

# Catalytic Conversion of Methane into Aromatic Hydrocarbons over Iron Oxide Loaded ZSM-5 Zeolites\*\*

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The catalytic conversion of methane to desirable commodity chemicals is a challenging approach to the utilization of natural gas resources; consequently, considerable effort has been devoted to the development of novel catalytic systems. Oxygen has generally been used to activate the methane, even at the expense of losing some of the feedstock as carbon dioxide. The most extensively studied processes are oxidative coupling of methane,<sup>[1, 2]</sup> partial oxidation of methane to synthesis gas,<sup>[3]</sup> and the formation of such oxygenated compounds as methanol.<sup>[4]</sup> Recent studies have demonstrated that methane can be selectively converted into benzene over Mo/H-ZSM-5 catalysts in the absence of an oxidant such as O<sub>2</sub>.<sup>[5–10]</sup>

We report here on a stable and selective bifunctional catalyst for the conversion of methane into aromatic hydrocarbons such as benzene, toluene, and naphthalene in the absence of an oxidant. The catalyst consists of iron oxides dispersed on the surface of an acidic ZSM-5 zeolite. Methane activation occurs on supported iron oxide clusters, and the primary product, ethylene, undergoes subsequent oligomerization and cyclization reactions at Brønsted-acidic sites to form the aromatic products. The Fe/H-ZSM-5 catalyst is typically prepared by incipient wetness impregnation through addition of an aqueous iron(III) nitrate solution to the H-ZSM-5 zeolite, followed by drying at 90 °C and calcination in oxygen at 500 °C. The resulting orange material is characterized by a broad electron paramagnetic resonance (EPR) signal with a *g*-value of 2.47 and a peak-to-peak width (ppw) of 1515 G (Figure 1 A). The signal broadens upon

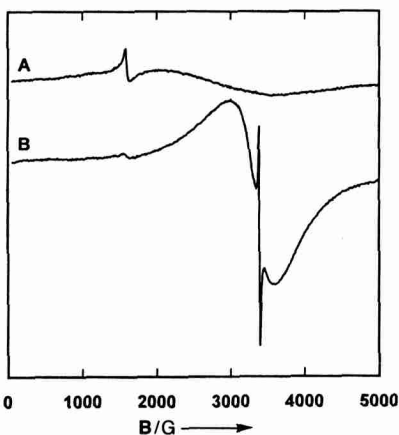


Figure 1. EPR spectra of A) a 0.6 wt% Fe/H-ZSM-5 catalyst calcined at 500 °C for 1 h, and B) an active 0.6 wt% Fe/H-ZSM-5 catalyst prereduced in CO and treated for 1 h in methane at 700 °C. The spectra were measured at 120 K, and the signal at *g* = 4.3 is due to distorted tetrahedral Fe<sup>3+</sup> ions from the parent H-ZSM-5 material[12].

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cooling and does not follow the Curie–Weiss law. Such behavior is typical for  $\text{Fe}_2\text{O}_3$  clusters.<sup>[11, 12]</sup> The presence of iron(III) was further confirmed by X-ray photoelectron spectroscopy (XPS). The corresponding  $2p_{3/2}$  and  $2p_{1/2}$  binding energies (BE) of iron(III) were obtained at 710.7 eV and 724.5 eV, respectively. The spin-orbital splitting was 13.8 eV, and an accompanying weak  $3d \rightarrow 4s$  shake-up satellite peak was detected at 718.7 eV, all typical for iron(III).<sup>[13]</sup>

The calcined material was first reduced with CO at 500 °C for 6 h, heated to 700 °C in He, and then subjected to a continuous methane flow at 700 °C. Conversion and product formation were monitored by on-line gas chromatography. As an example, we will discuss the catalytic performance of a 2 wt% Fe/H-ZSM-5 catalyst in some detail (Figure 2). Similar results were

obtained for the initial activation period, but then declined slowly with increasing time on stream. For toluene, a maximum selectivity of 3% was observed. Thus, after a sufficiently long reaction time, mainly benzene was produced, along with some toluene and naphthalene, and the maximum selectivity toward aromatic hydrocarbons exceeded 85%. On the other hand, selectivity toward  $\text{C}_2$  and  $\text{C}_3$  hydrocarbons (mainly ethylene) increased continuously with increasing reaction time, as coke deposition gradually deactivated acidic sites in the zeolite where the ethylene undergoes secondary reaction. It is also remarkable that a stable conversion of 4% could be sustained even after 16 h on stream. The catalyst could be regenerated by heating the material in  $\text{O}_2$  at 500 °C for 8 h; however, the resulting maximum methane conversion was only 3.5% at a benzene selectivity of 65%.

The black active catalyst had the typical EPR spectrum shown in Figure 1 B. Besides the sharp isotropic signal at  $g \approx 2$  with  $\text{ppw} = 11.5$  G, a broad EPR signal was observed with  $g = 2.06$  and  $\text{ppw} = 600$  G. The former signal followed the Curie–Weiss law, indicating the presence of organic radicals; that is, the formation of coke. This signal gradually increased in intensity during the course of reaction. The other EPR signal, centered at  $g \approx 2.06$ , broadened upon cooling and did not follow the Curie–Weiss law.<sup>[14]</sup> The nature of the species responsible for this signal was further analyzed by XPS. After passing methane gas over the catalyst, the Fe  $2p_{3/2}$  and  $2p_{1/2}$  BE values were determined to be 710.5 eV and 724.4 eV, respectively, and no other peaks were observed. In addition, no weak  $3d \rightarrow 4s$  shake-up satellite peak was detected at 718.7 eV. Thus, upon methane activation, the catalyst is partially reduced from  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ .<sup>[13]</sup> Furthermore, the C 1s signal at 283.5 eV increased in intensity. This was due to coke formation during methane activation. Such coke may explain the decrease in selectivity toward aromatics.

By changing the CO prereduction time and temperature we were able to change the extent of the EPR-active Fe clusters. This resulted in materials with different catalytic activities, as shown in Figure 3. It is clear that an almost linear relationship exists between the level of EPR-active Fe clusters and methane-conversion activity of the catalyst at maximum benzene selectivity. This in turn suggests that such clusters may be involved in the activation of methane.

The primary products of methane activation, mainly ethylene, undergo further reaction at zeolitic acidic sites, result-

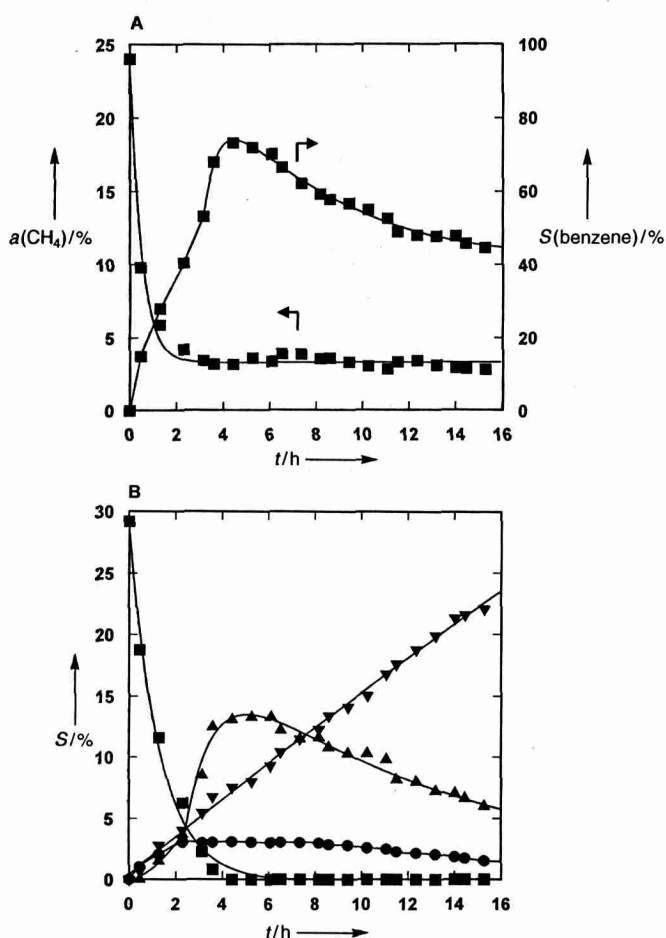


Figure 2. The catalytic performance of a Fe/H-ZSM-5 catalyst with 2 wt% iron: A) overall conversion  $a(\text{CH}_4)$  [%] and benzene selectivity  $S(\text{benzene})$  [%], and B) selectivities  $S$  [%] toward CO (■), naphthalene (▲), toluene (●) and  $\text{C}_2$ – $\text{C}_3$  hydrocarbons (▼).

obtained for a 0.6 wt% Fe/H-ZSM-5 material. After an initial activation period of 4 h, a benzene selectivity of 74% was reached at a methane conversion of about 4%. During the first half-hour on stream, virtually no hydrocarbon products were formed, and the major gas-phase products were CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . Because the catalyst was pretreated in He at high temperature before initiating the reaction, the only oxygen source for formation of oxygen-containing products is lattice oxygen from the catalyst. In addition to benzene, toluene and naphthalene were also formed, but with much lower selectivities. Naphthalene selectivity reached a value of 13% immediately follow-

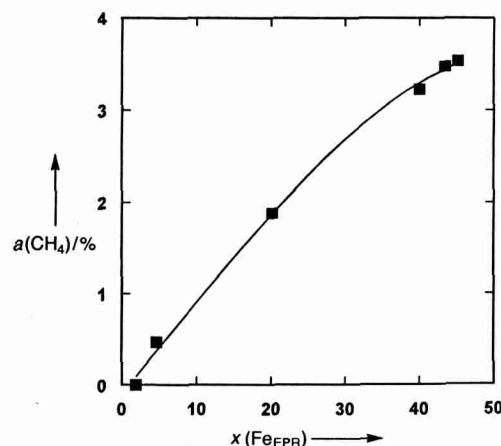


Figure 3. Methane activation behavior of Fe/H-ZSM-5 catalysts as a function of the extent of EPR-active Fe clusters,  $x(\text{FeEPR})$  (in arbitrary units). The extent of such Fe clusters was determined by double integration of the recorded EPR spectra and subtraction of the contribution from a sharp isotropic signal at  $g \approx 2$ . Methane conversions refer to conversions at maximum benzene selectivity.

ing in the formation of benzene, toluene, and naphthalene. The occurrence of such oligomerization and cyclization reactions has been demonstrated by partially and even fully exchanging the Brønsted acid sites of the starting H-ZSM-5 material with  $\text{Na}^+$  ions. Treatment in this way resulted in a gradual decrease in the number of Brønsted acid sites, as evidenced by FT-IR spectroscopy, as well as a decrease in catalytic activity and selectivity of the catalyst. Thus, Brønsted acid sites play a crucial role in the catalytic performance of these materials. In another experiment we prepared solid-state, ion-exchanged Fe/H-ZSM-5 zeolites by using  $\text{Fe}^{\text{III}}\text{Cl}_3$ . The freshly prepared materials were totally inactive for methane activation. Only after CO treatment at relatively high temperatures was some activity detected. However, such materials were always catalytically inferior to those prepared by impregnation, and no naphthalene could be detected.

In conclusion, we have found that iron oxides supported on H-ZSM-5 zeolites are able to convert methane into aromatic hydrocarbons with a selectivity greater than 85%. The activity is based on a unique balance between formation of iron clusters on the surface of the zeolite and the presence of a sufficient number of Brønsted acid sites. It is also worth mentioning here that unsupported iron oxides are used industrially for the dehydrogenation of ethylbenzene to styrene under conditions similar to those applied in this study.<sup>[15]</sup> The XPS results confirm that neither metallic iron nor iron carbides are formed on this catalyst, which is significant in view of the fact that similar activation of  $\text{CH}_4$  over an Mo/H-ZSM-5 catalyst has been proposed to involve  $\text{Mo}_2\text{C}$ , the presence of which was confirmed by XPS.<sup>[9, 10]</sup> Recently, Marczewski et al. have shown that methane can be converted into aromatics under nonoxidative conditions in a two-stage catalytic system.<sup>[16]</sup> Methane was converted into ethylene over a Mn/Na/SiO<sub>2</sub> catalyst (10% Mn, 3.4% Na) at 800 °C. The initially formed ethylene was then further converted into benzene and toluene over an H-ZSM-5 catalyst at 600 °C. Further studies on the mechanism of methane activation in the absence of oxygen, and extension to other transition metal oxides such as  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{WO}_3$  are in progress and should increase our understanding of these novel catalytic materials.

### Experimental Section

Fe/H-ZSM-5 catalysts were prepared by impregnation with an aqueous solution of iron (III) nitrate onto commercial PQ Corp. H-ZSM-5 (CBU 5020 E, with a Si/Al ratio of 25/1). The resulting materials were dried at 90 °C overnight (14 h) and calcined at 500 °C for 5 h. Reactions were carried out in a flow system, in reactors constructed from alumina tubes. The flow reactor had an internal diameter of 6.4 mm, and the amount of catalyst used was 1.0 g. To minimize contributions from possible gas-phase reactions, quartz chips filled the space above and below the catalyst beds in the flow reactors. A thermocouple in a smaller alumina tube was attached to the outside wall of each of the reactors. The gases, which included 10%  $\text{N}_2/\text{CH}_4$  (UHP),  $\text{O}_2$  (UHP), He (UHP), and CO (UHP) were obtained from Matheson and used without further purification. Gas flows were regulated by mass flow controllers (MKS Model 1159 A). In the flow system the catalyst was heated in a 50 mL min<sup>-1</sup> flow of  $\text{O}_2$  to 500 °C, calcined for 1 h, and flushed in a 50 mL min<sup>-1</sup> flow of He for 30 min. Reduction treatments were carried out at 500 or 700 °C for several hours in a 25 mL min<sup>-1</sup> flow of CO. The total GHSV (gas hour space velocity) during methane conversion was 800 h<sup>-1</sup>. The gas feed consisted of  $\text{CH}_4$  that contained 10%  $\text{N}_2$ . The  $\text{N}_2$  was used as an internal standard so that  $\text{CH}_4$  conversion could be determined accurately. Coke formation during the reaction could be evaluated from a carbon mass balance. The mass balance indicated that about 5–10% of the  $\text{CH}_4$  was converted into coke during methane activation. Reaction mixtures were analyzed by on-line gas chromatography (HP 5890 A) using a 5% Bentone-34 on Chromosorb W-AW column and a HayeSepD column. All studies were carried out at atmospheric pressure. FT-IR spectra were obtained on a Perkin Elmer 2000 FT-IR spectrometer. Self-supporting wafers of 10–15 mg cm<sup>-2</sup> were pressed from the powdered catalysts. Wafers were mounted on a fused-quartz bracket placed in an IR cell. The cell was equipped with KBr windows and a heated region into which the wafer could be raised and pretreated. For EPR spectroscopy, a Bruker ESP 300 spectrometer at X-band (ca. 9.5 GHz) was used. EPR spectra of the active catalysts were obtained with a specially designed quartz

reactor tube with a side-arm for EPR measurements. XPS spectra were acquired on a Perkin Elmer (PHI) model 5500 spectrometer. A quartz reactor system with in situ transfer capability made it possible to duplicate the conditions present in the catalytic reaction experiments.

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- [1] J. H. Lunsford, *Angew. Chem.* **1995**, *107*, 1059; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 970.
- [2] J. H. Lunsford, *Stud. Surf. Sci. Catal.* **1993**, *75*, 103.
- [3] S. C. Tsang, J. B. Claridge, M. L. H. Green, *Catal. Today* **1995**, *23*, 3.
- [4] M. Faraldos, M. Banares, J. A. Anderson, H. Hu, I. E. Wachs, J. L. G. Fierro, *J. Catal.* **1996**, *160*, 214; O. V. Krylov, *Catal. Today* **1993**, *18*, 209; N. D. Parkyn, C. I. Warburton, J. D. Wilson, *ibid.* **1993**, *18*, 385.
- [5] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu, *Catal. Lett.* **1993**, *21*, 25.
- [6] Y. Xu, S. Liu, L. Wang, M. Xie, X. Guo, *Catal. Lett.* **1995**, *30*, 135.
- [7] F. Solymosi, A. Erdohelyi, A. Szöke, *Catal. Lett.* **1995**, *32*, 43.
- [8] F. Solymosi, A. Szöke, J. Csere'nyi, *Catal. Lett.* **1996**, *39*, 157.
- [9] D. Wang, J. H. Lunsford, M. P. Rosynek, *Top. Catal.* **1996**, *3*, 289.
- [10] F. Solymosi, J. Csere'nyi, A. Szöke, T. Ba'nsa'gi, A. Oszko', *J. Catal.* **1997**, *165*, 150.
- [11] F. E. Mabbs, D. Collison, *Electron Paramagnetic Resonance of d Transition Metal Compounds*, Elsevier, Amsterdam, **1992**.
- [12] D. Goldfarb, M. Bernardo, K. G. Strohmaier, D. E. W. Vaughan, H. Thomann, *J. Am. Chem. Soc.* **1994**, *116*, 6344; B. D. McNicol, G. T. Pott, *J. Catal.* **1972**, *25*, 223; E. G. Derouane, M. Mestdagh, L. Vielvoe, *J. Catal.* **1974**, *33*, 169; P. Ratnasami, R. Kumar, *Catal. Today* **1991**, *9*, 328.
- [13] *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy* (Eds.: D. Briggs, M. P. Seah), Wiley, New York, **1983**; C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenburg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin Elmer, Eden Prairie, MN, **1979**.
- [14] Temperature-dependence EPR spectroscopy shows that the  $g = 2.06$  and  $g = 4.3$  signals correspond to different iron species. In addition, the two EPR signals respond differently toward different microwave powers, and the  $g = 2.06$  signal saturates more readily at liquid  $\text{N}_2$  temperature than the  $g = 4.3$  signal. The behavior of the  $g = 2.06$  signal must be due to cooperative magnetic phenomena (e.g., ferro-anti-ferromagnetism and dipole–dipole interaction).
- [15] E. H. Lee, *Catal. Rev.* **1973**, *8*, 285.
- [16] M. Marczewski, H. Marczewska, K. Mazowiecka, *React. Kinet. Catal. Lett.* **1995**, *54*, 81.

## Carbene Complex Modified Glycols: Synthesis and Reactivity\*\*

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Electrophilic carbene complexes are versatile reagents in stereoselective synthesis. They are applied in metal- and ligand-centered cycloaddition reactions<sup>[1]</sup> such as [3 + 2]benzannulation with alkynes<sup>[1a, b]</sup> and cyclopropanation,<sup>[1c, d]</sup> serve as precursors of photochemically generated ketene equivalents,<sup>[1e]</sup> and can be deprotonated to give organometallic analogues of enolates that are of interest in aldol and Michael addition reactions.<sup>[1f, g]</sup> The synthetic potential of organometallic compounds has been exploited only in rare occasions in carbohydrate chemistry. So far, reagents for the umpolung of the

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