The effect of active site distribution in bi-functional Pt-zeolite catalysts for ethane dehydroaromatization

Goodarzi, Farnoosh; Christensen, David Benjamin; Joensen, Finn; Kegnæs, Søren; Mielby, Jerrik Jørgen

Published in:
Applied Catalysis A: General

Link to article, DOI:
[10.1016/j.apcata.2019.117383](https://doi.org/10.1016/j.apcata.2019.117383)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Goodarzi, F., Christensen, D. B., Joensen, F., Kegnæs, S., & Mielby, J. J. (2020). The effect of active site distribution in bi-functional Pt-zeolite catalysts for ethane dehydroaromatization. *Applied Catalysis A: General*, 592, [117383]. <https://doi.org/10.1016/j.apcata.2019.117383>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Journal Pre-proof

The effect of active site distribution in bi-functional Pt-zeolite catalysts for ethane dehydroaromatization

Farnoosh Goodarzi, David Benjamin Christensen, Finn Joensen, Søren Kegnæs, Jerrik Mielby

PII: S0926-860X(19)30538-1

DOI: <https://doi.org/10.1016/j.apcata.2019.117383>

Reference: APCATA 117383

To appear in: *Applied Catalysis A, General*

Received Date: 9 October 2019

Revised Date: 5 December 2019

Accepted Date: 22 December 2019

Please cite this article as: Goodarzi F, Christensen DB, Joensen F, Kegnæs S, Mielby J, The effect of active site distribution in bi-functional Pt-zeolite catalysts for ethane dehydroaromatization, *Applied Catalysis A, General* (2020), doi: <https://doi.org/10.1016/j.apcata.2019.117383>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier.

The effect of active site distribution in bi-functional Pt-zeolite catalysts for ethane dehydroaromatization

Farnoosh Goodarzi,^a David Benjamin Christensen,^a Finn Joensen,^b Søren Kegnæs^a and Jerrik Mielby^{,a}*

^a DTU chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kgs, Lyngby, Denmark.

^b Haldor Topsøe A/S, Haldor Topsøes Allé 1, 2800 Kgs, Lyngby, Denmark.

* Corresponding author Email: jjmie@kemi.dtu.dk , Tel: +45 45252402

Graphical Abstract

Highlights

- Pt/ZSM-5 catalysts with different porosity and metal distribution were synthesized
- The catalysts were tested for direct dehydroaromatization of ethane
- The distribution of acid and metal active sites had a large effect on activity
- Adjacent active sites situated inside ZSM-5 resulted in the highest yield of aromatics

Abstract:

The direct conversion of ethane to higher-valued petrochemical feedstock such as benzene, toluene and xylenes (BTX) has become more economically attractive because of the recent shale gas revolution. The selectivity towards BTX and catalyst deactivation represent significant technical challenges in this process. In this work, we synthesized a series of bi-functional Pt on acidic ZSM-5 catalysts to investigate the effect of platinum nanoparticle distribution and location on selectivity and deactivation. The best catalyst was Pt encapsulated in desilicated ZSM-5 that remained stable after 15 hours of reaction resulting in 60% higher conversion and 75% higher BTX selectivity than Pt supported on conventional acidic ZSM-5 zeolite.

KEYWORDS: bi-functional catalysts; dehydroaromatization; zeolite; encapsulated metal nanoparticles; ethane

1. Introduction

Aromatics such as benzene, toluene and xylenes (BTX) are high-valuable raw materials for manufacturing industries.[1] ZSM-5 with microporous three-dimensional channel structure is the primary catalyst applied in the direct conversion of light alkanes such as ethane into aromatics (dehydroaromatization). The pore size of around 5.4 Å in the ZSM-5, which has similar size as BTX molecules, makes this zeolite the perfect size selective catalyst for BTX. Acidic ZSM-5 is usually combined with effective hydrogenating metals such as Pt[2,3], Pd[4] and Ru[5] or metal cations (e.g. Zn, Ga)[6–8], to achieve higher catalytic activity.

Despite the excellent performance of conventional acidic ZSM-5, the small size of the pores imposes a diffusion barrier that leads to severe coke formation in the micropores and catalyst deactivation.[9,10] To address this drawback, different solutions have been proposed to minimize the mean diffusion path length.[10–13] The introduction of mesopores can suppress coke formation by facilitating the molecular diffusion. Mesopores can be created during

synthesis by using hard or soft templates [14–16] or via post-synthetic approaches such as alkali/acid treatments [17–19]. In addition, the presence of mesopores can increase the external surface area to facilitate the dispersion of supported metal nanoparticles.[20,21]

Previous reports have indicated that the proximity of the metal and acid sites influences the conversion, selectivity and deactivation in the direct transformation of ethane to aromatics. For instance, Reschetilowski *et al.* [2] proposed that higher dispersion and smaller particle size of Pt leads to closer proximity of metal and acid sites, which increases the electron deficiency of the metal. The authors suggested that this stabilizes the chemisorbed platinum-ethylene complex, which assists consecutive reactions that convert the olefin intermediates into coke and consequently leads to rapid deactivation. Furthermore, Steinberg *et al.* [22] investigated the importance of the catalyst bed and demonstrated that the optimum packing has Pt/ZSM-5 in the top bed and pure ZSM-5 in the bottom bed. The authors therefore concluded that dehydroaromatization is initiated in the first bed and the process is followed by aromatization on the bottom bed. Based on these results, Xiang *et al.* [23] recently suggested that for combining these beds into one catalyst bed, an optimum design would be a catalyst that consists of a core of Pt on ZSM-5 with a shell of pure ZSM-5. Despite previous investigations on Pt/ZSM-5, the importance of the metal and acid site distribution is still not fully understood because of the lack of proper model catalysts. Based on our previous work with metal nanoparticles and mesoporous zeolites [20,21], we therefore decided to encapsulate Pt in the core of a hierarchical ZSM-5 catalyst.

Here, we prepared four ZSM-5 zeolites with similar strong acid site concentration but different morphology and pore size distribution in order to investigate the effect of the metal nanoparticles size, location and distribution and proximity of Pt and acid sites. The zeolites were then impregnated with Pt and tested for the direct conversion of ethane into BTX by dehydroaromatization. The first catalyst is conventional ZSM-5 with Pt primarily located on the zeolite external surface (Pt/C-ZSM-5), please see figure 1. The second catalyst is selectively desilicated ZSM-5, where mesopores and voids are created inside the zeolite framework and platinum is mainly located inside these voids (Pt/D-ZSM-5). The third and fourth catalysts are Pt encapsulated in mesoporous ZSM-5 (Pt/M-ZSM-5) and recrystallized mesoporous ZSM-5 with Pt surrounded by a thin microporous shell of ZSM-5 (Pt/R-ZSM-5), respectively. Under the same reaction conditions, Pt/D-ZSM-5 exhibited the highest catalytic activity and remained stable for over 15 hours of conversion. Furthermore, the catalyst accommodated the largest amount of coke.

Figure 1. Schematic illustration of the four different catalysts. From left to right: Pt supported on conventional ZSM-5 (Pt/C-ZSM-5), Pt supported on desilicated ZSM-5 (Pt/D-ZSM-5), Pt supported on mesoporous carbon-templated ZSM-5 (Pt/M-ZSM-5) and Pt supported on carbon-templated and recrystallized ZSM-5 (Pt/R-ZSM-5).

2. Experimental

Tetrapropylammonium hydroxide (TPAOH, Sigma-Aldrich, 1.0 M in H₂O) and tetraethyl orthosilicate (TEOS, Sigma-Aldrich, ≥99.0 %) were used as the structure directing agent (SDA) and silicon source, respectively, in all of the syntheses.

2.1 Synthesis

2.1.1 Conventional ZSM-5 (C-ZSM-5)

For synthesis of conventional ZSM-5 (C-ZSM-5) with Si/Al ratio of 100, 0.016 g of sodium aluminate (NaAlO₂, Sigma-Aldrich, anhydrous) was dissolved in 7.26 ml TPAOH. Then 4.46 mL of TEOS was added dropwise to the solution while stirring in a Teflon beaker. The mixture was stirred for 1 hour and then heated in a Teflon-lined stainless steel autoclave at 180 °C for 24 h under autogenous pressure. The product was separated from the liquid phase by filtration, washed several times with distilled water, dried at 80 °C overnight and then calcined for 20 h at 550 °C to yield NaZSM-5. NaZSM-5 was ion exchanged as described in section 2.1.5 to achieve C-ZSM-5.

Selectively desilicated ZSM-5 (D-ZSM-5)

1.0 g of NaZSM-5 was added to a solution of 0.7 g cetyltrimethylammonium bromide (CTAB, as surfactant) in 50 ml ammonium hydroxide (15 % ammonia in H₂O) and stirred for 3 hours at room temperature. The mixture was then heated in a Teflon-lined stainless steel autoclave at 90 °C for 24 hours under autogenous pressure. Products were washed and calcined for 10 h at 550 °C to yield desilicated NaZSM-5. Finally, the product was ion exchanged as described in section 2.1.5 to achieve D-ZSM-5.

2.1.2 Mesoporous ZSM-5 (M-ZSM-5)

Following the procedure by Jacobsen *et al.*, [14] mesoporous ZSM-5 was synthesized using carbon black particles (BP-2000), with average particle diameter of 12 nm, as hard template. First, 0.016 g of sodium aluminate was dissolved in 7.26 mL TPAOH and then 2 g of carbon black was impregnated with the solution in a Teflon beaker and dried overnight at room temperature. The dried mixture was impregnated with 4.46 mL of TEOS and dried overnight at room temperature. The Teflon beaker was placed in a Teflon-lined stainless steel autoclave and 15 ml of distilled water was added into the autoclave, around the beaker, to produce saturated steam. The autoclave was heated at 180 °C for 72 h. After the autoclave was quenched, synthesized powder was collected, washed with distilled water, dried at 80 °C for 24 h and finally calcined at 550 °C for 20 h to yield mesoporous NaZSM-5. The sample was ion exchanged as described in section 2.1.5 to achieve M-ZSM-5.

2.1.3 Steam-assisted recrystallized mesoporous ZSM-5 (R-ZSM-5)

The as-synthesized mesoporous NaZSM-5 was pulverized in a mortar, dried in vacuum oven at 80 °C overnight. First, 0.016 g of sodium aluminate was dissolved in 7.26 mL TPAOH and used for impregnating 1 g of the ZSM-5 powder in a Teflon beaker. The mixture was mixed for 15 minutes and dried overnight at room temperature. Then the material was impregnated with 4.46 mL TEOS again and dried overnight at room temperature. The beaker was placed in a Teflon-lined stainless steel autoclave and 15 ml of distilled water was added into the autoclave, around the beaker, to produce saturated steam. The autoclave was heated at 180 °C for 72 h. After the autoclave was quenched, synthesized powder was collected, washed with distilled water, dried at 80 °C for 24 h and finally calcined at 550 °C for 20 h to yield recrystallized NaZSM-5. The product was ion exchanged as described in section 2.1.5 to achieve R-ZSM-5.

2.1.4 Ion exchange protocol and Impregnation of the zeolites

All ZSM-5 samples were ion exchanged by stirring 1 g of zeolite in 80 ml of 1 mol/L ammonium nitrate aqueous solution at 80 °C for 1 hour. The process was repeated three times while the last ion exchange was carried out overnight. The powder was washed, dried in the oven for 12 h at 80 °C and calcined for 10 h at 550 °C to achieve protonated ZSM-5 zeolites. Prior to metal impregnation, the zeolite powder was placed in vacuum oven at 50 °C overnight. The zeolite powder was impregnated with H_2PtCl_6 solution in water until incipient wetness. Finally, the powder was dried at 80 °C for 12 h, calcined at 350 °C (heating ramp of 0.5 °C/min) for 3 h and reduced in H_2 at 600 °C for 3 h to achieve 1 wt% Pt in ZSM-5 zeolite.

2.2 Characterizations

Powder X-ray diffraction was performed for all Pt on acidic ZSM-5 catalysts and pure acidic ZSM-5 zeolite on a Huber G670 diffractometer operated in transmission mode with $\text{Cu K}\alpha_1$ irradiation from a focusing quartz monochromator.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was done for elemental analysis on an Agilent 720 ICP-OES spectrometer to determine the amount of Si, Al and Pt.

Transmission electron microscopy (TEM) was performed on a FEI Tecnai T20 G2 microscope operated at 200 KV to investigate crystal sizes and morphology of the samples and platinum location on different ZSM-5 supports.

N_2 physisorption was operated for protonated ZSM-5 zeolites at liquid nitrogen temperature on a 3FLEX surface area and porosimetry analyzer. Prior to the test, samples were outgassed under vacuum at 400 °C overnight. The specific surface area (S_{BET}) was calculated by the BET method. Micropore volumes (V_{micro}) were determined using t-plot method. The total pore volumes (V_{total}) and the external surface were calculated from the amount of adsorbed nitrogen at the relative pressure of $P/P_0=0.95$.

Temperature programmed desorption of ammonia (NH_3 -TPD) was measured by Ammonia TPD on a Mettler Toledo TGA-DSC1. Prior to the analysis, the samples were heated to 500 °C in a mix flow of N_2 and Ar. Afterwards, samples were cooled down to 150 °C and NH_3 was purged for 30 min followed by flushing with inert gases for 3 hours to remove physically adsorbed NH_3 . Eventually, desorption of NH_3 was carried out by increasing the temperature to 500 °C with a heating ramp of 5 °C/min.

The amount of coke was quantified by thermo-gravimetric analysis (TGA) on a Mettler Toledo equipment. The catalysts were heated at a rate of 5 °C min^{-1} in synthetic air to 700 °C.

2.3 Catalytic Test

Ethane dehydroaromatization experiments were performed in a continuous fixed bed stainless steel reactor with an inner diameter of 9 mm at 550 °C and under 2 barg pressure. The reactor and thermowells, which were in contact with the stream, were coated with SilcoNert®1000[24] (Silicosteel®, thickness of 100-500 nm). Catalyst fraction size was between 0.6-1 mm and 1.0 g of the fractionated catalyst was loaded into the reactor. All of the catalysts were pretreated at 550 °C for 1 h under 12 NL h⁻¹ flow of N₂ to remove impurities and any traces of oxygen from the catalysts. The gas was then switched to 10 % ethane in N₂ with total flow of 3 NL h⁻¹ corresponding to a gas hourly space velocity (GHSV) of 0.3 NL/g_{cat} /h. The outlet gases were analyzed online in an Agilent 7890B gas chromatograph equipped with two capillary columns of CP-Al₂O₃-KCl (25m×0.32mm×5μm) and HP-INNOWax, (30mm×0.32mm×0.25μm), a thermal conductivity detector (TCD) and two flame ionization detectors (FID). The conversion and products selectivity were calculated based on carbon mole balance.

3. Results and Discussion

3.1 Characterization results

The X-ray diffraction (XRD) patterns of all the platinum containing ZSM-5 catalysts and pure conventional ZSM-5 zeolite are shown in Figure 2. As expected, the patterns show that all ZSM-5 samples were crystalline and had the characteristic peaks of the ZSM-5 zeolite framework. In addition, a very weak peak appeared around $2\theta=39.9^\circ$ in all of the ZSM-5-supported Pt samples except for Pt/R-ZSM-5. We assign this peak to the diffraction from Pt (111). The absence of the Pt (111) peak in Pt/R-ZSM-5 indicates that the nanoparticles are smaller than in the other samples. Furthermore, we found that the diffraction peak of Pt (111) is slightly broader in Pt/D-ZSM-5, indicating that the nanoparticles in this sample are smaller than in Pt/M-ZSM-5 and Pt/C-ZSM-5.

Figure 2. XRD patterns of the prepared catalysts (normal (left) and zoomed in (right)).

Figure 3 shows the N_2 physisorption analysis of all ZSM-5 zeolite without platinum. The isotherms are type I for both C-ZSM5 and D-ZSM-5 with a small step around $P/P^\circ = 0.15$. This step is not related to pores in the MFI materials, but a result of the so-called fluid-to-crystalline like phase transition of the adsorbed nitrogen.[25] Moreover, D-ZSM-5 has a small H4 hysteresis loop at P/P° above the forced closure at $P/P^\circ = 0.4$, which is attributed to the created internal voids and mesopores in the sample with broad pore size distribution.[20,21] Figure S1 shows the pore size distribution (PSD) obtained from BJH analysis of the desorption branch which confirms that PSD in the D-ZSM-5 is between 6 to 70 nm. However, M-ZSM-5 shows a type IV isotherm with a hysteresis loop at $P/P^\circ > 0.8$. Typically, this loop is assigned to mesopores[26] and BJH analysis shows that PSD is between 5 to 50 nm (Figure S1). Similarly, R-ZSM-5 exhibits a type IV isotherm but with hysteresis loop of H2 that has a steep closing at $P/P^\circ = 0.4$. This well-known phenomenon is referred to as an inkbottle-type of porosity and indicates that the mesopores are only accessible through the inherent zeolite micropores.[27] Based on these results, the four ZSM-5 zeolites have different types of pore systems and different pore size distributions. All textural properties of the ZSM-5 supports are summarized in Table S1. The results show that the modified zeolites D-ZSM-5, M-ZSM-5 and R-ZSM-5 have a higher external surface area and total pore volume than C-ZSM-5, while the microporous surface area remain in the same range.

Figure 3. N₂ physisorption analysis with offset of 2 mmol/g between isotherms for conventional (C-ZSM-5), selectively desilicated (D-ZSM-5), mesoporous ZSM-5 (M-ZSM-5) and steam-assisted recrystallized mesoporous ZSM-5 (R-ZSM-5) performed at 77K.

Elemental analysis results obtained from ICP-OES revealed that all four catalysts have similar Pt content of about 0.7 wt% as well as a similar Si/Al ratios of around 100 (See Table S2). X-ray photoelectron spectroscopy (XPS) analysis of Pt/C-ZSM-5 shows two weak peaks from Pt 4d_{5/2} and 4d_{3/2}. This indicates that Pt particles are present on the surface of this sample. The other samples showed no detectable peaks between 300-350 eV, which confirms that a significant part of the platinum nanoparticles were encapsulated in the interior of the zeolites.

Figure 4. XPS of the Pt on different support.

The TEM images in Figure 5 illustrate very different zeolite morphologies as well as dispersion and location of the Pt nanoparticles. The C-ZSM-5 and D-ZSM-5 have the typical coffin-shape morphology for the MFI structure with average crystal size of 250 nm. Moreover, in D-ZSM-5 the created voids and mesopores are obvious inside the zeolite crystals. As for M-ZSM-5 and R-ZSM-5, the crystals are larger in size (around 1000 nm), which are more clear in figure S4 and S5. Figure 5d also shows reconstructed surface via steam-assisted recrystallization around R-ZSM-5 that makes the surface smoother, while M-ZSM-5 has a rough surface (Figure

5c). The Pt nanoparticles are rather large in Pt/C-ZSM-5 (around 10 to 50 nm) compared to other samples. Furthermore, metal nanoparticles are agglomerated and mostly situated on the surface of the Pt/C-ZSM-5. In the Pt/D-ZSM-5 where Pt nanoparticles are encapsulated in the recrystallized ZSM-5, the small metal nanoparticles (less than 10 nm) are well distributed in the zeolite voids and mesopores inside the interior region of the zeolite crystal. In the case of Pt/M-ZSM-5, the Pt particles are difficult to detect in the TEM images due to the thickness of the zeolite particles. However, we speculate that Pt nanoparticles are situated inside the mesoporous ZSM-5 crystals since there are no particles found on the external surface. For Pt/R-ZSM-5 sample, Pt nanoparticles (smaller than 10 nm) are well dispersed inside the zeolite and encapsulated by the thin shell surrounding them. The observed size of Pt nanoparticles in TEM are in good agreement with XRD results (more TEM images are presented in SI). In addition, the TEM images confirm XPS analysis results that Pt nanoparticles are mainly located on the surface of Pt/C-ZSM-5, whereas for the other samples the metal particles are primarily located in the interior.

Figure 5. TEM images of a) Pt/C-ZSM-5, b) Pt/D-ZSM-5, c) Pt/M-ZSM-5 and d) Pt/R-ZSM-5, respectively.

NH₃-TPD shows that the concentration of strong acid sites is similar in all ZSM-5 catalysts considering the degree of uncertainty for the analysis, which is 0.02 mmol/g.

3.2 Catalytic results

We tested the four catalysts for the direct dehydroaromatization of ethane into BTX-type aromatics. Figure 6a shows the conversion as function of the time-on-stream at 550 °C. The overall catalytic behavior of all four catalysts is that their initial conversion begins to decrease over time with different rates. Among the catalysts, Pt/D-ZSM-5 resulted in the highest activity and selectivity towards BTX during the 15 hour experiment. The least active catalyst is Pt/M-ZSM-5 that showed low conversion, low selectivity and significant deactivation. Based on a previous study by Reschetilowski *et al.* [2], it is likely that this catalyst is less active firstly due to the large size of Pt nanoparticles and secondly because metal nanoparticles are located inside the mesopores and not in the zeolite framework. This means that platinum nanoparticles are situated distant from Brønsted acid sites.

The selectivity of the catalysts towards the desired BTX products in Figure 6b shows that Pt/D-ZSM-5 has the highest selectivity, which is about 38% and it increases slightly over time to about 42%. In contrast, the Pt/M-ZSM-5 shows the lowest selectivity towards BTX and decreases from 20% to below 10% after 6 h. In spite of the same conversion of ethane over Pt/C-ZSM-5 and Pt/R-ZSM-5 during the first 5 h of reaction, the latter catalyst exhibits a more stable and higher conversion. In addition, the BTX selectivity of Pt/R-ZSM-5 is higher, and significantly more stable, only decreasing from 36% to 33% while BTX selectivity drops from 28 to 21% for Pt/C-ZSM-5. Direct conversion of ethane to aromatics is thermodynamically limited by the initial reaction, which is dehydrogenation of ethane into ethylene. Therefore, ethylene is required to be transformed to aromatics to overcome the thermodynamic limitation and increase the overall conversion.[28] As NH₃-TPD results showed similar strong acid site concentration for all four zeolites, it may be assumed that the consumption of ethylene is favored by the close proximity of metal and acid sites which catalyze the oligomerization and cyclization transformation.[29,30] For this reason, both distribution and location of metal active sites in the catalysts probably play a crucial role with respect to both activity and BTX selectivity. This would explain the higher selectivity for Pt/D-ZSM-5 and Pt/R-ZSM-5 where Pt nanoparticles are more evenly distributed in the interior and surrounded by ZSM-5 framework compared to the other two catalysts in which nanoparticles are located on the external surface as shown in TEM. Furthermore, we believe that Pt/D-ZSM-5 gives the highest

conversion and BTX selectivity compared to Pt/R-ZSM-5 due to the optimum location of Pt nanoparticles, which is in the inner region. This also confirms the discussed mechanism in the literature[22] that first ethane dehydrogenates on the metal nanoparticles active sites. Subsequently, ethylene reacts further on zeolite Brønsted acid sites, while diffusing out of the catalyst, to convert into BTX. Therefore, if Pt nanoparticles are not distributed near the framework (i.e. close proximity to the acid sites), the conversion will be limited, which is projected more clearly in Pt/C-ZSM-5.

Figure 6. Ethane conversion and BTX selectivity for different catalysts at 550 °C, 2 barg and $GHSV=0.3 \text{ h}^{-1}$

Figure 7 shows the selectivity towards different by-products: methane, ethylene, propane, propylene, butane, butenes, ethyl benzene and heavy aromatics such as naphthalene derivatives. Methane formation is the consequence of higher conversion and BTX selectivity that involves more secondary reactions. Therefore, the catalysts Pt/D-ZSM-5 and Pt/R-ZSM-5 with higher conversion and BTX selectivity have higher selectivity to methane. Ethylene product is lower in these catalysts compared to Pt/C-ZSM-5 and Pt/M-ZSM-5, which also confirms that ethylene is consumed more efficiently in these catalysts to form aromatics. Olefins and alkanes consisting of C_3 and C_4 are considered as secondary products, which is why their production reach a maximum and then declines as the result of their further transformation in all of the catalysts. In general, a small amount of heavy aromatics are formed over all of the catalysts but the selectivity towards these products is too small for comparison.

Figure 7. Selectivity towards methane, ethylene, alkanes, olefins, BTX and heavy aromatics for the different catalysts at 550 °C, 2 barg and GHSV=0.3 h⁻¹.

The TGA results in Figure 8 indicate that the most active catalyst of Pt/D-ZSM-5 has the largest amount of coke content around 12.6 wt% while Pt/R-ZSM-5 contains the least amount of coke (1.3 wt%). It is likely that higher porosity of Pt/R-ZSM-5 enhances the diffusion to suppress the coke formation more effectively than Pt/D-ZSM-5, which has less voids and mesopores. It is remarkable however, that the desilicated sample maintains superior activity and selectivity throughout, despite the high amount of coke deposition. Carbon deposition on Pt/M-ZSM-5 and Pt/R-ZSM-5 zeolites are almost similar, although the latter catalyst exhibited higher conversion and selectivity towards BTX. Based on the small coke content of these two catalysts, the main reason for the deactivation in Pt/M-ZSM-5 might be sintering and loss of

metal active sites rather than coking. Furthermore, Pt/C-ZSM-5 has high content of deposited coke (around 10%), which indicates that the decrease in activity and selectivity was mainly caused by pore blockage. Based on all above discussed results, Pt/D-ZSM-5 is the most active and selective catalyst that preserved its activity which we may attribute to successful metal encapsulation in the core region and presence of mesoporosity which provides accessibility to the active sites.

Figure 8. TGA results of catalysts with heating ramp of 5°/min in synthetic air.

4. Conclusion:

Four platinum containing acidic ZSM-5 with similar strong acid site concentration but different morphology, where metal nanoparticles are located in different regions of zeolite, were synthesized and tested in the direct conversion of ethane to aromatics. The two catalysts, Pt on conventional ZSM-5 and Pt on mesoporous ZSM-5, in which Pt nanoparticles were larger and located distant from the acid sites showed the least activity and selectivity towards BTX. Furthermore, the conversion and selectivity decreased after 15 hours.

Desilicated ZSM-5 and recrystallized ZSM-5-encapsulated Pt nanoparticles showed significantly higher activity and selectivity towards BTX. The metal active sites in these catalysts were sitting in close proximity to the acid sites. Furthermore, in desilicated ZSM-5-encapsulated Pt, where Pt nanoparticles are situated mainly in the core of zeolite surrounded by zeolite framework, resulted in highest conversion of ethane and selectivity towards BTX. The BTX selectivity of this catalyst was significantly stable because of presence of mesopores despite containing the highest amount of coke. Desilicated ZSM-5 encapsulated Pt catalyst proved to be the optimum design for the bi-functional Pt/ZSM-5 catalyst. Thus, we believe the new design of the synthesized catalyst holds promise to achieve a selective and stable catalyst for ethane dehydroaromatization.

Acknowledgements

The authors are grateful for funding from Haldor Topsøe A/S, Independent Research Fund Denmark (grant no. 6111-00237) and Villum Fonden (Grant No. 13158). Finally, we acknowledge Aino Nielsen for help with FTIR analysis.

References:

- [1] A.A. Dergachev, A.L. Lapidus, *Russ. J. Gen. Chem.* 79 (2009) 1244–1251. doi:10.1134/S1070363209060413.
- [2] W. Reschetilowski, U. Mroczek, K.H. Steinberg, K.P. Wendlandt, *Appl. Catal.* 78 (1991) 257–264. doi:10.1016/0166-9834(91)80110-I.
- [3] O. V. Chetina, T. V. Vasina, V. V. Lunin, *Appl. Catal. A, Gen.* 131 (1995) 7–14. doi:10.1016/0926-860X(95)00126-3.
- [4] U. Mroczek, W. Reschetilowski, K. Pietzsch, K.H. Steinberg, *React. Kinet. Catal. Lett.* 43 (1991) 539–544. doi:10.1007/BF02064725.
- [5] U. Mroczek, F. Roessner, K.H. Steinberg, *React. Kinet. Catal. Lett.* 43 (1991) 559–563. doi:10.1007/BF02064728.
- [6] O.P. Keipert, D. Wolf, P. Schulz, M. Baerns, *Appl. Catal. A, Gen.* 131 (1995) 347–365. doi:10.1016/0926-860X(95)00148-4.
- [7] T. Liang, H. Toghiani, Y. Xiang, *Ind. Eng. Chem. Res.* (2018) acs.iecr.8b03735. doi:10.1021/acs.iecr.8b03735.
- [8] V.B. Kazansky, I.R. Subbotina, N. Rane, R.A. Van Santen, E.J.M. Hensen, *Phys. Chem. Chem. Phys.* 7 (2005) 3088–3092. doi:10.1039/b506782k.
- [9] J. Glatthorn, E. Feldmann, V. Tabaku, C. Leuschner, P. Meyer, *BMC Ecol.* 18 (2018) 493–502. doi:10.1186/s12898-018-0203-y.
- [10] L. Su, L. Liu, J. Zhuang, H. Wang, Y. Li, W. Shen, Y. Xu, X. Bao, *Catal. Letters.* 91 (2003) 155–168. doi:10.1023/B:CATL.00000007149.48132.5a.
- [11] I.I. Ivanova, E.E. Knyazeva, *Chem. Soc. Rev.* 42 (2013) 3671–3688. doi:10.1039/c2cs35341e.
- [12] J.C. Groen, W. Zhu, S. Brouwer, S.J. Huynink, F. Kapteijn, J.A. Moulijn, J. Pérez-Ramírez, *J. Am. Chem. Soc.* 129 (2007) 355–360. doi:10.1021/ja065737o.
- [13] M.Y. Gim, C. Song, T.H. Kim, J.H. Song, D.H. Kim, K.Y. Lee, I.K. Song, *Mol. Catal.* 439 (2017) 134–142. doi:10.1016/j.mcat.2017.07.001.
- [14] C.J.H. Jacobsen, C. Madsen, J. Houzvicka, I. Schmidt, A. Carlsson, *J. Am. Chem. Soc.*

- 122 (2000) 7116–7117. doi:10.1021/ja000744c.
- [15] H. Wang, T.J. Pinnavaia, *Angew. Chemie - Int. Ed.* 45 (2006) 7603–7606. doi:10.1002/anie.200602595.
- [16] H. Chen, M. Yang, W. Shang, Y. Tong, B. Liu, X. Han, J. Zhang, Q. Hao, M. Sun, X. Ma, *Ind. Eng. Chem. Res.* 57 (2018) 10956–10966. doi:10.1021/acs.iecr.8b00849.
- [17] M. Ogura, S. Shinomiya, J. Tateno, Y. Nara, M. Nomura, E. Kikuchi, M. Matsukata, *Appl. Catal. A Gen.* 219 (2001) 33–43. doi:10.1016/S0926-860X(01)00645-7.
- [18] J.C. Groen, J.A. Moulijn, J. Pérez-Ramírez, *Microporous Mesoporous Mater.* 87 (2005) 153–161. doi:10.1016/j.micromeso.2005.07.050.
- [19] M. Ogura, S. Shinomiya, J. Tateno, Y. Nara, E. Kikuchi, M. Matsukata, *Chem. Lett.* 29 (2000) 882–883. doi:10.1246/cl.2000.882.
- [20] F. Goodarzi, L. Kang, F.R. Wang, F. Joensen, S. Kegnæs, J. Mielby, *ChemCatChem.* 10 (2018) 1566–1570. doi:10.1002/cctc.201701946.
- [21] J. Mielby, J.O. Abildstrøm, F. Wang, T. Kasama, C. Weidenthaler, S. Kegnæs, *Angew. Chemie - Int. Ed.* 53 (2014) 12513–12516. doi:10.1002/anie.201406354.
- [22] K.H. Steinberg, U. Mroczek, F. Roessner, *Appl. Catal.* 66 (1990) 37–44. doi:10.1016/S0166-9834(00)81625-5.
- [23] Y. Xiang, H. Wang, J. Cheng, J. Matsubu, *Catal. Sci. Technol.* 8 (2018) 1500–1516. doi:10.1039/c7cy01878a.
- [24] SilicoNert, (2019). <https://silcotek.de/coating>.
- [25] P.L. Llewellyn, J.P. Coulomb, Y. Grillet, J. Patarin, H. Lauter, H. Reichert, J. Rouquerol, *Langmuir.* 9 (1993) 1846–1851. doi:10.1021/la00031a036.
- [26] A.H. Janssen, I. Schmidt, C.J.H. Jacobsen, A.J. Koster, K.P. de Jong, *Microporous Mesoporous Mater.* 65 (2003) 59–75. doi:10.1016/j.micromeso.2003.07.003.
- [27] J.C. Groen, J. Pérez-Ramírez, *Appl. Catal. A Gen.* 268 (2004) 121–125. doi:10.1016/j.apcata.2004.03.031.
- [28] Y. Xiang, H. Wang, J. Cheng, J. Matsubu, *Catal. Sci. Technol.* 8 (2018) 1500–1516. doi:10.1039/C7CY01878A.
- [29] M. S Scurrrell, *Appl. Catal.* 32 (1987) 1–22. doi:10.1016/S0166-9834(00)80612-0.
- [30] A. Hagen, F. Roessner, *Catal. Rev. - Sci. Eng.* 42 (2000) 403–437. doi:10.1081/CR-100101952.

Table 1. Distribution of weak and strong acidic sites as determined by NH₃-TPD.

Catalyst	Weak acid sites ^a (mmol/g)	Strong acid sites ^b (mmol/g)	Total acid Sites (mmol/g)
C-ZSM-5	0.040	0.069	0.109
D-ZSM-5	0.039	0.081	0.120
M-ZSM-5	0.052	0.104	0.156
R-ZSM-5	0.040	0.086	0.126

^a Density of acid sites determined by NH₃-TPD for NH₃ desorbed at 180-280 °C, ^b Density of acid sites determined by NH₃-TPD for NH₃ desorbed at 280-550 °C.