Enhanced methane conversion to olefins and aromatics by H-donor molecules under non-oxidative condition

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ABSTRACT: We report that methane activation to olefins and aromatics over iron coated

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catalytic quartz reactor can be enhanced by hydrogen radicals, which are provided by the thermal decomposition of hydrogen-donor molecules, such as 1,2,3,4-tetrahydronaphthalene (THN) and benzene. Methane conversion increases from 17.5 % to 25.5% in the presence of 1.41 % THN in methane at 1323 K. The onset temperature of C_2H_4 formation decreases from 1143 to 1073 K by adding 7.7% C_6H_6 into methane feed. Isotope experiments confirm the involvement of H radicals in the reaction, which activate methane homogeneously according to the reaction: $H + CH_4 \rightarrow H_2 + CH_3$, besides the heterogeneous activation over iron sites.

KEYWORDS. Non-oxidative methane conversion, iron catalysts, catalytic reactor, H radicals, homogeneous methane activation

Direct conversion of methane into high value-added fuels and chemicals, such as light olefins and aromatics, is an attractive process which could play an important role in the landscape of chemical industry.[1] Significant progress has been made in the development of several catalytic processes, such as oxidative coupling of methane (OCM),[2-3] methane dehydroaromatization (MDA),[4-9] and the recently developed process of methane to olefins, aromatics and hydrogen (denoted as MTOAH).[1, 10] It was shown that the MTOAH process likely involves methane activation over single Fe atoms embedded in the SiO_2 lattice (Fe©SiO_2) forming methyl radicals, which subsequently go through gas phase reaction forming ethylene, benzene and naphthalene under non-oxidative conditions. Despite the further development of the MTOAH processes,[11-13] methane activation under non-oxidative conditions remains challenging due to the high reaction temperature and thermodynamic as well as kinetic limitations.[10] Therefore, new strategies to enhance methane activation are crucial in order to improve the overall efficiency of the MTOAH

reaction.

In the MTOAH reaction, alongside heterogeneous catalytic activation over Fe©SiO$_2$ active site, homogeneous methane activation occurs either via unimolecular dissociation reactions[14] (CH$_4$ (+M) → H+ CH$_3$ (+M)) or via free radical hydrogen abstraction[15] (R + CH$_4$ → RH + CH$_3$). Independently from the activation pathway, the involvement of methyl radicals in the OCM and MTOAH reactions was previously confirmed experimentally.[10,16-17] Besides methyl radicals, DFT calculations also suggested that the H radicals may also play an important role in the selective reaction pathway of the MTOAH reaction.[10] However, no experimental evidence was reported and their role in the reaction is not clear due to the expected relatively low concentration of H radicals, its high reactivity and therefore short lifetime under the MTOAH reaction conditions. The homogeneous hydrogen abstraction from methane by H radicals according to reaction (1) has been studied theoretically[16, 18-20] and experimentally,[21-23] however reaction (1) was studied so far only as a single event and not as part of a catalytic reaction network such as MTOAH.

$$H + CH_4 \rightarrow H_2 + CH_3 \tag{1}$$

Reaction (1) exhibits a moderate activation energy between 56-62 kJ/mol, an enthalpy of reaction ($\Delta_r H$) of 4.2 kJ/mol and a Gibbs free energy of reaction ($\Delta_r G$) of -31.8 kJ/mol at 1223 K.[21-22, 24] The homogeneous activation of methane according to reaction (1) is therefore energetically more favorable than the heterogeneous activation of methane in the MTOAH reaction over Fe©SiO$_2$[10] (theoretical predicted Ea = 279.8 kJ/mol) or unimolecular methane dissociation (Ea = 380-434 kJ/mol).[14] Thus, it is of interest to investigate if methane conversion can be enhanced by addition of H radicals into the reaction system and the effect of radicals on

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the selective pathway to olefins and aromatics.

Experimental kinetic studies of reaction (1) used either photolysis of NH_3[21] and HI[23] or microwave discharge of H_2[24] molecules to produce H radicals in the gas feed. However, each of these methods presents drawbacks when used in a catalytic process with complex gas mixture such as in the MTOAH. Thus in order to understand the role of the H radicals in MTOAH without external interference, we introduced hydrocarbon H-donor molecules into the reaction feed, such as 1,2,3,4-tetrahydronaphthalene (THN) or benzene, which produce H radicals upon their thermal decomposition (Scheme S1).[25-29] Thereby, the concentration of H radicals produced in the gas feed was determined from the concentration of molecular hydrogen evolved during the thermal decomposition of hydrogen-donor compounds in an inert feed assuming a homolytic splitting of the C-H bond. THN, which is a bicyclic aromatic compound with four labile hydrogen atoms, has been successfully used in coal liquefaction as an atomic hydrogen donor.[30-32] Thermal decomposition of THN in inert gas at 1223 K is described in the supporting information (SI). Naphthalene and H_2 were detected as the main products by gas chromatography (GC) and nuclear magnetic resonance (NMR) (Figure S1 and S2), accompanied with a small amount of benzene, polymethylated benzens and methane (Figure S4a). We estimate the formation rate of H radicals based on that of H_2. For example, at 1.4 vol.% THN in N_2 atmosphere, the H_2 formation rate is 0.07 μmol/s, corresponding to 0.14 μmol/s for H radicals at 1223 K (Figure S3). Note that THN is completely decomposed at 1223 K in CH_4 or Ar (Figure S4), meaning that the rates of H radicals formation measured in Ar are the same during the MTOAH reaction. At lower temperature, the estimated rate of THN thermal decomposition in CH_4 or Ar are also similar.

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In this study, an iron wall-coated quartz reactor (denoted as Fe-reactor) with inner diameter of 14 mm and effective length of 100 mm (see SI) was prepared by chemical vapor deposition. A wall-coated reactor was chosen over a fixed-bed reactor in order to increase the empty volume, which allowed homogeneous reaction to develop and reduce mass and heat transfer limitation.[33-34] All experiments were performed at atmospheric pressure. N_2 was used as internal standard for the gas analysis with a ratio CH_4/N_2=9/1. Methane conversion, product selectivity and coke formation are calculated following a previously reported method.[35] Activity of several Fe-reactors prepared with the same conditions show a good reproducibility in the MTOAH reaction (Figure S5). The concentration of iron in quartz at the surface (with a depth of measurement up to 38 μm calculated by using SRIM software package[36]) of the Fe-reactor, determined by Particle Induced X-ray Emission (see SI), was between 0.17 and 0.30 wt% (Figure S6). For comparison, the surface of the blank reactor shows only 3.6 ppm iron.

The nature of the Fe-reactor surface was characterized *post mortem* with XANES and UV-Vis spectroscopy after oxidation at 1023 K in order to remove the small quantity of coke formed during the reaction. Under those conditions, the surface exhibits mainly both isolated FeO_x and lager FeO_x clusters in Fe-reactor (Figure S7-S8 and SI).[37-38] As also shown in Figure S8, upon on methane activation at 1273 K and 90 ml/min for 30 min, the isolated FeO_x becomes evident, although signals assigned to lager FeO_x clusters remain. This work focuses mainly on the effect of radicals in the gas phase homogeneous reactivity and a more detailed study of the catalytic surface is in preparation and should be published in a follow-up work.

Figure 1a shows that methane conversion increases from 1.2 % over a blank reactor to 7.8 % over the catalytic Fe-reactor at 1273 K, which emphasizes the importance of catalytic activation

of methane in the MTOAH reaction. Upon addition of 1.41 vol.% THN in the methane feed over Fe-reactor at 1273 K, methane conversion is almost doubled from 7.8 % to 15.6 %, i.e. an enhancement of about 7.8%. Interestingly, methane conversion over the blank reactor is also enhanced by about 7.5% when the same amount of THN is added at 1273 K. The enhancement by a similar factor over the Fe-reactor and the blank reactor under the same conditions suggests that the contribution of THN is likely related with the gas phase reactions. Figure 1a shows that the selectivity toward ethylene was 22.7% vs. 26.0% with and without THN, respectively, while the selectivity toward benzene was 26.3% and 31.7% with and without THN, respectively. It indicates that the presence of THN slightly reduced the selectivity toward light products such as ethylene and benzene. Even at methane iso-conversion, the difference of the ethylene selectivity lies within a few points for these two cases (Figure S9). The slight changes on the selectivity and the obvious promotion on the methane conversion demonstrate that the THN mainly takes part in the homogeneous methane activation, acting as the initial step to activate methane forming methyl radicals, without affecting significantly the subsequent reaction pathway.

Figure 1b displays that methane conversion as well as the product yields in the presence of THN are stable with time on stream at 1273 K. When THN is switched off, methane conversion drops to 7.8%, and the yields of C_2H_4 and C_6H_6 decrease to 2.0% and 2.5%, respectively. When THN is switched on, methane conversion jumps up to 15.5% while the yields of C_2H_4 and C_6H_6 increase to 3.5% and 4.1%. The periodic switch on and off for several cycles does not perturb the performance of methane conversion and no obvious degradation of the activity is observed. Furthermore, no deactivation of methane conversion and C_2H_4 selectivity was observed during a 40 h stability test at 1273 K and 85 ml/min in the presence of 0.5% THN (Figure S10). The

results indicate a stable reaction and also confirm the enhancing effects of the THN in methane conversion.

The influence of H radicals on the methane conversion in the MTOAH reaction depends on its concentration, which is controlled by varying the concentration of H-donor molecules. (Figure S11 and Figure 1c). The rate of methane conversion increases almost linearly with the rate of H radicals below 0.20 $\mu mol_H \cdot s^{-1}$ in the reaction feed (Figure 1c). Above this concentration of H radicals, the conversion of methane levels off to 0.60 $\mu mol_{CH4} \cdot s^{-1}$. The efficiency of H radicals in the MTOAH reaction is shown in Figure S12. At low concentration, the presence of H radicals in the reaction seems to induce an "autocatalyzed" phenomenon; *e.g.* at 0.05 $\mu mol_H \cdot s^{-1}$ one H radical can activate almost three methane molecules (Figure S8). At higher concentration of H radicals, the probability increases for two H radicals to recombine to H_2 instead of reacting with methane. Furthermore, H_2 is detrimental for the MTOAH reaction according to the Le Chatelier principle (Figure S13), and the efficiency of H radicals at higher concentration toward methane activation decreases. Similar suppression phenomenon by H_2 had been observed previously for the MDA,[39] MTOAH[13] and methane pyrolysis.[40-41] It is estimated that the homogeneous methane activation with H radicals contributes about 45% - 71% in addition to the heterogeneous activation over the iron catalyst (Figure S12).

The effect of H radicals in the MTOAH reaction was further investigated with benzene as H-donor molecules. The thermal decomposition of benzene in inert gas is resumed in SI and the formation of H_2 with a trace amount of polymethylated benzens is observed (Figure S14-S16), which is in agreement with previous report.[25-26] Figure 1c shows that the rate of CH_4 conversion as a function of the rate of H radicals formed from benzene decomposition (denoted as red

triangle) falls on the same line as that from THN decomposition. This result reveals that methane conversion is only a function of the H radicals concentration independently of the specific H-donor molecules; *i.e.* the properties of the counter hydrocarbon radicals generated from THN (*e.g.* dihydronaphthyl radicals) or from benzene (*e.g.* phenyl radicals) have no significant effect on the conversion of methane in the MTOAH reaction. This observation is further supported by the use of decahydronnaphthalene (DHN), dihydronaphthalene (HHN) and pyridine as H-donor molecules. For each of those molecules, the rate of methane conversion as function of the rate of H radicals falls again on the same line as that of THN and benzene, as shown in Figure 1c.
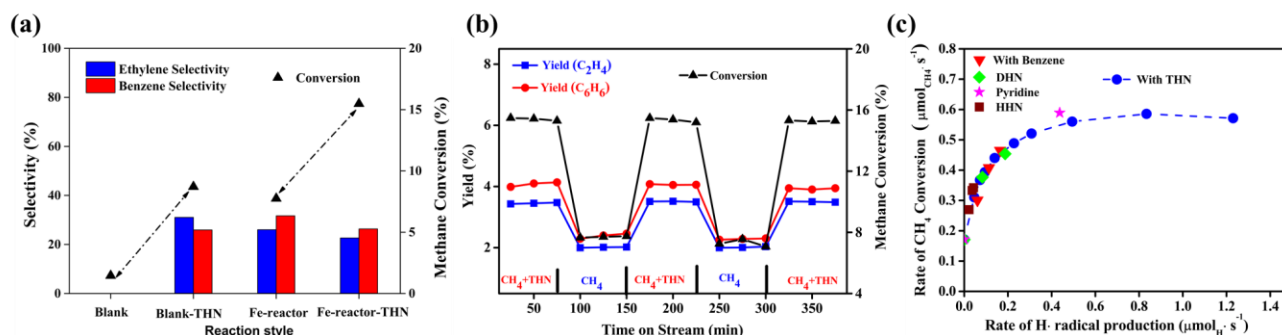

Figure 1. (a) Methane conversion (denoted by the black triangle), selectivity of ethylene and benzene over the Fe-reactor in comparison to that in a blank reactor in the presence and absence of THN. 1273 K, $CH_4/N_2 = 9/1$, F = 60 ml/min, 1.4% THN (if THN present in the feed). (b) Periodic switching on and off THN as a function of time on stream over Fe-reactor. 1273 K, $CH_4/N_2 = 9/1$, F = 60 ml/min, 1.4% THN (if THN present in the feed). (c) Rate of methane conversion as a function of the rate of H radical, which is controlled by varying content of different H-donor molecules, over Fe-reactor, $CH_4/N_2 = 9/1$, F = 30 ml/min, 1223 K.

Interestingly, the addition of H radicals also lowers the onset temperature of ethylene formation, as evidenced by temperature programmed reaction, which was performed over the catalytic Fe-

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reactor using TOF-MS photoionization to monitor the formation of ethylene with a high sensitivity and avoid fragmentation of higher hydrocarbons. In absence of any H-donor molecules, ethylene formation starts at 1143 K as shown in Figure 2a. However upon addition of 7.7 % benzene in the reaction feed, C_2H_4 is already observed at 1073 K (Figure 2b), *i.e.* the homogeneous activation of methane by H radicals lowers the onset reaction temperature for the methane conversion to ethylene by 70 K compared to the heterogeneously catalyzed MTOAH reaction over Fe-reactor. Note that a control experiment with the same concentration of benzene without methane under the same conditions does not yield ethylene (Figure S17). Thermodynamic considerations (Figure S18) show that reaction (1) could take place at room temperature ($\Delta_rG < 0$). However, a temperature as high as 1073 K is needed here, which could be attributed to the minimum temperature required for benzene decomposition and H radicals formation (Figure S19). By substituting benzene (C_6H_6) with C_6D_6, HD molecules are observed (Figure 2c) and their onset temperature (1073 K) is similar to the temperature needed for ethylene formation with C_6H_6 as shown in Figure 2b. The formation of HD molecules further supports the above assumption that the deuterium atoms decomposing from benzene (C_6D_6) participate in the activation of methane process similar to reaction (1), *i.e.* $D + CH_4 \rightarrow HD + CH_3$. The above results demonstrate that H radicals could initiate methane activation process homogeneously via reaction (1) at a lower temperature than the catalytic activation heterogeneously. The produced CH_3 radicals in reaction (1) likely go through gas phase reaction forming C_2 products as in the catalytic MTOAH process and hence the product distribution is also similar.
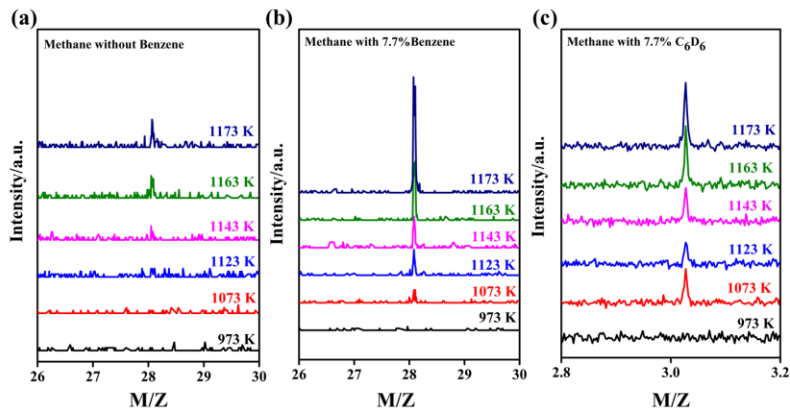
Figure 2. MTOAH over the Fe-reactor at different temperatures monitored by TOF-MS. (a) Ethylene formation in the absence of benzene (C_6H_6). (b) Ethylene formation in the presence of 7.7% benzene (C_6H_6). (c) HD formation in presence of 7.7% deuterated benzene (C_6D_6). Reaction Conditions: 1% He/ 99% CH_4, 20 ml/min.

Figure 3a shows that methane conversion increases with the reaction temperatures and flow rate over Fe-reactor, thereby the flow rate is increased with the temperature in order to avoid coke formation. Furthermore, the enhancement induced by the addition of THN appears to be rather constant in the temperature range of 1223 – 1323 K, i.e. methane conversion increases by about 6.0% in the presence 1.4% THN reaching 25.5% at 1323 K with the selectivity of C_2 hydrocarbons at 26.4% and BTX at 28.9% (Figure 3b). Note that a small amount of coke is formed at the 1373 K. In addition, a higher temperature also facilitates the formation of acetylene. For example, from 1223 to 1323 K, the concentration of C_2H_2 in the C_2 hydrocarbons distribution changes from 19.5% to 36.0%, while C_2H_4 decreases from 74.8% to 60.8% (Figure S20). The selectivity of naphthalene increases from 26.1% to 39.0%. Such an increase in the naphthalene selectivity with temperature rising is also observed without THN.
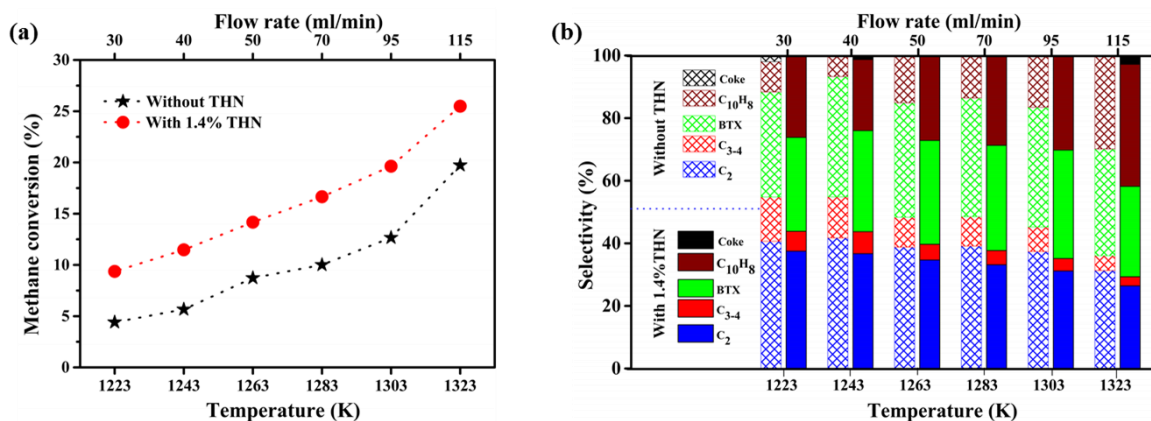
Figure 3. (a) Methane conversion and (b) products selectivity as a function of reaction temperature and flow rate over Fe-reactor without and with 1.4% THN.

In summary, we demonstrate here that methane conversion to olefins and aromatics over Fe-reactor can be enhanced by hydrogen radicals, which are added into the reaction by H-donor molecules, while the selectivity of the main products is not impacted significantly. This enhancement effect is independent of the specific hydrogen-donor molecules and increases with the available amount of hydrogen radicals in the reaction system at a low concentration. The rate of methane conversion levels off at a higher H radical concentration due to recombination of H radicals into H_2 and hence losing efficiency. Interestingly, isotopic experiments confirm that hydrogen radicals activate methane homogeneously by extracting one hydrogen atom from methane, which serves as the initial step to activate methane and forms methyl radicals, which could take place at a lower temperature than the activation over iron based catalytic surface. The major limiting factor to reduce further the reaction temperature appears to be the temperature at which hydrogen radicals are generated; e.g. by the H-donor molecules decomposition. The hereby presented enhancement effect points to new strategies to increase the efficiency of methane activation under non-oxidative conditions. In a recent effort to study the gas phase

mechanism of the MTOAH reaction in detail, hydrogen free radicals were detected *in-situ* in MTOAH by H-Rydberg Tagging spectroscopy and those results will be publish in a follow-up work.

ASSOCIATED CONTENT

Supporting Information

Fe-reactor preparation and characterization, benzene and THN decomposition, MTOAH reaction, isotopic experiments of online TOF-MS and the results (PDF).

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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