A Radical Twist to the Versatile Behavior of Iron in Selective Methane Activation**

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The availability of large reserves of methane, which is the main component of most natural gas, makes it a very important feedstock molecule for the production of base chemicals (e.g., ethylene, propylene, and aromatics) and energy carriers (e.g., transportation fuels). More recently, the shale gas bonanza—particularly in the USA—as well as the presence of vast amounts of gas methane hydrates at several places on earth, has further spurred great interest to develop economically viable, large-scale routes for the selective activation of methane.

Current commercial routes for methane activation involve the conversion of methane into syngas, which is a mixture of CO and H₂, and its subsequent conversion into hydrocarbons such as propylene, aromatics, and fuels.[1–3] More specifically, methanol-to-hydrocarbon (MTH) catalysis involves the catalytic conversion of syngas-derived methanol (or dimethyl ether) into mixtures of, for example, ethylene, propylene, and aromatics, depending on the specific zeolite material and reaction conditions applied. On the other hand, one can make use of the syngas produced from methane and convert it with either iron- or cobalt-based Fischer–Tropsch synthesis (FTS) catalysts into, for example, waxes, which can then be back-cracked into chemicals and transportation fuels, such as diesel, with zeolite-based catalysts. Unfortunately, both syngas conversion routes are complex multistep catalytic operations, which are energy intensive, due to, for example, the syngas generation, costly in terms of the different reaction and separation steps involved, and far from optimal in terms of atom efficiency.

In view of these inherent disadvantages, researchers both in academia and industry are searching for more cost- and resource-effective routes for the direct utilization of methane. An example of such an approach is the oxidative coupling of methane (OCM), generating methyl radicals in the gas phase which then recombine to ethylene.[4,5] Unfortunately, the currently developed OCM catalyst materials and related reactor (membrane) designs do not provide the required performance, both in terms of activity and more importantly selectivity (e.g., CO₂ generation and formation of coke deposits). However, in recent announcements, companies like Siluria and UOP report on the (pre)-commercialization of methane coupling routes to ethylene.[6]

In a recent study, Guo and co-workers reported on a new catalyst material, which could circumvent the disadvantages of, for example, OCM technology.[7] It was found that the novel catalyst, consisting of lattice-confined single iron sites (Figure 1), produces in a nonoxidative manner high yields of ethylene, benzene, and naphthalene. Very remarkable is the negligible amount of coke deposits formed at the relatively high operational temperature of 1363 K, which results in an

Figure 1. Structural motif of the designed 0.5 wt % Fe@SiO₂ catalyst material, active in the selective activation of methane and producing ethylene, benzene, and naphthalene without the substantial formation of coke deposits at high reaction temperatures.
The active site in this catalyst material is proposed to consist of a single iron atom, coordinated to one silicon and two carbon atoms (Figure 1). This conclusion has been derived from extended X-ray absorption fine structure (EXAFS) studies, complemented with high-angle dark field (HAADF) scanning transmission electron microscopy (STEM) measurements. The active site can therefore be regarded as a local mixed iron silicide carbide phase (Fe_xSi_yC_z with x = 1, y = 1, and z = 2) with an iron atom in a trigonal environment embedded within a seemingly very inert, porous SiO_2 matrix. As there is a vast amount of literature in the areas of for example, metallurgy, mineralogy, and materials electronics, further characterization studies will have to clarify the precise nature of this peculiar active center. This is possible by using additional methods, such as Mössbauer spectroscopy (MS), Auger electron spectroscopy (AES), and electron energy loss spectroscopy (EELS) (preferably in combination with TEM), although each of these methods, as well as the originally reported EXAFS measurements, will require a set of well-defined iron silicide and iron carbide reference compounds for proper spectral analysis.

In this context it is important to mention the unique synthesis method employed for making the low-surface-area catalyst material containing lattice-confined single iron sites, which is referred to the 0.5 wt% Fe@SiO_2 catalyst. A ferrous metasilicate (Fe_2SiO_4, better known as fayalite, is fused with SiO_2 at very high temperatures (1973 K) in air, and the resulting material is ball-milled and treated with aqueous HNO_3. The discovered 0.5 wt% Fe@SiO_2 catalyst clearly outperforms the more classically prepared high-surface-area Fe/SiO_2 and Fe/ZSM-5 catalysts, especially in terms of coke deposit formation. As these classically prepared iron-based catalysts do not possess—at least not to the same extent—their iron sites with the peculiar coordination environment, the new catalyst indeed illustrates the requirement of suppressing the formation of adjacent (multiatom) iron sites, which typically catalyze the unwanted C-C coupling that ultimately leads to coke deposit formation.

This brings us to the reaction pathway followed by this unique 0.5 wt% Fe@SiO_2 catalyst. Guo et al. performed density functional theory (DFT) calculations, backed by vacuum ultraviolet soft photoionization molecular-beam mass spectrometry (VUV-SP1-MBMS) measurements to determine the presence of methyl radicals in the gas phase above the catalytic surface. The overall reaction mechanism is outlined in Figure 2. The methane activation process starts with the generation of methyl radicals on the isolated iron site, as is the case for OCM chemistry. Two of these methyl radicals then combine in the gas phase to form ethane, which is, however, not observed in the gas phase. Instead, ethane is readily dehydrogenated to ethylene under the applied conditions. This ethylene then may undergo hydrogen abstraction with the formation of an C_2H_5 radical. These radicals can then react with other ethylene molecules and after subsequent dehydrogenation and cyclization benzene is formed. Benzene in itself can also undergo dehydrogenation and further chain growth and cyclization leads to the formation of naphthalene. In contrast to OCM chemistry, ROO radicals are avoided, which significantly reduces unwanted peroxide routes that typically lead to large amounts of oxygenates and/or CO_2. In other words, the main gas-phase products are ethylene, benzene, naphthalene, and hydrogen.

Remarkably, the chemistry reported by Guo et al. closely resembles some of the chemistry in the commercial benchmark for ethylene production—the steam cracking of hydrocarbons (e.g. naphtha). In essence, this conventional technology also comprises radical chemistry in which hydrocarbon fragments, including ethylene, benzene, and naphthalene, are formed at high temperature (1073–1123 K), albeit the process is much less selective due to the intrinsic nature of the feedstock (complex mixtures). In steam cracking, significant amounts of coke deposits are formed on the wall of the cracking coils. The unique feature of the catalytic route reported by Guo et al. is that it starts with cheap methane feedstock and that several of the regular radical pathways appear to be blocked.

The biggest mystery of the catalytic chemistry described by Guo et al. is the (almost) complete absence of the unwanted formation of coke deposits. This is a very encouraging result in the ongoing quest to develop selective routes for the direct utilization of methane. In addition, improvements of the relative yields of ethylene, benzene, and naphthalene are required to make this novel catalytic cracking route attractive for implementation in the petrochemical industry. Just as important for the further development of this technology is the long-term stability of the catalyst system as the current investigations are limited to run times up to 60 h. Future research will show whether the reported high-selectivity yields of ethylene and aromatics can be maintained with this special catalyst formulation for extended run times under these relatively harsh reaction conditions.

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[1] J. H. Lunsford, Catal. Today 2000, 63, 165.
[2] N. O. Elbashir, C. Mirodatos, A. Holmen, D. B. Bukur, *Catal. Today* **2014**, *228*, 1.

[3] H. Torres Galvis, K. P. de Jong, *ACS Catal.* **2013**, *3*, 2130.

[4] G. E. Keller, M. M. Bhasin, *J. Catal.* **1982**, *73*, 9.

[5] J. H. Lunsford, *Angew. Chem.* **1995**, *107*, 1059; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 970.

[6] E.g., D. Ramesh, *Chemical Week*, June 2 **2014**; T. Black, *Bloomberg*, April 25 **2012**.

[7] X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng, M. Wie, D. Tan, R. Si, S. Zhang, J. Li, L. Sun, Z. Tang, X. Pan, X. Bao, *Science* **2014**, *344*, 616.

[8] M. K. Kolel-Veetil, T. M. Keller, *Materials* **2010**, *3*, 1049.