Fe-HZSM5 Catalysts for Methane Upgrading

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Introduction
Benzene is one of the most important organic intermediates in the petrochemical industry. Currently, it is mainly produced from crude oil processing. However, the increasing price difference between oil and natural gas due to the availability of abundant shale gas has renewed interest in the development of a process for the direct conversion of methane to benzene. This can be achieved via methane dehydroaromatization (DHA) with reported methane conversions of up to ~10% XCH4 with 80% benzene selectivity at a typical reaction temperature of 700°C over bi-functional Mo/HZSM5 (catalysts)1. Over this catalyst, methane is activated on Mo sites (present in their active form as oxacarbide clusters) and the generated methyl radicals oligomerize on Bronsted acid site (BAS) of HZSM5 to form benzene (i.e. the high benzene selectivity is attributed to the shape selectivity of ZSM5 micropores)2. While the existing literature for DHA predominantly focuses on Mo/HZSM5 catalysts, the sensitivity of the Mo-oxycarbide species motivates the search for alternate metals, which can efficiently activate methane for the following oligomerization.

Iron is an attractive candidate due to low cost and low toxicity. Recent work by Bao3 and coworkers confirmed that the well-established potential of Fe as a C-C coupling catalyst, but also demonstrated the propensity of Fe to result in extensive coke formation. Intriguingly, however, they demonstrated that atomically dispersed Fe results in the formation of methyl radicals without coke formation, which then underwent C-C coupling in the gas phase at the high temperatures of their reaction conditions. Based on this, we hypothesize that highly dispersed Fe in HZSM5 catalyst should result in a selective Fe-HZSM5 catalyst for methane DHA. In this work, we hence used three different synthesis approaches to prepare Fe-HZSM5 with different Fe dispersion and demonstrate the correlation between dispersion and benzene yield.

Materials and Methods
Three synthesis approaches were employed to prepare Fe-HZSM5 catalysts. The first one (”Fe@HZSM5”) was prepared by using size controlled Fe nanoparticles embedded in a silica matrix (prepared via a reverse-micromulsion mediated sol-gel process as precursor for a hydrothermal conversion to Fe@HZSM5). The second synthesis path (”H-(Fe)ZSM5”) followed an isomorphous substitution route, by using Fe(NO3)3 mixed with Tetraethoxysilane as the precursor mixture for the hydrothermal synthesis. The third route (”Fe/HZSM5”) is a conventional wet-chemical ion exchange where pre-synthesized HZSM5 was ion exchanged with Fe(NO3)3 aqueous solution at 80°C for 6h. All prepared catalysts were washed, dried and calcined to 500°C for 4-6hr, and then characterized via XRD, TEM, SEM, EDX and UV-vis spectroscopy. Activity for DHA evaluated in a fixed bed reactor with a 50vol% CH4 in He feed at a GHSV 3750 h⁻¹. Product gases were analyzed via GC and MS.

Results and Discussion
As expected, the three different synthesis routes resulted in different Fe dispersions in HZSM5. For Fe@HZSM5, only 3-5 nm iron oxide particles present, both embedded within and between HZSM5 crystals. In contrast, the isomorphous substitution route results in highly dispersed iron species in the zeolite micropores, while the wet ion exchange catalyst contains both highly dispersed Fe in micropores and nanoparticles on the external surface.

The catalytic performance of these catalysts is shown in Figure 1a and 1b. Fe@HZSM5 shows a higher initial activity, but rapid deactivation and poor benzene yield (with predominantly C2 products). In contrast, Fe/HZSM5 and H-(Fe)ZSM5 show lower, but sustained activity and much improved benzene yields. Increasing the reaction temperature to 900°C, both conversion and benzene yield are strongly improved over the latter two catalysts, with higher benzene yield (Figure 1c) for the H-(Fe)ZSM5 catalysts. Overall, increased Fe dispersion hence correlates directly with benzene yield for these catalysts, confirming our initial hypothesis that highly dispersion iron species allow the formation of methyl radicals, which then oligomerized on the BAS of the zeolite to form benzene. Our current efforts concentrate on a further improvement of the Fe dispersion towards monatomic dispersion.

Significance
Our results confirm that Fe-ZSM5 catalysts are promising, inexpensive catalysts for methane dehydroaromatization, and that selectivity of this catalyst for DHA is strongly determined by the Fe dispersion. This suggests that further improvement towards true monatomic dispersion of the catalyst should yield further increase in benzene yield.

![Figure 1. Reactivity data for the three Fe-HZSM5 catalysts: Methane conversion (a) and benzene yield (b) at 700°C for H-(Fe)ZSM5 (blue), Fe@HZSM5 (green) and Fe/HZSM5 (red); (c) benzene yield for H-(Fe)ZSM5 (blue) and Fe/HZSM5 (red) at 900°C.](image)

References