolite-binder samples with regard to EB conversion and practically 100% PX-approach; however, selectivity has obviously improved. The xylene loss is remarkably lower, and there are less C_9-/C_{10}-aromatics on iron and molybdenum containing samples.
- Under the same conditions, the platinum containing zeolite-binder extrudate shows an almost complete conversion of EB and a high concentration of nonaromatics due to a significant hydrogenation of the aromatic ring. Obviously the subsequent cracking of the cyclic compounds results in high xylene losses.
- Due to the lower hydrogenation degree of the aromatic ring, considerably lower xylene losses could be obtained at increased reaction temperatures. A further decrease of the xylene loss, associated with a slightly lower EB conversion, was observed when reducing the acidity of the catalyst. In all cases, the PX-approach was practically 100%.

Based on the results obtained with the platinum-zeolite binder system, a procedure has been developed for the manufacturing of a commercial catalyst. Under the general process conditions of catalyst 8835 (Table 1), the PX-approach over 99% shows an excellent isomerization activity for xylenes. Under commercial conditions, an EB conversion in the range 55–80% can be realized with the proviso of stable operation. Even under severe conditions of up to 80% EB conversion, there is only a moderate increase in xylene loss, which is noteworthy under commercial aspects (Fig. 4).

The results from three commercial plants operated with different targets and various PX-recovery technologies (Table 5) indicate a high stability (cycle periods up to 36 months), good activity (EB conversion up to 80% at an LHSV of 2.8) and a high selectivity of catalyst 8835.

Another important feature of this catalyst is its selective hydrocracking activity of nonaromatics (Table 6). This is a prerequisite for processing of nonaromatics containing feedstocks, as these compounds will be kept at a constant level in the recycle stream, i.e. building-up of the nonaromatics level will be avoided.

3.4. Comparison between mordenite- and pentasil-based catalysts

The small differences in the process conditions for both catalysts 8832 and 8835 (Table 1) allow to use them in existing commercial plants for PX-production without technical changes.

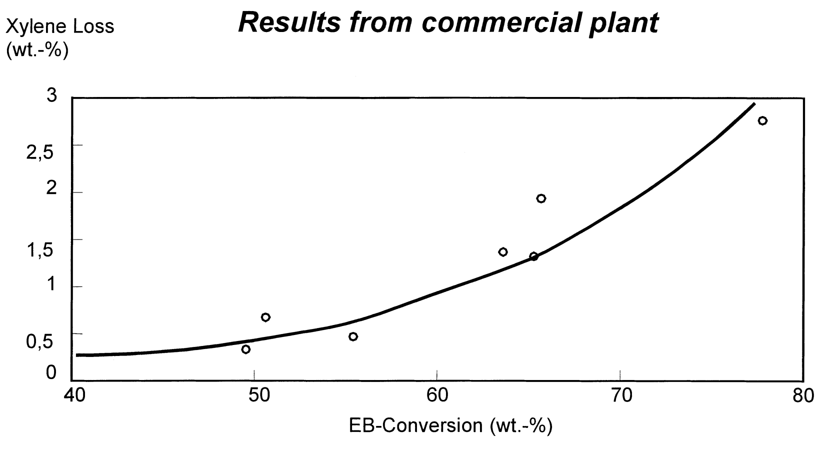


Fig. 4. Xylene loss and EB conversion at catalyst 8835.

Table 5
Typical performance of catalyst 8835

Target Separation technology	Plant 1	Plant 2	Plant 3
	PX; OX	OX	PX; OX
	Crystallization; distillation	Distillation	Parex; distillation
Cat-inventory (m^3)	20.2	12.6	23.2
Cat-inventory (lbs)	26 450	16 500	38 150
LHSV (v/v h)	2.6	2.5	2.8
PX-appr. (%)	99.5	99	>99.5
EBC (%)	55	55	65–80
X-loss (%)	0.8–1.2	0.8–1.2	1.5–3.0
Cycle time (month)	30–36	>36	12–28

Table 6
Hydrocracking of paraffins on catalyst 8835 at different severities

Component in wt%	Reactor	
	Inlet	Outlet
n-Octane	0.2	<0.01
n-Nonane	1.0	<0.01
Methyloctane	2.5	0.8…0.3
Ethylheptane	0.5	0.5…03
Dimethylheptane	1.0	0.9…0.5
Summary	5.2	2.2…1.1
EBC in %		55…83

The maximum PX-yield from the mixed xylene feed will be obtained with the mordenite-catalyst, due to the EB conversion into xylenes. The special qualities of the pentasil-based catalyst, however, offer some attractive points for using such a catalyst, which will be explained in the following examples.

Case 1 refers to the same final production yield of PX and OX (Table 7). It becomes obvious that the application of catalyst 8835 implies a minor catalyst inventory and less energy consumption.

The capacity of the PX-recovery unit is often the bottleneck in PX-production units. Therefore, in case 2, the equal flow rate through the Parex® unit serves as basis for the comparison of both catalysts. Fig. 5 shows how the PX/OX-production can be switched by using the EB-dealkylation catalyst 8835. A ratio of about 2.2 between PX and OX is being assumed.

With the EB-isomerization catalyst 8832, 182 000 t per annum PX and OX can be produced on the basis of 200 000 t per annum mixed xylene feed, i.e. 91% of

Table 7
Comparison of performance Leuna catalysts 8831 and 8835

	Catalyst 8831	Catalyst 8835
Catalyst inventory (tons)	20	12
Platinum inventory (kg)	80	3.6
Rector throughput (m^3/h)	62	46

Advantages of catalyst 8835
Diminution of the catalyst inventory by 40%
Decrease of the reactor throughput by 25%
Reduction of the fuel oil consumption by 22%
Reduction of the electric power consumption by 10%
Reduction of the hydrogen make up gas quantity by 15%

[b] All data are referring to the commercial plant. Basis for the comparison is a daily production of: 150 t of *p*-xylene and 90 t of *o*-xylene.

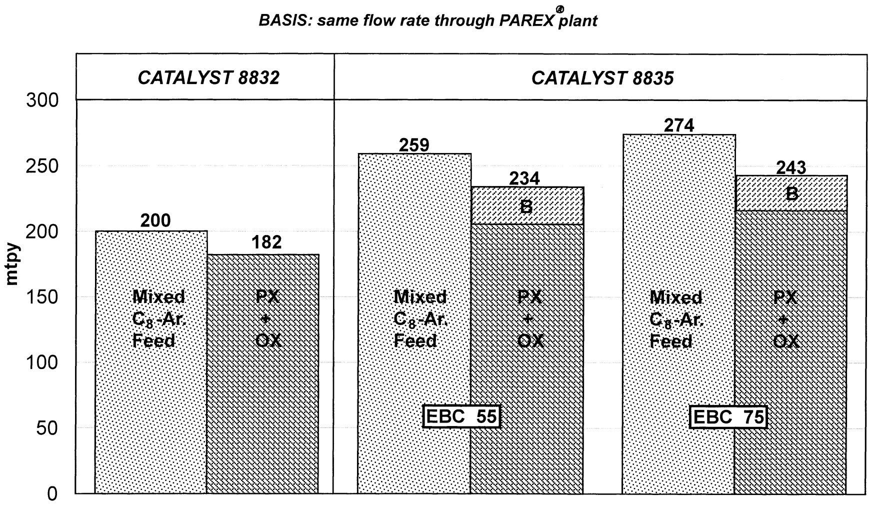


Fig. 5. Changing of EB-isomerization cat (8832) by a EB-dealkylation cat (8835).

the total feed. The same complex with the dealkylation catalyst 8835 can increase the PX/OX-yield to 207 000 t per annum at 55% EB conversion, based on 259 000 t per annum total feed. A further improvement can be obtained at the higher EB conversion of 75%. It is assumed that the downstream fractionators can process the additional benzene quantity of 27 000 and 28 500 t per annum, respectively. The total PX/OX-yield from the mixed xylene feed decreases to 80% and 78%, respectively. However, the complex can increase the total PX- and OX-production by 14–17%.

4. Summary

This paper demonstrates that catalysts for C_8-aromatics processing on the basis of two different catalyst systems – mordenite-containing catalyst with a high Pt-content and pentasil containing catalyst with a very low Pt-content (see Table 8) – have been in commercial operation for more than 20 years. The latest mordenite-catalyst 8832 isomerizes EB from the mixed C_8-aromatics mainly into xylenes at a high space velocity. The pentasil catalyst 8835 allows to attain an EB conversion of 55–80%, with

Table 8
Survey of C_8-aromatics isomerization catalyst

Type	Shape/size	Bulk density (kg/dm^3) sock loading	Application
Mordenite-based catalysts (about 0.4 wt% Pt)			
8831	Extrudates/diam. 1.7 mm	Approx. 0.60	Isomerization of C_8-aromatics mixtures; ethylbenzene approach of 30–40%; ethylbenzene is partially converted into xylenes
8832	Extrudates/diam. 1.3 mm	Approx. 0.63	Isomerization of C_8-aromatic mixtures; ethylbenzene approach of 50–60%; ethylbenzene is mainly converted into xylenes
Pentasil-based catalysts (very low content of Pt)			
8835	Extrudates/diam. 1.7 mm	Approx. 0.63	Isomerization of C_8-aromatics and dealkylation of ethylbenzene; ethylbenzene conversion of 50–80%

moderate xylene loss. Both catalysts can be regenerated and offer attractive possibilities to increase the output of PX or PX and OX in existing C_8-processing units.

5. Abbreviations/definitions

$$\text{PX-/OX-approach}\ (\%) = \frac{X_\mathrm{O} - X_\mathrm{I}}{X_\mathrm{E} - X_\mathrm{I}} \times 100,$$

where X_O is the concentration of PX resp. OX related to xylenes in wt% at the reactor outlet, X_I the concentration of PX resp. OX related to xylenes in wt% at reactor inlet and X_E is the equilibrium concentration of PX (24 wt%) resp. OX (23.5 wt%) at typical reactor temperature.

$$\text{EB-approach}\ (\%) = \frac{\mathrm{EB_I} - \mathrm{EB_O}}{\mathrm{EB_I} - \mathrm{EB_E}} \times 100,$$

where $\mathrm{EB_I}$ is the reactor inlet concentration of EB related to C_8-aromatics in wt%, $\mathrm{EB_O}$ the reactor outlet concentration of EB related to C_8-aromatics in wt% and $\mathrm{EB_E}$ is the equilibrium concentration of EB related to C_8-aromatics of 8.5 wt%.

$$\text{Xylene gain}\ (\%) = \frac{\mathrm{XYL_O} - \mathrm{XYL_I}}{\mathrm{XYL_I}} \times 100,$$

where $\mathrm{XYL_{O,I}}$ represents xylenes in reactor feed ($\mathrm{XYL_I}$) resp. reactor product ($\mathrm{XYL_O}$) in wt%.

References

[1] N.Y. Chen, W.E. Garwood, F.G. Dwyer, Shape Selective Catalysis in Industrial Applications, Marcel Dekker, New York, 1989, pp. 207–215.

[2] P.B. Weisz, in: Advances in Catalysis, vol. 13, Academic Press, London, 1962, pp. 137–190.

[3] S.T. Sie, A.F. de Vries, C.M.A.M. Mesters, A.Q.M. Boon, K. Bottenberg, B. Trautrims, Erdöl Erdgas Kohle 112 (1996) 463.

[4] H. Heinemann, Catal. Rev.-Sci. Eng. 23 (1981) 315.

[5] D.S. Santilli, J. Catal. 99 (1986) 327.

[6] K. Becker, H. John, H. Franke, J. Klempin, H.-J. Barz, J. Dermietzel, Chem. Tech. (Leipzig) 30 (1978) 407.

[7] H. Franke, J. Klempin, E. Schreiber, H. Limmer, E. Höpfner, F. Lippold, K. Becker, H. John, J. Dermietzel, Chem. Tech. (Leipzig) 31 (1979) 402.

[8] J. Klempin, H. Franke, E. Schreiber, H. Limmer, E. Höpfner, F. Lippold, Chem. Tech. (Leipzig) 33 (1981) 356.

[9] K. Becker, H. John, K.-H. Steinberg, M. Weber, K.-H. Nestler in: D. Kalló, Kh.M. Minachev (Eds.), Catalysis on Zeolites, Akadémiai Kiadó, Budapest, 1988, pp. 529–536.

[10] P. Birke, H. John, H.-D. Neubauer, J. Klempin, E. Schreiber, Oil Gas European Magazine, vol. 17 (no. 4), 1991, p. 28.