A EUROPEAN JOURNAL

<u>CHEMPHYSCHEM</u>

OF CHEMICAL PHYSICS AND PHYSICAL CHEMISTRY

Accepted Article

Title: Non-oxidative Coupling of Methane to Ethylene Using Mo2C/ [B]ZSM-5

Authors: Huibo F Sheng and Raul Francisco Lobo

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemPhysChem 10.1002/cphc.201701001

Link to VoR: http://dx.doi.org/10.1002/cphc.201701001



WILEY-VCH

www.chemphyschem.org

WILEY-VCH

Non-oxidative Coupling of Methane to Ethylene Using Mo₂C/[B]ZSM-5

Huibo Sheng, Edward P. Schreiner, Weiqing Zheng, and Raul F. Lobo*[a]

Abstract: Methane non-oxidative coupling to ethylene was investigated on Mo₂C/[B]ZSM-5 catalyst at 923 K and atmospheric pressure. In contrast to Mo₂C/[AI]ZSM-5 catalysts for methane aromatization, this material exhibits very high ethylene selectivity (>90%) and low aromatics (benzene and naphthalene) selectivity. The much weaker Brønsted acidity of [B]ZSM-5 leads to a slow rate of ethylene oligomerization. The stability of the catalyst is greatly enhanced with 93% of the initial reaction rate remaining after 18 h of time on stream. In-situ UV/VIS spectra indicate that prior to carburization, mono/binuclear Mo oxides are initially well dispersed onto the zeolite support. Mo carbides clusters, formed during carburization with methane, appear similar to clusters formed in [AI]ZSM-5, as indicated by the X-ray Absorption Spectroscopy (XAS) data.

Introduction

Effective utilization of methane is of great interest and importance to the chemical industry because of the rapid growth of shale gas production and the low cost of this raw material.^[1] The conversion of methane to higher hydrocarbons can be categorized into indirect methods and direct methods. Indirect methods use carbon monoxide and hydrogen—produced via methane steam reforming, carbon dioxide reforming, or partial oxidation—as intermediates.^[2] Direct methods involve methane coupling with or without the presence of an oxidant, known respectively as oxidative coupling of methane (OCM) and non-oxidative coupling of methane (NCM).^[3]

One of the methane coupling products is ethylene and according to a PwC(PricewaterhouseCoopers) report, the capital cost of ethylene produced using NCM is estimate as \$316/ton, while the current ethylene price from crude oil steam cracking is \$1717/ton.^[4] Non-oxidative coupling of methane to ethylene is thus a promising alternative to generate a carbon stream that can be fed directly into the existing structure of the chemical industry, with potentially less than one fifth of the current cost.

Wang and co-workers pioneered non-oxidative methane dehydroaromatization reaction on Mo/ZSM-5.^[5] It is reported that only 1.4% of methane was fully converted to benzene at 973 K on HZSM-5 catalysts. A higher conversion of 7.2% was

 [a] H. Sheng, E. P. Schreiner, Dr. W. Zheng, Prof. Dr. R. F. Lobo Center for Catalysis Science and Technology Department of Chemical and Biomolecular Engineering University of Delaware
 150 Academy Street, Newark, DE, 19716 (USA) E-mail: lobo@udel.edu

Supporting information for this article is given via a link at the end of the document $\$

achieved in the presence of Mo in the sample.^[5] An induction period was observed with MoO₃/HZSM-5, implying that the actual active phase was formed in-situ from the MoO₃/HZSM-5 starting material.^[6, 7] Further research has revealed that the primary reaction of C–H bond dissociation occurs on Mo₂C nanoparticle surface.^[8] At the surface, a molybdenum-carbenelike intermediate, CH₂=Mo, is involved in the proposed mechanism. Ethylene is believed to be the primary product from the coupling of the surface carbene species in these samples.^[8, 9] Ethylene oligomerization reactions take place simultaneously leading to the formation of aromatics species, the thermodynamically favored products at the high reaction temperature.^[10] The formation of aromatics is catalyzed by Brønsted acid sites in the zeolite pores and the material operates as a bi-functional catalysts.^[11]

The acidic OH groups of the zeolite catalyst, however, also promote coke formation and fast catalyst deactivation at high temperature.^[12] By removal of external acid sites^[13] or of part of the framework aluminum,^[14] the catalyst activity and stability can be significantly improved. In the rich literature of methane aromatization to benzene, the selectivity of ethylene has not been investigated in much detail. Considering the nature of the bi-functional Mo/HZSM-5 catalysts, one may assume that ethylene could be selectively produced solely on molybdenum carbide, where the methane C-H bond dissociation and coupling reactions occur. However, unsupported Mo₂C shows very limited methane reactivity (0.1 ~ 0.3% conversion), has poor selectivity (hydrogen, carbon, and a minor amount of ethane are produced), and suffers from fast deactivation.^[10] In contrast, in this report we describe an investigation of methane coupling to ethylene on molybdenum carbide nanoparticles supported on non-acidic [B]ZSM-5. Different from Mo₂C/[AI]ZSM-5 catalysts for methane aromatization reaction, this material exhibits very high ethylene selectivity (>90%) instead of producing aromatics (benzene and naphthalene). Due to the low acidity of the zeolite support, the stability of the catalyst is also greatly improved with a deactivation rate of less than 0.5% h⁻¹ during an 18 h reaction test period, while Mo₂C/[AI]ZSM-5 usually deactivates within a few hours.^[11]

Results and Discussion

[B]ZSM-5 was synthesized under hydrothermal crystallization conditions as indicated in the experimental section. The samples were analyzed by Inductively Coupled Plasma (ICP) measurements to quantify composition. A high Si/B ratio of 70 is obtained by this technique. 2% of Mo is introduced to the zeolite by wetness impregnation. The impregnated sample is then calcined in air at 823 K for 4 h. Before the methane reaction, the

This article is protected by copyright. All rights reserved.

calcined sample is carburized in 20% CH_4/H_2 at 923K (detailed information can be found below). Different types of characterization techniques were applied to the above four samples, namely [B]ZSM-5, impregnated, calcined, and carburized 2% Mo/[B]ZSM-5.



Figure 1. XRD patterns of Mo/[B]ZSM-5 (Peaks marked are from 10% wt. Si internal standard), [Al]ZSM-5 reference: $H_{0.32}(Si_{95.68}Al_{0.32}O_{192})^{[15]}$

As shown in Figure 1, the X-ray powder diffraction patterns of the synthesized B-containing MFI-type zeolites samples have a well-defined diffraction pattern consistent with the formation of the pure MFI-type structure. There is no evidence for the presence of any amorphous material in any of the samples. Furthermore, in all the 2% Mo/[B]ZSM-5 samples, the peak positions are slightly shifted towards lower angles as compared to silicalite, which indicates a decrease of the unit cell dimensions of the boron-containing zeolite upon impregnation and calcination of the Mo precursor (Figure S1). This is consistent with the small size of B with respect to Si. No diffraction peaks for molybdenum oxides are observed in any of the samples ruling out the formation of (detectable) large Mo particles in the exterior of the zeolite crystals. This is likely due to the low Mo loading and is an indication of good dispersion of the Mo precursors before and after the experiments.

To measure accurately the zeolite unit cell volume, 10 wt.% of pure Si powder was mixed with each sample and used as internal standard.^[16] Calculated unit cell volumes and u.c. parameters are listed in Table 1. This table shows that zeolite unit cell expanded after the calcination and carburization steps, indicating the loss of framework boron during both reactions. Deboronation is facilitated at the high temperature range and in the presence of water generated in both calcination and caburization steps. Unlike dealumination in aluminosilicate zeolite, boron can be removed from the framework even under mild conditions (e.g. stirring in water at room temperature), an in the presence of high temperatures and water vapor this process is accelerated.^[17] The amount of framework B can be estimated on the basis of the size of the unit cell because unit cell dimensions are linearly correlated with the boron content in the unit cell.^[18, 19] According to the published correlation,^[19] the asmade zeolite B-MFI sample contained about 2.5 boron atoms per unit cell, this number decreased to 1.7 after calcination and decreased further to 1 per unit cell after carburization.

Table 1. Unit cell volume (UCV) a	nd parameters of 2% Mo/IBIZSM-5

parameter	UCV / Å ³	a/Å	b / Å	c / Å
[B]ZSM-5	5322	19.853	20.067	13.360
2%Mo/[B]ZSM-5 (impregnated)	5323	19.845	20.080	13.357
2%Mo/[B]ZSM-5 (calcined)	5337	19.847	20.087	13.387
2%Mo/[B]ZSM-5 (carburized)	5350	19.904	20.094	13.378

Textural and micropore volume estimates of the catalyst were measured using N_2 adsorption isotherms (Table 2). Both BET surface area and the micropore volume decreased after Mo was loaded onto the zeolite, suggesting that the Mo species are entering the channels of the zeolite in this step.

Table 2. BET surface areas and micropore volumes of 2% Mo/[B]ZSM-5				
Material	BET surface area m²/g	Micropore volume cm ³ /g		
[B]ZSM-5	403.8	0.136		
2%Mo/[B]ZSM-5 (impregnated)	391.1	0.112		
2%Mo/[B]ZSM-5 (calcined)	358.5	0.101		
2%Mo/[B]ZSM-5 (carburized)	337.5	0.099		

We carried out an in-situ UV/VIS investigation of molybdenum oxides particles formed in the samples upon impregnation and calcination. Oxomolybedenum species can give strong absorption bands in the UV/VIS region due to the ligand-to-metal charge transfer ($O^{2-} \rightarrow Mo^{6+}).^{[20]}$ The bands are usually relatively narrow and can be observed between 200 and 400 nm due to the nature of π to π^* charge-transfer transition. $^{[21]}$ For the ligand-to-metal charge transfer, the energy of the electronic transitions have a strong dependence on the ligand field symmetry surrounding the molybdenum center. In this work for oxo-ligands, a more energetic transition is expected for tetrahedral Mo(VI) than for octahedral Mo(VI).^{[21]} Therefore in the literature, most bands for pure tetrahedral oxomolybdenum were reported at 260-280 nm, while bands for pure octahedral oxomolybdenum were observed at 300-320 nm.^{[22]}

In Figure 2, a broad band around 250-350 nm with a shoulder at 235 nm was observed for the impregnated Mo/[B]ZSM-5, while after a calcination a sharp band at 260 nm with a shoulder at 235 nm was formed. The broad band can be considered as the overlapping of the bands at 260-280 nm and 300-320 nm, suggesting the fact of polymeric structure of both tetrahedral and octahedral molybdenum centers of the supported oxomolybdate species.^[23] Since the precursor (NH₄)₆Mo₇O₂₄ is only composed of 7 MoO_6 octahedra linked by sharing oxo-edges, we believe the tetrahedral molybdenum centers are formed during the impregnation and the drying steps, since the blue shift of the absorption bands is also reported during the impregnation step in other metal oxide catalysts due to the near surface pH changes.^[24] After a calcination, the material presents two bands at 235 nm and 260 nm, implying the formation of tetrahedral molybdednum centers and the disappearance of octahedral centers. In fact these two bands are very typically observed for CaMoO₄ or Na₂MoO₄, where MoO₄²⁻ anions are isolated from each other either by Ca^{2+} or Na^{+} [25]



WILEY-VCH

The UV/VIS spectra of Mo/[AI]ZSM-5 are also very well studied in the literature by other authors. Vasenin et al.^[26] reported a band at 330 nm for the initial 10% Mo/[AI]ZSM-5 after drying 373K and assign the band to the precursor (NH₄)₆Mo₇O₂₄. Martinez and Peris^[27] only observed bands at 220-250 nm for the calcined 3% Mo/[AI]ZSM-5 catalyst, indicating the molybdenum mainly exists as highly dispersed tetrahedral oxomolybdate species. Ngobeni et al.^[28] also reported the bands at 220-250 nm for 2% Mo/[AI]ZSM-5 and found the addition of boron or silver as dopants does not influence the coordination sphere of molybdenum species.



Figure 2. UV/VIS diffused reflectance spectra of 2%Mo/[B]ZSM-5

As the narrowing and the blue shift of the band are observed when there is a decrease of the oxomolybdates cluster size or the counter-cation numbers,^[23] the UV/VIS spectra suggest that the surface oxomolybdates species have been well dispersed and anchored onto the zeolite support, but how small the cluster is remains unclear. Weber^[29] reported that the average number of adjacent molybdenum cations in very small oxide clusters is linearly correlated with the optical band gap energy of the bulk oxide, and this property can be readily determined using UV/VIS spectroscopy (Figure 3). According to the correlation the polyoxomolybdates turn into mono/binuclear molybdenum oxides after calcination implying not only that the molybdenum migrates into the zeolite pores but also that these species are anchored onto the silanol groups and/or the weak Brønsted acid boron sites.



Figure 3. UV/VIS edge energies of 2%Mo/[B]ZSM-5

After the formation of mono/binuclear molybdenum oxides, the samples were carburization in a flow of 20% CH₄/H₂ (20 sccm) at 973 K for 8 h. A temperature programmed oxidation experiment (TPO) was carried out on these samples to quantify the ratio of Mo and carbon after the carburization step (Figure 4). The trace with negative values depicts the consumption of O2 and the positive signals are due to the generation of CO and CO2. At the beginning of the experiment, in the low temperature regime (400-600 K), CO is the favored oxidation product and as the temperature increased (700-823 K), CO2 exceeded the CO produced to become the main product. However Ding et al.^[8] reported that the reoxidation of the 4% Mo₂C/[AI]ZSM-5 occurs as a single fast process with sharp evolutions of both CO and CO_2 at about 725 K. For bulk Mo_2C the CO_x evolution temperature is even higher at about 1000 K.^[8] The lowest CO_x evolution temperature suggests the best reactivity and oxygen dissociation ability of the Mo₂C/[B]ZSM-5. In addition, by comparing the oxygen consumed by carbon and by molybdenum, a Mo/C ratio of 1.9 was estimated, indicating the carburization process was almost completed with all the oxides turning into carbides.

WILEY-VCH



Figure 4. Temperature programmed oxidation of carburized 2% Mo/[B]ZSM-5

A transmission electron microscope (TEM) image of the carburized 2% Mo/[B]ZSM-5 is shown in Figure 5. In the image, black dots of ~1 nm in diameter can be identified inside the particle as well-dispersed Mo₂C particles. However a few larger particles around 2 nm are also observed. This can be explained by the "knock-on" effect observed during the electron beam irradiation, where the Mo₂C particles are squeezed out from the zeolite channel to the external surface (Figure S2).



Figure 5. TEM image of 2% Mo/[B]ZSM-5 after carburization

a rate of 2 K/min. Growth of the pre-edge feature was observed, that is, there is an increase of the tetrahedral symmetry of the Mo center.^[30] During the second step (upper right), when the temperature was increased to 923 K at 1 K/min, a plateau was reached with no major structure change. In the third step (lower left) the pre-edge feature became less and less intense as the temperature was increased to 973 K at 1 K/min. The disappearance of the pre-edge absorption feature - indicates that the Mo(VI)-oxo species were reduced and carbidic Mo species are formed.^{(8, 31]} The spectra did not change further at 973 K. The lower right figure shows the overall change of the Kedge through the whole carburization process. The Mo-K absorption edge shifts to lower energies ($\Delta E = 4.5 \text{ eV}$) during the carburization process, and the ΔE is about 5 eV with Mo/[AI]ZSM-5 according to Ding et al.^[8] The final oxidation state of the Mo was close to the oxidation state of Mo in Mo₂C, suggesting that the sample contains a mixture of molybdenum carbide and molybdenum oxycarbide. This result is consistent with other XANES analysis during the carburization process of Mo/[AI]ZSM-5, where Mo center is anchored either onto the silanol groups and/or Brønsted acid aluminum sites. [32, 33]



Figure 6. X-ray absorption near edge structure (XANES) of 2% Mo/[B]ZSM-5 during in-situ carburization process

The Extended X-ray Absorption Fine Structure (EXAFS) of the Mo in the 2% Mo/[B]ZSM-5 and standard compounds are displayed in Figure 7. The sample calcined at 773 K showed doublet peaks at ~1.2 Å while the intensity of all features beyond

The structural coordination and electronic state of Mo can be described with in-situ X-ray absorption fine structure (XAFS) spectroscopy during the carburization process. The Mo K-edge X-ray absorption near edge structure (XANES) was recorded and is shown in (Figure 6). A three-step K-edge feature change was observed during the carburization: The first step (upper left) was performed ramping the temperature from 298 K to 723 K at



ChemPhysChem

3 Å are much weaker; these results reveal that MoO3 crystallites are dissociated into smaller particles such as mono/binuclear molybdenum oxides.[33] The peaks at ~1.2 Å indicate the formation of Mo centers in tetrahedral coordination instead of the initial octahedral coordination environment. This observation is also in consistence with our previous discussion from the UV/VIS results. After the carburization with 20% CH₄/H₂, the molybdenum oxide species were reduced and carburized to form molybdenum carbide. As shown in Figure 6, the newly formed MoC_x species give rise to two peaks at ~1 and 2 Å. These peaks however cannot be described only using carbon neighbors in the first shell simulation, which usually only present one strong peak at ~2.5 Å as reported by others.^[8, 13, 32] Instead they can be well described by one oxygen neighbor near 1.7 Å and three carbon neighbors near 2 Å and was also reported by Li et al. when describing the mechanism of the formation of MoC_x species on [AI]ZSM-5.^[33] In the bulk Mo₂C, Mo has three carbon neighbors at a distance of 2.1 Å and twelve Mo neighbors at distances from 2.9 to 3.1 Å.[8] The absence of Mo-Mo pairs at the distance around 3 Å for the carburized sample suggests that the Mo small species formed upon calcination do not aggregate into larger clusters upon carburization.



Figure 7. Radical structure function of Mo in standard compounds and in 2% Mo/[B]ZSM-5 before and after *in-situ* carburization

In the typical [AI]ZSM-5 catalysts for the methane aromatization reactions the zeolite offers anchoring sites for the metal to disperse, and as the co-catalyst, the Brønsted acid sites catalyze the ethylene oligomerization reaction to aromatics.^[32] Diffused reflectance FT-IR experiments were carried out to compare the role of [B]ZSM-5 to that of the [AI]ZSM-5 (Figure 8). The 2% Mo/[Al]ZSM-5 showed two IR bands assigned to OH stretching vibrations: the band at 3743 cm⁻¹ attributed to terminal silanol groups,^[34] and the band at 3610 cm⁻¹ is typical for the acidic bridging OH of Si-OH-AI.^[17] For the [B]ZSM-5, the OH vibration signal from silanol groups is slightly red-shifted to 3735 cm⁻¹, and the OH vibration band from Si–OH…B is observed at 3724 cm⁻¹ and 3709 cm⁻¹. In a zeolite framework, the boron atom is coplanar with three oxygens due to its small atomic diameter, and the distance to the fourth oxygen is too long to form strong bond.^[34] Therefore the acidity of the bridging OH in [B]ZSM-5 is much weaker than that of [AI]ZSM-5. After the Mo impregnation the intensity of the IR bands decreased,

implying the substitution of the molybdenum oxides to the protons of the exchangeable OH groups. The intensity further decreased after a calcination at 773 K as a result of the molybdenum oxides being better dispersed as smaller clusters onto more anchoring sites, which is in agreement with the previous results from UV/VIS and XAS.



Figure 8. FT-IR spectra of 2%Mo/[AI]ZSM-5 and 2%Mo/[B]ZSM-5

Catalytic Tests

The catalytic properties were evaluated in a flow reactor under conditions similar to conditions reported in the literature for [Mo]-AI-ZSM-5 (923 K, 1 atm, 5% CH₄/He flow of 20 sccm, 50mg Mo₂C/[B]ZSM-5). Typically, 50 mg of the calcined Mo/[B]ZSM-5 was loaded into the reactor followed by carburization in 20% (vol.) CH₄/H₂. This step takes about 16 hours with the temperature ramping from 298 K to 623 K at 2 K/min, then to 973 K at 1 K/min, and held at 973 K for 8 hours. After this step, the system was cooled to the reaction temperature in He.^[35] After the temperature was stabilized, a reaction gas consisting of 5% (vol) CH₄/He was fed into the system and the products are analysed with an online GC equipped with TCD and FID detectors (Figure 9). Due to thermodynamic limitations, the conversion of methane around 1% with a 90%+ selectivity to ethylene instead of benzene. In terms of the catalyst stability of the methane aromatization reactions on Mo/[AI]ZSM-5, the Brønsted acid sites catalyzed oligomerization reaction may cause carbon deposition, which further covers the active site and leads to catalyst deactivation within a few hours.[11] According to this catalyst deactivation mechanism, Mo/[B]ZSM-5 is expected to have higher stability for methane activation reaction due to the nature of low acidity. Our result shows that the catalyst is very stable through the run, as the rate only decreases to 93% of initial reaction rate after 18 h.

The noisy data of methane reaction rate in Figure 9, is presented here because the rate is calculated from a subtraction of two large numbers (methane concentration before and after reaction). Therefore a linear regression was fitted with the rate of methane as a function of time on stream. A null hypothesis $H_0=0$ of the slope and the intercept is tested to verify if there is significant linear relationship between the methane rate and the

time on stream. The P-value for the slope is ~0.001 and for the intercept is 0. In both cases, the null hypothesis is rejected, suggesting that both slope and intercept value does not equal to zero. The details of the t-test can be found in the supporting information.



Figure 9. Catalytic rates and selectivity of methane activation on 2%Mo/[B]ZSM-5 at 923 K. The average rate is *r*=0.3 mmol h⁻¹ g_{cat} ⁻¹ at ~0.8% conversion. Based on an equilibrium conversion of 2.4%, the forward rate is estimated as $r_{t} = 0.34$ mmol h⁻¹ g_{cat} ⁻¹.

The Mo/[AI]ZSM-5 has been extensively studied since Wang^[5] first discovered its novel property of methane direct dehydroaromatization to benzene.^[3, 6-11, 14, 32, 36] As shown in Scheme 1, in comparison to Mo₂C/[AI]ZSM-5, Mo₂C/[B]ZSM-5 showed 90% selectivity towards ethylene, with only 7% selectivity to benzene. In contrast Li^[37] has reported a similar selectivity for this reaction with Mo₂C/[B]ZSM-5 to that with Mo₂C/[Al]ZSM-5 (88% benzene and 3% ethylene at initial and 68% benzene and 24% ethylene after 120 min). The difference in selectivity between the results reported here and those of Li et al is due to the presence of aluminum impurities in their boron source, impurities that would introduce strong acid sites into their samples. Note too that a different catalyst synthesis method was applied in their report where Mo precursor MoO₃ and [B]ZSM-5 were physically mixed and grinded, although both impregnation and physical mixture synthesis showed similar methane conversion and products selectivity in the case of [AI]ZSM-5, as Borry and co-workers reported.[7]



Scheme 1. Methane activation products selectivity of $Mo_2C/[AI]ZSM-5$ vs. $Mo_2C/[B]ZSM-5$

Conclusions

A highly selective methane non-oxidative coupling catalyst Mo₂C/[B]ZSM-5 was synthesized and characterized. Boron is employed instead of aluminium in the zeolite framework, which leads to a dramatic decrease in the zeolite acidity. 2% wt. of molybdenum was loaded into the zeolite by wetness impregnation. After calcination, mono and binuclear Mo oxide species were anchored onto the zeolite surface, as a high UV/VIS band gap energy (4.1 eV) was observed.[29] Molybdenum oxides were reduced and carburized to form well dispersed and isolated molybdenum carbides, as proved by the absence of Mo-Mo pairs in the EXAFS measurement. Due to the low acidity of the support, the catalyst shows a high selectivity towards ethylene (~90%) instead of aromatics. Ethylene oligomerization reaction, which is responsible for heavy coke formation, was thus inhibited. As a result, no significant catalyst deactivation was observed during the 18-hour long test.

Experimental Section

1.0 Catalyst preparation

[B]ZSM-5 was synthesized by the hydrothermal method using tetrapropylammonium bromide (TPABr) as the organic structure director. Fumed silica was used as the silica source and boric acid as the boron source. Typically, 0.3112 g H₃BO₃ (Sigma Aldrich), 4.5479 g SiO₂ (Cabosil, M5), 0.4540 g NaOH (Fisher), 2.6201 g TPABr (Sigma Aldrich) were dispersed in 60 mL DI water and stirred until it became homogeneous. The resulting gel was transferred to a 125 mL Teflon-lined stainless steel autoclave (Parr 4748) and heated to 423 K for 3 days under static conditions. The as-made product was filtered, washed with DI water and dried in an oven at 353 K overnight. After calcination at 823 K and NH₄⁺ ion (0.05 M NH₄NO₃, Sigma Aldrich) exchange, 2% ammonium heptamolybdate (Sigma Aldrich) was impregnated onto the zeolite support. Before reaction, the catalyst was calcined at 773 K and carburized at 973 K.

2.0 Catalyst evaluation

The catalyst was evaluated in a quarter inch quartz tube reactor. Typically, 50 mg of sample will be loaded into the reactor between two layers of quartz wool. The reactor was installed in a flow reactor system, which also includes a gas flow system, a heating system, and products analysis system. Multiple gases can be fed using Brooks mass flow controller E5850. The quartz reactor is heated by a furnace and the gas line after the reactor are properly wrapped with heating tapes. An online gas chromatography (GC, Shimadzu 2014) and a mass spectroscopy (Pfeiffer, Thermostar GSD 320T) are employed to collect and analyse the products.

3.0 Catalyst characterization

3.1 X-ray diffraction (XRD) and Transmission electron microscopy (TEM)

XRD analysis were performed using Bruker D8 x-ray powder diffractometer with monochromatic Cu K α 1 line (k = 1.540 Å). TEM image was obtained by a JEM-2010F. N₂ adsorption experiments were performed with 3Flex surface characterization analyzer. BET Surfaces were calculated using the MicroActive for 3Flex software.

3.2 UV/vis spectroscopy

Diffused reflectance UV/vis study was carried out using a flow cell and a Jasco V550 UV/vis spectroscopy. The in-situ flow cell is made of U-shaped quartz round tube with a UV window made of square quartz tube (Quartz Plus, Inc.). Typically 100 mg of the catalyst sample was loaded into the flow cell at the window. Other auxiliary systems (a heating

system and gas flow control system) are included to perform the in-situ UV/vis study. All the spectra were taken at room temperature with inert gas flowing through the sample bed.

3.3 Temperature programmed oxidation (TPO)

TPO experiment was conducted with the quartz reactor as mentioned in section 2.0. About 100 mg of the calcined catalyst was loaded into the reactor and a carburization was performed before the TPO experiment. After the catalyst bed was cooled down to room temperature in He flow, a 20% O2/He gas was introduced with a ramping rate of 10 K/min until 823 K. The gas products were collected and analysed by a mass spectroscopy (Pfeiffer, Thermostar GSD 320T).

3.4 X-ray absorption spectroscopy (XAS)

In-situ XAS studies were carried out in Argonne National Lab (ANL) at beamline 11B.The impregnated 2% wt. Mo/[B]ZSM-5 was loaded into an in-situ reaction cell.^[40] The sample was first calcined at 773 K and then carburized with 20% CH₄/H₂ at 973 K. Full EXAFS spectra were taken at the beginning and the end of each process. XANES spectra were taken every 5 min during the in-situ treatment.

3.5 In situ Fourier transform infrared (FT-IR) characterization

The FT-IR measurements were performed using an in situ diffused reflectance infrared Fourier transform (DRIFT) cell with ZnSe windows (15 x 2 mm, Harrick Sci.). The IR cell consists of a cell body, sample holder and aluminium heating block. About 50 mg of the catalyst sample was required to load into the sample holder as a pellet. Proper gases could be fed through the sample by mass flow controllers (Brooks 5850E series). IR spectra were collected using a Fourier transform infrared spectrometer (Nicolet Nexus 470). The IR spectral data were analysed by OMNIC software. The catalyst sample was pre-treated with He at 773 K (5 K/min ramping rate) for 4 hours to remove moisture and other surface contaminates. After cooling down to room temperature, IR spectra were collected in He flow.

Acknowledgements

We gratefully acknowledge the funding from US Air Force. The authors thank Dr. Jason Loiland and Chen-Yu Chou for their help in the XAFS data collection at Argonne National Laboratory.

Keywords: methane activation • C1 chemistry • ethylene • molybdenum carbide • boron ZSM-5

- J. H. Lunsford, Catalysis Today 2000, 63, 165-174. [1] [2] A. T. Ashcroft, A. K. Cheetham, M. L. H. Green, P. D. F. Vernon, Nature
- 1991. 352. 225-226.
- T. V. Choudhary, E. Aksoylu, D. W. Goodman, Catalysis Reviews-[3] Science and Engineering 2003, 45, 151-203.
- PwC, Vol. 2016, http://www.pwc.com/us/en/industrial-[4]
- products/publications/shale-gas-chemicals-industry-potential.html, 2013. L. S. Wang, L. X. Tao, M. S. Xie, G. F. Xu, J. S. Huang, Y. D. Xu, *Catalysis Letters* **1993**, *21*, 35-41. [5]
- [6] B. M. Weckhuysen, D. J. Wang, M. P. Rosynek, J. H. Lunsford, Journal of Catalysis 1998, 175, 338-346.
- R. W. Borry, Y. H. Kim, A. Huffsmith, J. A. Reimer, E. Iglesia, Journal of [7]
- Physical Chemistry B 1999, 103, 5787-5796.
 W. P. Ding, S. Z. Li, G. D. Meitzner, E. Iglesia, *Journal of Physical Chemistry B* 2001, *105*, 506-513.
 Y. D. Xu, S. T. Liu, L. S. Wang, M. S. Xie, X. X. Guo, *Catalysis Letters* 1005, 506-514. [8]
- [9] 1995, 30, 135-149.
- F. Solymosi, J. Cserenyi, A. Szoke, T. Bansagi, A. Oszko, Journal of [10] Catalysis **1997**, *165*, 150-161. D. J. Wang, J. H. Lunsford, M. P. Rosynek, *Journal of Catalysis* **1997**, [11]
- 169, 347-358.
- B. M. Weckhuysen, M. P. Rosynek, J. H. Lunsford, Catalysis Letters [12] 1998. 52. 31-36.

- W. P. Ding, G. D. Meitzner, E. Iglesia, Journal of Catalysis 2002, 206, [13] 14-22.
- [14] D. Ma, Y. Lu, L. L. Su, Z. S. Xu, Z. J. Tian, Y. Xu, L. W. Lin, X. H. Bao, Journal of Physical Chemistry B 2002, 106, 8524-8530.
- [15] H. Vankoningsveld, J. C. Jansen, H. Vanbekkum, Zeolites 1990, 10, 235-242.
- [16] D. T. On, S. Kaliaguine, L. Bonneviot, Journal of Catalysis 1995, 157, 235-243
- H. Koller, C.-Y. Chen, S. I. Zones, Topics in Catalysis 2015, 58, 451-[17] 479.
- A. Cichocki, J. Datka, A. Olech, Z. Piwowarska, M. Michalik, Journal of [18] the Chemical Society-Faraday Transactions **1990**, *86*, 753-756. B. L. Meyers, S. R. Ely, N. A. Kutz, J. A. Kaduk, E. Vandenbossche,
- [19] Journal of Catalysis 1985, 91, 352-355.
- L. Wang, W. K. Hall, Journal of Catalysis 1982, 77, 232-241.
 F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6 ed., Wiley, New York, 1999. [21]
- J. H. Ashley, P. C. Mitchell, Journal of the Chemical Society a -[22]
- Inorganic Physical Theoretical 1968, 2821-& [23] M. Fournier, C. Louis, M. Che, P. Chaquin, D. Masure, Journal of
- Catalysis 1989, 119, 400-414. [24]
- L. G. van de Water, J. A. Bergwerff, T. A. Nijhuis, K. P. de Jong, B. M. Weckhuysen, *Journal of the American Chemical Society* 2005, 127, 5024-5025.
- [25] P. C. Mitchell, F. Trifiro, Journal of the Chemical Society a -Inorganic
- Physical Theoretical **1970**, 3183-&. N. T. Vasenin, V. F. Anufrienko, I. Z. Ismagilov, T. V. Larina, E. A. Paukshtis, E. V. Matus, L. T. Tsikoza, M. A. Kerzhentsev, Z. R. [26] Ismagilov, Topics in Catalysis 2005, 32, 61-70.
- A. Martinez, E. Penis, Applied Catalysis a-General 2016, 515, 32-44.
 M. W. Ngobeni, A. F. Carley, M. S. Scurrell, C. R. Nicolaides, Journal of Molecular Catalysis a-Chemical 2009, 305, 40-46. [27] [28]
- R. S. Weber, Journal of Catalysis 1995, 151, 470-474
- [30] S. B. Xie, K. D. Chen, A. T. Bell, E. Iglesia, Journal of Physical
- Chemistry B 2000, 104, 10059-10068 [31]
- J. Bedard, D.-Y. Hong, A. Bhan, *Journal of Catalysis* **2013**, *306*, 58-67. S. T. Liu, L. Wang, R. Ohnishi, M. Ichikawa, *Journal of Catalysis* **1999**, *181*, 175-188. [32]
- [33] W. Li, G. D. Meitzner, R. W. Borry, E. Iglesia, Journal of Catalysis 2000, 191, 373-383.
- [34] J. Datka, Z. Piwowarska, Journal of the Chemical Society-Faraday Transactions / 1989, 85, 47-53.
- [35] A. Mehdad, R. E. Jentoft, F. C. Jentoft, Journal of Catalysis 2017, 347, 89-101.
- V. T. T. Ha, L. V. Tiep, P. Meriaudeau, C. Naccache, *Journal of Molecular Catalysis a-Chemical* **2002**, *181*, 283-290; D. Ma, Y. Y. Shu, M. J. Cheng, Y. D. Xu, X. H. Bao, *Journal of Catalysis* **2000**, *194*, 105-[36] 114; R. Ohnishi, S. T. Liu, Q. Dong, L. Wang, M. Ichikawa, Journal of *Catalysis* **1999**, *182*, 92-103; J.-P. Tessonnier, B. Louis, S. Rigolet, M. J. Ledoux, C. Pham-Huu, *Applied Catalysis a-General* **2008**, 336, 79-88. S. Li, D. Ma, Q. B. Kan, P. Wu, Y. B. Peng, C. L. Zhang, M. S. Li, Y. H.
- [37] Fu, J. Y. Shen, T. H. Wu, X. H. Bao, Reaction Kinetics and Catalysis Letters 2000, 70, 349-356.
- S. Y. Xing, D. H. Zhou, L. Cao, X. Li, Chinese Journal of Catalysis 2010, [38] 31, 415-422.
- D. H. Zhou, D. Ma, Y. Wang, X. C. Liu, X. H. Bao, Chemical Physics [39] Letters 2003, 373, 46-51.
- [40] P. J. Chupas, K. W. Chapman, C. Kurtz, J. C. Hanson, P. L. Lee, C. P. Grey, Journal of Applied Crystallography 2008, 41, 822-824.

This article is protected by copyright. All rights reserved.