

Highly Selective Nonoxidative Coupling of Methane over Pt-Bi Bimetallic Catalysts

Yang Xiao[®] and Arvind Varma^{*®}

Davidson School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907-2100, United States

Supporting Information

ABSTRACT: There is widespread interest in converting methane, primary component of natural gas and shale gas, into valuable chemicals. As an important direct methane transformation technique, despite extensive research conducted for decades, oxidative coupling of methane (OCM) remains industrially uneconomical owing to low selectivity toward valuable target products (C₂ species, ethane/ethylene). In the present work, we describe that ZSM-5 zeolite supported bimetallic Pt-Bi catalysts stably and selectively convert methane to C₂ species with high carbon selectivity (>90%) at relatively moderate temperatures (600–700 °C). On the basis of experimental observations, it is proposed that the surface Pt in the catalysts functions as the active site for methane activation, while Bi addition as promoter plays an important role in C₂ species formation and catalyst stability.



KEYWORDS: shale and natural gas utilization, nonoxidative coupling of methane (NOCM), Pt-Bi bimetallic catalysts, high selectivity toward C_2 species, Bi promoter effect on C_2 species formation

The abundance of methane, the main component of natural gas (~95%) and shale gas (typically >70%), on Earth makes it an attractive source for energy and chemicals for at least the next century. Catalytic transformation of methane to value-added chemicals plays an important role in methane utilization.^{1,2} Various routes have been considered, including indirect transformation, which converts methane to syngas as an intermediate followed by its further conversion to other compounds, and direct transformation, which converts methane to higher hydrocarbons (e.g., ethylene, benzene) or oxygenates (e.g., methanol, formaldehyde) without any intermediate products.³ Direct transformation is more attractive because it saves both operating costs and capital investment. Among direct transformation technologies, oxidative coupling of methane (OCM) is promising because the primary products (C₂ species, ethane/ethylene) are precursors for a variety of more valuable products: e.g., plastics and resins. Tuning the selectivity toward C₂ species in OCM, however, has been a longstanding challenge since the 1980s, owing to the unavoidable presence of overoxidized species (CO/CO_2) under oxidative conditions. Hundreds of catalyst candidates have been prepared and tested for OCM, while selectivity toward CO/CO_2 is typically about 50%, indicating uneconomical conversion of carbon atoms.⁴

Nonoxidative conversion of methane to aromatics, first reported in 1993,⁵ improves carbon atom economy. Using Mo supported on zeolites, existing nonoxidative technologies generate benzene as the main product, but unavoidable coke formation limits the catalyst lifetime and process commercialization.⁶ Although the selectivity toward benzene is typically

about 80–90%, other aromatic hydrocarbons (C_7-C_9) as well as C_2 species (both ethane and ethylene) have also been reported.^{7–9} In a recent report, 2–3% methane conversion was reached over Bi/SiO₂ at 900 °C under nonoxidative conditions, while the selectivity toward C_2 products was about 40%.¹⁰

Nonoxidative coupling of methane (NOCM) to form C_2 hydrocarbons has been considered since the 1990s. Extensive investigations have been focused on the two-step process, involving first feeding methane for dissociative adsorption on catalyst surface, followed by feeding hydrogen to generate higher hydrocarbons.^{11–16} By only feeding methane continuously, Belgued et al.¹⁷ reported that C_2H_6 and H_2 were immediately produced over a commercial 6 wt % Pt/SiO₂ catalyst at low temperature (250 °C), while owing to catalyst deactivation, both products disappeared for a time on stream (TOS) of more than 8 min. This indicates that methane can be activated at temperatures lower than those typically used in OCM (>700 °C). Soulivong et al.¹⁸ showed that ethane with >98% carbon selectivity was produced over silica-supported tantalum hydride catalyst at temperatures <500 °C, although methane conversion was less than 0.5%. Guo et al.¹⁹ reported 48% conversion of methane under nonoxidative conditions over Fe/SiO₂ catalyst at 950 °C, producing ethylene, benzene, and naphthalene with carbon selectivities of 53%, 22%, and 25%, respectively. Gerceker et al.²⁰ also found similar products

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Figure 1. Product distribution at 650 °C and 0.1 atm methane partial pressure over (a) 1% Pt, (b) 1% Pt-0.1% Bi, (c) 1% Pt-0.2% Bi, (d) 1% Pt-0.5% Bi, (e) 1% Pt-0.8% Bi, and (f) 1% Pt-1% Bi catalysts.



Figure 2. Performance of different Pt-Bi/ZSM-5 catalysts at various methane conversions for (a) ethane selectivity and (b) turnover frequency (TOF) at 650 $^{\circ}$ C and 0.1 atm methane partial pressure.

over PtSn catalyst supported on SiO₂ and ZSM-5 at 700 $^{\circ}$ C, however, the methane conversion was less than 0.3%.

In the present report, under nonoxidative conditions, we describe that Pt-Bi bimetallic catalysts supported on ZSM-5 zeolite selectively convert methane to ethane with high carbon selectivity (>90%) and typical methane conversion of ca. 2%, along with equivalent molar hydrogen generated as a byproduct. The catalyst exhibits little deactivation during an 8 h test, indicating good stability and prevention of coke formation. This is the first report of stable methane coupling in a continuous flow reactor, at relatively moderate temperatures (600–700 °C), with methane conversion ~2% and carbon selectivity to C_2 hydrocarbon species >90%.

Various ZSM-5 zeolite supported Pt-Bi bimetallic catalysts were prepared, characterized, and tested in a fixed-bed reactor (see Materials and Methods in the Supporting Information). As noted in Materials and Methods, the Pt and Bi loadings were both by weight %, while H-ZSM-5 was the H-form ZSM-5 with

an Si/Al ratio of 40. For brevity, in later sections the term weight % is not noted explicitly. These fresh catalysts exhibit similar BET surface areas (372-412 m²/g), pore sizes (2.8-3.5 nm), pore volumes (0.33-0.41 cm³/g) (Table S1), and Pt metal dispersions (22-29%) (Table S2). Tables S1 and S2 show that, for the used 1% Pt catalyst, all of these values dramatically decreased (BET surface area 234 m²/g, pore size 1.3 nm, pore volume 0.14 cm^3/g , and metal dispersion 16%). For the used bimetallic 1% Pt-0.8% Bi catalyst, however, only a slight decrease was observed in these values (BET surface area $329 \text{ m}^2/\text{g}$, pore size 2.3 nm, pore volume 0.31 cm³/g, and metal dispersion 20%). TEM scans (Figure S1) show that metals (dark dots) were successfully loaded on the ZSM-5 support and the metal dispersion (calculated by TEM-based particle size²¹) values were consistent with the H₂-O₂ titration²² data in Table S2. The XRD patterns (Figure S2) for various Pt-Bi/ZSM-5 catalysts are compared to diffraction patterns for unsupported MFI (ZSM-5) reported in the International Zeolite Association

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Figure 3. Temperature-programmed investigations: (a) H_2 desorption (H_2 -TPD) from different Pt-Bi/ZSM-5 catalysts and (b) surface reaction (TPSR) profiles for 1% Pt-0.8% Bi/ZSM-5 catalyst at 0.1 atm methane partial pressure and 600 min g_{cat} /mol contact time.

(IZA) structure database.²³ Fresh supported (Figure S2a–g) and unsupported ZSM-5 (Figure S2h) exhibit similar patterns, likely due to low metal loading (1 wt % or less) and high Pt dispersion (20-30%).²⁴ The used 1% Pt catalyst (Figure S2i) exhibited fewer peaks in comparison to other materials, indicating that the crystallinity was changed slightly, likely owing to coke deposit. The used 1% Pt-0.8% Bi catalyst (Figure.S2j) showed the same MFI structure as well, implying less coke deposit and thus better stability in comparison to the pure Pt catalyst. Table S3 shows that the fresh and used catalysts contained essentially the same amounts of Pt and Bi as designed.

As shown in Figure 1, by varying the contact time of feed methane with packed catalysts, different methane conversions were obtained, as plotted by blue lines, while detailed product distributions are illustrated as bar charts. (Definitions for Methane Conversion, Product Selectivity and Yield in the Supporting Information). All methane conversions were less than 7%, limited by thermodynamic equilibrium under the operating conditions, corresponding to

$$CH_4 \rightarrow 0.5C_2H_6 + 0.5H_2$$
 (1)

$$CH_4 \rightarrow 0.5C_2H_4 + H_2 \tag{2}$$

For the 1% Pt catalyst, methane conversions were between 3% and 6%, while no hydrocarbon but only hydrogen was detected, owing to coke formation over the pure Pt surface.²⁵ For the 1% Pt-0.1% Bi catalyst, methane conversion was similar to results for the 1% Pt catalyst, with 0.5–8% benzene (C_6H_6) selectivity but no C_2 hydrocarbons generated. For four other bimetallic catalysts with 1% Pt and 0.1–1% Bi in Figure 1, ethane as the target product in the present work was produced with a variety of selectivity values ranging from 17% to 95%, while benzene and ethylene (C_2H_4) were formed as byproducts as well.

Figure 2a additionally shows that the selectivity toward ethane always decreased with an increase in methane conversion for these four catalysts. For the 1% Bi catalyst, on the other hand, no methane conversion (<0.1%) was found. In particular, for the 1% Pt-0.8% Bi catalyst, selectivity toward

ethane was 85-95% when methane conversion was 1-5%. Note that equilibrium methane nonoxidative conversion to C_2 species is about 2-3% at 650 °C. (Thermodynamic Consideration and Figure S4 in the Supporting Information), while higher than equilibrium conversion was typically observed for methane nonoxidative conversion at short time on stream (TOS) in the literature.^{7,8,26,27} For consistency, all data reported in our work for catalytic performance comparison were taken at 1 h TOS. As reported in the literature, Bi addition to Pt could tune catalytic activity, where Bi functions as site blocker,^{28,29} while Bi alone shows poor catalytic activity. For increasing amounts of Bi addition to Pt, chemisorption of small molecules (e.g., H_2 , CO,³⁰ and $C_2H_4^{31}$) was found to be attenuated, indicating relatively lower activity for reaction and higher tolerance for poison species. Coverage values of chemisorbed species, influenced by both geometric and electronic effects,^{32,33} also depend on molecular size, which indicates that, for a specific reaction, a particular Pt/Bi composition is favored. For example, Greeley et al.³⁴ reported that $Pt_{1.00}Bi_{0.95}$ exhibits excellent activity for hydrogen evolution, while our prior work described that 3% Pt-0.6% Bi provides the highest 1,3-dihydroxyacetone yield from glycerol selective oxidation.³⁵ In the present work, we observe that, for NOCM conversion, 1% Pt-0.8% Bi gives the best catalytic performance. Figure 2b shows that over various catalysts tested in Figures 1 and 2a, turnover frequencies (TOF) based on Pt surface dispersion (Table S2) and methane conversion were essentially constant $(0.042-0.053 \text{ s}^{-1})$. This feature demonstrates that surface Pt is the active site for methane activation, as reported previously.³⁶

 H_2 temperature-programmed desorption (H_2 -TPD) profiles in Figure 3a demonstrate that hydrogen uptake at room temperature was attenuated with increasing Bi addition to 1% Pt/ZSM-5. For 1% Bi catalyst, no hydrogen uptake was found, indicating an inactive nature for Bi as shown in Figure 2a. Temperature-programmed surface reaction (TPSR) profiles in Figure 3b describe that below 500 °C methane cannot be activated efficiently, owing to the chemical stability of the methane molecule. Between ca. 500 and 650 °C, methane was converted to equivalent molar amounts of ethane and



Figure 4. Effects of operating conditions and catalyst stability over 1% Pt-0.8% Bi: (a) temperature effect at 0.1 atm methane partial pressure and 600 min g_{cat} /mol contact time; (b) methane partial pressure effect at 650 °C and 600 min g_{cat} /mol contact time; (c) contact time effect at 0.1 atm methane partial pressure and 650 °C; (d) catalyst stability at 0.1 atm methane partial pressure, 650 °C, and 300 min g_{cat} /mol contact time.

hydrogen, as indicated by eq 1. From ca. 700 to 800 °C, methane conversion continued to increase, while ethane concentration decreased from ca. 2.5% to nearly 0. The hydrogen production rate from 700 to 900 °C, however, continued to increase, implying further dehydrogenation of methane and leading to coke formation. As reported in the literature, 25,36,37 not only initial activation of methane (CH₄ \rightarrow $CH_3 + H$) but also further dehydrogenation of methane (e.g., forming CH₂, CH, and C species) occurs over the Pt surface, owing to relatively low reaction barriers of C-H bond cleavage (<1 eV). Thus, in comparison to C-C coupling (reaction barrier typically >2 eV over a flat surface³⁸ and 1-2 eV over a step surface³⁹), Pt catalysts preferably promote further dehydrogenation of methane rather than C-C coupling,⁴ eventually forming coke, which is consistent with the 1% Pt curve in Figures 1 and 2a. In addition to the Pt surface, C-C coupling could also occur at acidic sites of ZSM-5, as reported previously.^{41,42} Since the 1% Pt/ZSM-5 catalyst, as described in Figures 1 and 2, did not lead to any C₂ product, the acidic site in ZSM-5 appears to be inactive for C-C coupling in NOCM conversion in the present study. Ethane dehydrogenation to ethylene and/or acetylene could occur over pure Pt surfaces.^{43,44} With the addition of a second metal to Pt, binding of molecules is typically weaker over bimetallic surfaces,^{45,46} indicating relatively higher reaction barriers. As reported in the literature, a shorter contact time favors lower reactivity of ethane dehydrogenation.47,48 These are likely reasons for the limited ethane dehydrogenation product in the present study.

Figure S3a,b shows temperature-programmed oxidation (TPO) profiles for used 1% Pt and used 1% Pt-0.8% Bi catalysts, respectively. Initial oxidation of used 1% Pt occurred at ca. 300 °C, followed by two clear peaks at 440 and 540 °C (see also Table S4). For used 1% Pt-0.8% Bi, however, only one distinguished peak was identified, although it was followed by slight dragging (indicating another small peak). As given in

Table S4, by integrating curves in Figure S3, accumulated coke amounts were obtained. Table S5, demonstrating various coke amount calculation methods, indicates good mass balance. The used 1% Pt-0.8% Bi contained much less coke (27 mg/g_{cat}) than used 1% Pt (497 mg/ g_{cat}). These observations suggest that by addition of Bi to Pt/ZSM-5 catalyst, methane was activated at relatively low temperature (600-700 °C), while further dehydrogenation of methane, leading to coke deposits, was suppressed owing to the less active Pt-Bi surface in comparison to the pure Pt surface.⁴⁹ In our prior works, Bi was used as a promoter for either tuning selectivity toward target products^{35,50} or improving catalyst stability.⁵¹ With the participation of guaiacol molecules over Pt-Bi catalysts, it was proposed that CH₄ decomposed on the Pt surface and methyls coupled to form ethane.⁵¹ It appears that, in the present work, Bi addition to Pt combines these two functions: promoting NOCM selectivity to ethane and extending catalyst lifetime.

Figure 4a shows temperature effects on NOCM over the range 500-700 °C. Similar to the case for Figure 3b, methane conversion increased with temperature while ethane selectivity decreased, reaching a maximum ethane yield (selectivity × conversion) of 1.8% at 650 °C. For standard operating conditions (Materials and Methods), the methane partial pressure was 0.1 atm. Figure 4b shows that 0.1-1 atm of methane partial pressure gave essentially the same C_2 selectivity yet higher methane conversion at lower methane partial pressure. This feature occurs when thermodynamics dominates NOCM conversion (Thermodynamic Considerations and Figure S5 in the Supporting Information). Figure 4c illustrates the contact time effect on NOCM conversion. When a long contact time was used, the main byproduct was aromatic coke, although small amounts of ethylene and benzene were detected as well. It has been proposed that, in all nonoxidative conversions of methane, C2 species were produced as intermediates for either higher hydrocarbon or coke formation.⁷ Thus, methane conversion typically follows the reaction

network series $CH_4 \rightarrow C_2H_6 \rightarrow C_xH_y$ (x > 2, y \geq 0). In the present work, since the intermediate $\dot{\mathrm{C}}_2$ species was the target product, as shown in Figure 4c, it exhibited a selectivity maximum at ca. 600 min g_{cat} /mol, as expected from kinetic analysis (Kinetic Considerations and Figure S6 in the Supporting Information). Figure 4d shows that, following an initial transient activation period, both methane conversion and selectivity toward ethane were stable over the entire 8 h test. Note that for longer TOS (24-48 h), methane conversion slowly dropped to ca. 1%, while ethane selectivity was still maintained at about >80%. In comparison to stable values at 1-8 h TOS, in the initial activation period it appears that methane conversion was higher (4-5%), while the ethane selectivity was lower (50-80%). This suggests that carbonaceous deposits occurred during the initial activation period. As reported in the literature, these deposits may contribute to nonoxidative dehydrogenation of light hydrocarbons.⁵²⁻⁵⁵ This is the likely reason for irregular higher conversion than equilibrium values at short TOS, which was also observed in other methane nonoxidative conversion publications.^{7,8,26,27} At long TOS, as shown in Figure 4d, the methane conversion decreased below equilibrium values.

In general, current technologies for direct transformation of methane are not followed industrially owing to inefficient carbon atom utilization. In the present report, we describe a heterogeneous catalytic process at relatively moderate temperatures (600–700 °C) for stable methane conversion into ethane with carbon selectivity >90% and methane conversion ~2%. This is a promising start toward technologies suitable for exploitation on the industrial scale.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b00156.

Materials and methods, definitions for methane conversion, product selectivity, and yield, thermodynamic considerations, kinetic considerations, notation, and tables and figures as described in the text (PDF)

AUTHOR INFORMATION

Corresponding Author

*A.V.: e-mail, avarma@purdue.edu; tel, 765-494-8484; fax, 765-494-0805.

ORCID 💿

Yang Xiao: 0000-0003-1705-2213 Arvind Varma: 0000-0002-3472-5929

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Kondratenko, E. V.; Peppel, T.; Seeburg, D.; Kondratenko, V. A.; Kalevaru, N.; Martin, A.; Wohlrab, S. Methane Conversion Into Different Hydrocarbons or Oxygenates: Current Status and Future Perspectives in Catalyst Development and Reactor Operation. *Catal. Sci. Technol.* **2017**, *7*, 366–381.

(2) Schwach, P.; Pan, X.; Bao, X. Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects. *Chem. Rev.* 2017, *117*, 8497–8520.

(3) Karakaya, C.; Kee, R. J. Progress in the Direct Catalytic Conversion of Methane to Fuels and Chemicals. *Prog. Energy Combust. Sci.* **2016**, *55*, 60–97.

(4) Galadima, A.; Muraza, O. Revisiting the Oxidative Coupling of Methane to Ethylene in the Golden Period of Shale Gas: A Review. *J. Ind. Eng. Chem.* **2016**, *37*, 1–13.

(5) Wang, L.; Tao, L.; Xie, M.; Xu, G.; Huang, J.; Xu, Y. Dehydrogenation and Aromatization of Methane under Non-oxidizing Conditions. *Catal. Lett.* **1993**, *21*, 35–41.

(6) Spivey, J. J.; Hutchings, G. Catalytic Aromatization of Methane. *Chem. Soc. Rev.* 2014, 43, 792–803.

(7) Wang, D.; Lunsford, J. H.; Rosynek, M. P. Catalytic Conversion of Methane to Benzene over Mo/ZSM-5. *Top. Catal.* **1996**, *3*, 289–297.

(8) Tessonnier, J.-P.; Louis, B.; Rigolet, S.; Ledoux, M. J.; Pham-Huu, C. Methane Dehydro-Aromatization on Mo/ZSM-5: About the Hidden Role of Brønsted Acid Sites. *Appl. Catal., A* **2008**, *336*, 79–88.

(9) Ismagilov, Z. R.; Matus, E. V.; Tsikoza, L. T. Direct Conversion of Methane on Mo/ZSM-5 Catalysts to Produce Benzene and hydrogen: achievements and perspectives. *Energy Environ. Sci.* 2008, 1, 526–541.

(10) Nishikawa, Y.; Ogihara, H.; Yamanaka, I. Liquid-Metal Indium Catalysis for Direct Dehydrogenative Conversion of Methane to Higher Hydrocarbons. *ChemistrySelect* **2017**, *2*, 4572–4576.

(11) Koerts, T.; Deelen, M. J.; van Santen, R. A. Hydrocarbon Formation from Methane by a Low-Temperature Two-Step Reaction Sequence. J. Catal. **1992**, *138*, 101–114.

(12) Wu, M.-C.; Lenz-Solomun, P.; Goodman, D. W. Two-step, Oxygen-Free Route to Higher Hydrocarbons from Methane over Ruthenium Catalysts. J. Vac. Sci. Technol., A 1994, 12, 2205–2209.

(13) Guczi, L. Non-oxidative Methane Coupling over Co-Pt/NaY Bimetallic Catalysts. *Catal. Lett.* **1996**, *39*, 43–47.

(14) Wang, L.; Xu, Y.; Wong, S.-T.; Cui, W.; Guo, X. Activity and Stability Enhancement of MoHZSM-5-based Catalysts for Methane Non-Oxidative Transformation to Aromatics and C_2 Hydrocarbons: Effect of Additives and Pretreatment Conditions. *Appl. Catal., A* **1997**, 152, 173–182.

(15) Amariglio, A.; Belgued, M.; Pareja, P.; Amariglio, H. Oxygenfree Conversion of Methane to Higher Hydrocarbons through a Dual-Temperature Two-Step Reaction Sequence on Platinum and Ruthenium: 1. Chemisorption of CH_4 at a Fixed Temperature. *J. Catal.* **1998**, *177*, 113–120.

(16) Tshabalala, T. E.; Coville, N. J.; Scurrell, M. S. Methane Dehydroaromatization over Modified Mn/H-ZSM-5 Zeolite Catalysts: Effect of Tungsten as a Secondary Metal. *Catal. Commun.* **2016**, *78*, 37–43.

(17) Belgued, M.; Pareja, P.; Amariglio, A.; Amariglio, H. Conversion of Methane into Higher Hydrocarbons on Platinum. *Nature* **1991**, *352*, 789–790.

(18) Soulivong, D.; Norsic, S.; Taoufik, M.; Coperet, C.; Thivolle-Cazat, J.; Chakka, S.; Basset, J.-M. Non-Oxidative Coupling Reaction of Methane to Ethane and Hydrogen Catalyzed by the Silica-Supported Tantalum Hydride:SiO₂Ta-H. *J. Am. Chem. Soc.* **2008**, *130*, 5044–5045.

(19) Guo, X.; Fang, G.; Li, G.; Ma, H.; Fan, H.; Yu, L.; Ma, C.; Wu, X.; Deng, D.; Wei, M.; Tan, D.; Si, R.; Zhang, S.; Li, J.; Sun, L.; Tang,

Z.; Pan, X.; Bao, X. Direct, Nonoxidative Conversion of Methane to Ethylene, Aromatics, and Hydrogen. *Science* **2014**, *344*, 616–619.

(20) Gerceker, D.; Motagamwala, A. H.; Rivera-Dones, K. R.; Miller, J. B.; Huber, G. W.; Mavrikakis, M.; Dumesic, J. A. Methane Conversion to Ethylene and Aromatics on PtSn Catalysts. *ACS Catal.* **2017**, *7*, 2088–2100.

(21) Ertl, G.; Knozinger, H.; Schuth, F.; Weitkamp, J. Handbook of Heterogeneous Catalysis: 3.1.2 Particle Size and Dispersion Measurements, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2008; Vol. 1, pp 738–765.

(22) Benson, J. E.; Boudart, M. Hydrogen-Oxygen Titration Method for the Measurement of Supported Platinum Surface Areas. *J. Catal.* **1965**, *4*, 704–710.

(23) Baerlocher, C.; McCusker, L. B.; Olson, D. H. MFI - Pnma. *Atlas of Zeolite Framework Types*, 6th ed.; Elsevier Science: Amsterdam, The Netherlands, 2007; pp 212–213.

(24) Zhu, Z.; Lu, G.; Guo, Y.; Guo, Y.; Zhang, Z.; Wang, Y.; Gong, X.-Q. High Performance and Stability of the Pt-W/ZSM-5 Catalyst for the Total Oxidation of Propane: the Role of Tungsten. *ChemCatChem* **2013**, *5*, 2495–2503.

(25) Li, Y.; Li, D.; Wang, G. Methane Decomposition to CO_x -free Hydrogen and Nano-Carbon Material on Group 8–10 Base Metal Catalysts: a Review. *Catal. Today* **2011**, *162*, 1–48.

(26) Weckhuysen, B. M.; Rosynek, M. P.; Lunsford, J. H. Characterization of Surface Carbon Formed During the Conversion of Methane to Benzene over Mo/H-ZSM-5 Catalysts. *Catal. Lett.* **1998**, *52*, 31–36.

(27) Fila, V.; Bernauer, M.; Bernauer, B.; Sobalik, Z. Effect of Addition of a Second Metal in Mo/ZSM-5 Catalyst for Methane Aromatization Reaction under Elevated Pressures. *Catal. Today* **2015**, 256, 269–275.

(28) Kimura, H.; Tsuto, K.; Wakisaka, T.; Kazumi, Y.; Inaya, Y. Selective Oxidation of Glycerol on a Platinum-Bismuth Catalyst. *Appl. Catal., A* **1993**, *96*, 217–228.

(29) Villa, A.; Campisi, S.; Chan-Thaw, C. E.; Motta, D.; Wang, D.; Prati, L. Bismuth Modified Au-Pt Bimetallic Catalysts for Dihydroxyacetone Production. *Catal. Today* **2015**, *249*, 103–108.

(30) Paffett, M. T.; Campbell, C. T.; Taylor, T. N. The Influence of Adsorbed Bi on the Chemisorption Properties of Pt(111): H₂, CO, and O₂. J. Vac. Sci. Technol., A **1985**, 3, 812–816.

(31) Windham, R. G.; Koel, B. E.; Paffett, M. T. Studies of the Ensemble Size Requirements for Ethylene Adsorption and Decomposition on Platinum(111): Ethylene and Bismuth Coadsorption. *Langmuir* **1988**, *4*, 1113–1118.

(32) Gomez, R.; Feliu, J. M.; Aldaz, A. Effects of Irreversibly Adsorbed Bismuth on Hydrogen Adsorption and Evolution on Pt(111). *Electrochim. Acta* **1997**, *42*, 1675–1683.

(33) Pasti, I. A.; Mentus, S. V. Modification of Electronic Properties of Pt(111) Surface by Means of Alloyed and Adsorbed Metals: DFT Study. *Russian Journal of Physical Chemistry A* **2009**, *83*, 1531–1536.

(34) Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff; Norskov, J. K. Computational High-throughput Screening of Electrocatalytic Materials for Hydrogen Evolution. *Nat. Mater.* **2006**, *5*, 909–913.

(35) Hu, W.; Knight, D.; Lowry, B.; Varma, A. Selective Oxidation of Glycerol to Dihydroxyacetone over Pt-Bi/C Catalyst: Optimization of Catalyst and Reaction Conditions. *Ind. Eng. Chem. Res.* **2010**, *49*, 10876–10882.

(36) Vines, F.; Lykhach, Y.; Staudt, T.; Lorenz, M. P. A.; Papp, C.; Steinruck, H.-P.; Libuda, J.; Neyman, K. M.; Gorling, A. Methane Activation by Platinum: Critical Role of Edge and Corner Sites of Metal Nanoparticles. *Chem. - Eur. J.* **2010**, *16*, 6530–6539.

(37) Lin, Y.-Z.; Sun, J.; Yi, J.; Lin, J.-D.; Chen, H.-B.; Liao, D.-W. Energetics of Chemisorption and Conversion of Methane on Transition Metal Surfaces. *J. Mol. Struct.:* THEOCHEM **2002**, 587, 63–71.

(38) Cheng, J.; Hu, P.; Ellis, P.; French, S.; Kelly, G.; Lok, C. M. Chain Growth Mechanism in Fischer–Tropsch Synthesis: a DFT Study of C-C Coupling over Ru, Fe, Rh, and Re Surfaces. *J. Phys. Chem.* C 2008, *112*, 6082–6086.

(39) Yang, M.-L.; Zhu, Y.-A.; Fan, C.; Sui, Z.-J.; Chen, D.; Zhou, X.-G. DFT Study of Propane Dehydrogenation on Pt Catalyst: Effects of Step Sites. *Phys. Chem. Chem. Phys.* **2011**, *13*, 3257–3267.

(40) Wei, J.; Iglesia, E. Mechanism and Site Requirements for Activation and Chemical Conversion of Methane on Supported Pt Clusters and Turnover Rate Comparisons among Noble Metals. *J. Phys. Chem. B* **2004**, *108*, 4094–4103.

(41) Lukyanov, D. B.; Gnep, N. S.; Guisnet, M. R. Kinetic Modeling of Propane Aromatization Reaction over HZSM-5 and GaHZSM-5. *Ind. Eng. Chem. Res.* **1995**, *34*, 516–523.

(42) Vosmerikova, L. N.; Zaikovskii, V. I.; Volynkina, A. N.; Vosmerikov, A. V. Deactivation Features of Gallium-Containing Zeolites in the Propane Aromatization Process. *Pet. Chem.* **2017**, *57*, 85–92.

(43) Galvita, V.; Siddiqi, G.; Sun, P.; Bell, A. T. Ethane Dehydrogenation on Pt/Mg(Al)O and PtSn/Mg(Al)O Catalysts. J. *Catal.* **2010**, 271, 209–219.

(44) Wegener, E. C.; Wu, Z.; Tseng, H.-T.; Gallagher, J. R.; Ren, Y.; Diaz, R. E.; Ribeiro, F. H.; Miller, J. T. Structure and Reactivity of Pt-In Intermetallic Alloy Nanoparticles: Highly Selective Catalysts for Ethane Dehydrogenation. *Catal. Today* **2018**, *299*, 146–153.

(45) Greeley, J.; Norskov, J. K. Combinatorial Density Functional Theory-Based Screening of Surface Alloys for the Oxygen Reduction Reaction. J. Phys. Chem. C **2009**, 113, 4932–4939.

(46) Hook, A.; Massa, J. D.; Celik, F. E. Effect of Tin Coverage on Selectivity for Ethane Dehydrogenation over Platinum-Tin Alloys. *J. Phys. Chem. C* **2016**, *120*, 27307–27318.

(47) Wu, J.; Sharada, S. M.; Ho, C.; Hauser, A. W.; Head-Gordon, M.; Bell, A. T. Ethane and Propane Dehydrogenation over PtIr/Mg(Al)O. *Appl. Catal., A* **2015**, *506*, 25–32.

(48) Yu, Z.; Sawada, J. A.; An, W.; Kuznicki, S. M. PtZn-ETS-2: a Novel Catalyst for Ethane Dehydrogenation. *AIChE J.* **2015**, *61*, 4367–4376.

(49) Pasti, I.; Mentus, S. DFT Study of Adsorption of Hydrogen and Carbon Monoxide on $Pt_xBi_{1-x}/Pt(111)$ Bimetallic Overlayers: Correlation to Surface Electronic Properties. *Phys. Chem. Chem. Phys.* **2009**, *11*, 6225–6233.

(50) Xiao, Y.; Greeley, J.; Varma, A.; Zhao, Z.-J.; Xiao, G. An Experimental and Theoretical Study of Glycerol Oxidation to 1,3-Dihydroxyacetone over Bimetallic Pt-Bi Catalysts. *AIChE J.* **2017**, *63*, 705–715.

(51) Xiao, Y.; Varma, A. Catalytic Deoxygenation of Guaiacol Using Methane. ACS Sustainable Chem. Eng. 2015, 3, 2606–2610.

(52) Amano, H.; Sato, S.; Takahashi, R.; Sodesawa, T. Dehydrogenation of Cyclohexene over Carbon Deposited on Alumina. *Phys. Chem. Chem. Phys.* **2001**, *3*, 873–879.

(53) McGregor, J.; Huang, Z.; Parrott, E. P.; Zeitler, J. A.; Nguyen, K. L.; Rawson, J. M.; Carley, A.; Hansen, T. W.; Tessonnier, J.-P.; Su, D. S.; Teschner, D.; Vass, E. M.; Knop-Gericke, A.; Schlogl, R.; Gladden, L. F. Active Coke: Carbonaceous Materials as Catalysts for Alkane Dehydrogenation. J. Catal. **2010**, 269, 329–339.

(54) Nederlof, C.; Kapteijn, F.; Makkee, M. Catalysed Ethylbenzene Dehydrogenation in CO_2 or N_2 -Carbon Deposits as the Active Phase. *Appl. Catal., A* **2012**, *417–418*, 163–173.

(55) Collett, C. H.; McGregor, J. Things Go Better with Coke: the Beneficial Role of Carbonaceous Deposits in Heterogeneous Catalysis. *Catal. Sci. Technol.* **2016**, *6*, 363–378.

Supporting Information

Highly Selective Non-oxidative Coupling of Methane

over Pt-Bi Bimetallic Catalysts

Yang Xiao and Arvind Varma*

Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-2100,

U.S.A

E-mail: avarma@purdue.edu

Phone: 765-494-8484. Fax: 765-494-0805

^{*}To whom correspondence should be addressed

Materials and Methods

The chloroplatinic acid hexahydrate (99.9% metal basis) and bismuth (III) chloride (99.999%), both from Sigma Aldrich, were used as precursors for Pt and Bi, respectively. ZSM-5 (Si/Al=40) of ammonium form, from Zeolyst International, was transformed to the H-form (H-ZSM-5) by calcining in air at 500 °C for 4 hrs. The Pt-Bi catalysts were prepared by the following procedure as described in our prior works.^[1–3] Pt and Bi were loaded sequentially by the wet impregnation method. Briefly, Pt and Bi precursors were dissolved in dilute HCl solution with pH=5-6 and then added dropwise to the well-stirred ZSM-5 slurry, with continued stirring for 8 hrs at room temperature (20 °C). The slurry was then rinsed two times and dried in air at 100 °C before use for catalytic performance tests. Benzene (99%), from Alfa Aesar, was used as standard for GC calibration. Ultra high purity grade gases (99.98% O₂, 99.999% Ar, 99.99% CH₄, 99.99% C₂H₆, 99.99% C₂H₄, 99.999% N₂, 99.98% He and 99.999% H₂) were purchased from Indiana Oxygen. The 0.5% Pt/Al₂O₃ (metal dispersion=31 \pm 0.5%) standard, from Micromeritics, was used for calibration in H₂ chemisorption and H₂-O₂ titration experiments.

Various Pt-Bi catalysts used in the present work were characterized by BET (Brunauer-Emmett-Teller), H₂-TPD (temperature-programmed desorption), TPSR (temperature-programmed surface reaction), H₂-O₂ titration, ICP-AES (Inductively coupled plasma - atomic emission spectroscopy), TEM (transmission electron microscope), and powder XRD (X-ray Diffraction) techniques.

By N₂ adsorption and desorption at 77 K via a Micromeritics ASAP 2000 apparatus, BET measurements were conducted, giving physisorption properties of catalysts, including surface area, pore size and pore volume. Before measurements, degassing was carried out at 300 °C for 8 hrs. For bimetallic Pt-Bi catalysts supported on ZSM-5, both H₂ chemisorption and H₂-O₂ titration were carried out at room temperature. It was found that Pt metal dispersion values from both techniques were close (e.g. for 1 wt% Pt-0.8 wt%Bi, H₂ chemisorption value 22.2%, while H₂-O₂ titration value 23.1%). This is likely because at room temperature, Bi does not adsorb H₂ molecule, ^[4] and bismuth oxide does not react with H₂.^[5] Since H₂-O₂ titration gives higher sensi-

tivity than H_2 chemisorption,^[6] Pt dispersion was obtained by the H_2 -O₂ titration approach in the present work.

The TEM scans were operated at 200 kV with LaB₆ source (FEI-Tecnai). The TEM samples were prepared by suspending fine catalyst particles in ethanol, followed by dispersing them on 200 copper mesh grids with lacey carbon film coating, and then drying in air at room temperature. The powder XRD was carried out on a Rigaku SmartLab X-ray diffractometer with a CuK α radiation source. Elemental analysis of catalysts was carried out by the ICP-AES method (SPECTRO Instrument). For H₂-TPD tests, 5 vol% H₂ and 5 vol% O₂ in N₂, prepared in situ by adjusting flow rates via mass flow controllers, were used as oxidation and reduction gases, respectively. The standard H₂-TPD procedure included the following steps:

(i) Drying the sample at 200 $^{\circ}$ C in 5 vol% O₂ for 1 hr;

(ii) Reducing the sample at 400 $^{\circ}$ C in 5 vol% H₂ for 2 hr;

(iii) Feeding 5 vol% H₂ at room temperature for 2 hrs;

(iv) TPD measurements by increasing temperature from room temperature to 150 °C.

The heating rate was 5 °C/min, the standard catalyst packed weight was 0.50 g, and the total gas flow rate was 100 mL/min. The H₂ desorption was measured by a binary gas analyzer equipped with a thermal conductivity detector (TCD). For TPSR experiments, the catalyst was reduced using 5 vol% H₂ at 400 °C for 2 hrs before the TPSR measurement. Upon cooling to room temperature, a 5% CH₄ in N₂ gas mixture flow was fed at 20 mL/min, and the temperature was increased from room temperature to 900 °C at a heating rate 5 °C/min. A TCD was used to detect products. In the TPO process, 5% O₂ in N₂ gas mixture was used as the oxidizing gas. The used catalysts were packed in the reactor for TPO measurements without any pretreatment. The heating rate was 5 °C/min as well.

The catalytic performance tests were conducted in a fixed-bed reactor. Prior to reaction, the packed catalyst was activated at 400 °C for 4 hours under a gas mixture flow (H₂:N₂ = 1:2). The reactor was then purged by 50 mL/min N₂ for 15 min. The standard operating conditions were: 650 °C, 0.1 atm methane partial pressure, 0.50 g catalyst and 600 min g_{cat} /mol contact time. In

typical cases, following an initial transient period, the catalyst exhibited stable performance for several hours (3-6). Unless stated otherwise, all data sets were taken at 1 hr time on stream (TOS) during the stable period.

Blank tests of ZSM-5 support with no Pt or Bi loading were carried out under standard operating conditions, with methane conversion always less than 0.01%. A GC (Agilent GC6890) with both flame ionization detector (FID) and TCD, equipped with a Carboxen 1010 PLOT capillary column (30 m × 0.53 mm) was used for quantitative analysis of products. For detectable products (ethane, ethylene, benzene), Eqs. (1-3) were used to calculate methane conversion, product selectivity and yield, while for coke, mass balance was used to determine its selectivity and yield (*carbon of methane* – \sum *carbon of detectable products*). As shown in Table S5, whereas coke amount is calculated from CO₂ measured in TPO profiles, this approach is typically consistent with TPO mass measurements. All experiments were repeated at least twice and good repeatability, generally within less than 2% deviation, was achieved for all quantitative analysis.

Definitions for Methane Conversion, Product Selectivity and Yield

Methane conversion, product selectivity and yield are defined by Eqs. (1-3).

$$Methane\ Conversion\ =\ \frac{mol\ of\ Converted\ Methane}{mol\ of\ Methane\ Feed}\tag{1}$$

$$Product \ Selectivity = \frac{mol \ of \ Formed \ Product}{mol \ of \ Converted \ Methane}$$
(2)

$$Product Yield = \frac{mol \ of \ Formed \ Product}{mol \ of \ Methane \ Feed}$$
(3)

Thermodynamic Considerations

Regarding the main conversion in the present work, as described by Eqs. (4 - 5), the equilibrium methane conversion is calculated based on standard Gibbs formation energy of chemical species, provided by NIST JANAF database (http://kinetics.nist.gov/janaf/).

$$CH_4 \longrightarrow 0.5C_2H_6 + 0.5H_2 \tag{4}$$

$$CH_4 \longrightarrow 0.5C_2H_4 + H_2$$
 (5)

For a general reaction as described by Eq. (6), where C_i is chemical species i and α_i is the stoichiometric coefficient of C_i , the Gibbs free energy change ($\Delta_r G^0$) is calculated by Eq. (7),

$$\sum_{i} \alpha_{i} C_{i} = 0 \tag{6}$$

$$\Delta_r G^0 = \sum_i \alpha_i G_{f_i}^0 \tag{7}$$

The equilibrium constant of Eq. (6) is calculated by Eqs. (8 - 10).

$$\Delta_r G^0 = -RT \left(lnK \right) \tag{8}$$

$$K = exp\left(-\frac{\Delta_r G^0}{RT}\right) \tag{9}$$

$$K = \prod \left(\frac{P_i}{P_0}\right)^{\alpha_i} \tag{10}$$

Based on the above calculations, effects of temperature and methane partial pressure on methane equilibrium conversion to C_2 species are plotted in Figures S4 and S5, respectively. As shown in Figure S4, methane equilibrium conversion to C_2 species is about 2-3% at 650 °C, which is consistent with prior literature report.^[7] Note that equilibrium conversion values could be slightly

different, depending on the data set used for Gibbs formation energies of methane, ethane/ethylene and hydrogen. Also note that higher than equilibrium conversion is typically observed for methane non-oxidative reaction at short time on stream (TOS) in the literature.^[8–11] For consistency, all data reported in our work for catalytic performance comparison was taken at 1 hour TOS. As shown in Figure S5, at a given temperature (e.g. 650 °C), lower methane initial partial pressure leads to higher equilibrium methane conversion.

Kinetic Considerations

For the non-oxidative conversion of methane in the present work, C_2H_6 is the target product, while C_xH_y ($x > 2, y \ge 0$, e.g. C_6H_6 and C_2H_4) is formed as byproduct. Thus C_2H_6 is an intermediate in other hydrocarbon formation from methane, resulting in the series reaction network, described by Eq. (11)

$$CH_4(A) \xrightarrow{k_1} C_2H_6(B) \xrightarrow{k_2} C_xH_y(C)(x > 2, y \ge 0)$$
(11)

To qualitatively analyze product profiles for NOCM, both reactions in Eq. (11) are assumed to be first-order. In a continuous flow fixed-bed reactor, the following mass balance Eqs. (12 - 14) are obtained.

$$\frac{dF_A}{dW} = -k_1 P_A \tag{12}$$

$$\frac{dF_B}{dW} = k_1 P_A - k_2 P_B \tag{13}$$

$$\frac{dF_C}{dW} = k_2 P_B \tag{14}$$

leading to

$$F_A + F_B + F_C = F_{A_0} \tag{15}$$

where

$$P_i = F_i \times \frac{P_0}{F_{A0}} \tag{16}$$

By solving Eqs. (12 - 16), the following Eqs. (17 - 19) are obtained.

$$F_A = F_{A0} e^{-k_1 \tau}$$
, where $\tau = \frac{P_0}{F_{A0}} W$ (17)

$$F_{B} = \frac{F_{A0}k_{1}}{k_{2} - k_{1}} \left(e^{-k_{1}\tau} - e^{-k_{2}\tau} \right), \text{ for } k_{1} \neq k_{2}$$

$$F_{B} = F_{A0}k_{1}\tau e^{-k_{1}\tau}, \text{ for } k_{1} = k_{2}$$
(18)

$$F_C = F_{A0} - F_A - F_B \tag{19}$$

Considering various k_2/k_1 ratios, Figure S6 is plotted to show profiles of CH₄, C₂H₆ and C_xH_y at various dimensionless contact times ($k_1 \tau$). Figure S6 demonstrates that for all k_2/k_1 ratios, C₂H₆ exhibits a maximum at a specific contact time, depending on the k_2/k_1 value. When increasing k_2/k_1 value, the maximum shifts to the left (lower contact time), while the peak height decreases.

Notation

C_i	Chemical species i
F_0	Feed flow rate
F_i	Flowrate of species i
$G_{f_i}^0$	Standard gibbs formation energy of chemical species i
K	Equilibrium constant
k _i	Reaction rate constant of step i
P_0	Total pressure
P_i	Partial pressure of species i
R	Gas constant, 8.314 $J \cdot K^{-1} \cdot mol^{-1}$
Т	Temperature
W	Catalyst packing amount
X	Methane conversion
$k_1 \ au$	Dimensionless contact time, $k_1 P_0 W / F_{A0}$
Greek Letters:	
$lpha_i$	Stoichiometric coefficient of C_i
$\Delta_r G^0$	Reaction standard gibbs energy change

References

- Hu, W.; Knight, D.; Lowry, B.; Varma, A. Selective Oxidation of Glycerol to Dihydroxyacetone over Pt-Bi/C Catalyst: Optimization of Catalyst and Reaction Conditions. *Industrial & Engineering Chemistry Research* 2010, 49, 10876–10882.
- 2. Xiao, Y.; Varma, A. Catalytic Deoxygenation of Guaiacol Using Methane. ACS Sustainable Chemistry & Engineering 2015, 3, 2606–2610.
- Xiao, Y.; Greeley, J.; Varma, A.; Zhao, Z.-J.; Xiao, G. An Experimental and Theoretical Study of Glycerol Oxidation to 1,3-Dihydroxyacetone over Bimetallic Pt-Bi Catalysts. *AIChE Journal* 2017, *63*, 705–715.
- Paffett, M. T.; Campbell, C. T.; Windham, R. G.; Koel, B. E. A Multitechnique Surface Analysis Study of the Adsorption of H₂, CO and O₂ on BiPt(111) Surfaces. *Surface Science* **1989**, 207, 274 – 296.
- Shang, Z.; Sun, M.; Chang, S.; Che, X.; Cao, X.; Wang, L.; Guo, Y.; Zhan, W.; Guo, Y.; Lu, G. Activity and Stability of Co₃O₄-based Catalysts for Soot Oxidation: the Enhanced Effect of Bi₂O₃ on Activation and Transfer of Oxygen. *Applied Catalysis B: Environmental* **2017**, *209*, 33 – 44.
- Benson, J. E.; Boudart, M. Hydrogen-Oxygen Titration Method for the Measurement of Supported Platinum Surface Areas. *Journal of Catalysis* 1965, *4*, 704 710.

- Sheng, H. F.; Lobo, R. F. Non-oxidative Coupling of Methane to Ethylene Using Mo₂C/[B]ZSM-5. *ChemPhysChem* 2018, 19, 1–19.
- Wang, D.; Lunsford, J. H.; Rosynek, M. P. Catalytic Conversion of Methane to Benzene over Mo/ZSM-5. *Topics in Catalysis* 1996, *3*, 289–297.
- Weckhuysen, B. M.; Rosynek, M. P.; Lunsford, J. H. Characterization of Surface Carbon Formed During the Conversion of Methane to Benzene over Mo/H-ZSM-5 Catalysts. *Catalysis Letters* 1998, 52, 31–36.
- Tessonnier, J.-P.; Louis, B.; Rigolet, S.; Ledoux, M. J.; Pham-Huu, C. Methane Dehydro-Aromatization on Mo/ZSM-5: About the Hidden Role of Brønsted Acid Sites. *Applied Catalysis A: General* 2008, *336*, 79 – 88.
- Fila, V.; Bernauer, M.; Bernauer, B.; Sobalik, Z. Effect of Addition of a Second Metal in Mo/ZSM-5 Catalyst for Methane Aromatization Reaction under Elevated Pressures. *Catalysis Today* 2015, *256, Part 2*, 269 – 275.

Catalyst (wt%)	BET Surface Area, m^2/g	Pore Size, nm	Pore Volume, cm^3/g
1% Pt	412	3.1	0.38
1% Pt-0.1% Bi	409	3.5	0.41
1% Pt-0.2% Bi	388	2.9	0.31
1% Pt-0.5% Bi	391	3.0	0.35
1% Pt-0.8% Bi	372	3.2	0.37
1% Pt-1% Bi	383	3.4	0.33
1% Bi	407	2.8	0.39
ZSM-5	402	3.4	0.37
Used 1% Pt	234	1.3	0.14
Used 1% Pt-0.8% Bi	329	2.3	0.31

Table S1: BET Results for Pt-Bi Bimetallic Catalysts Supported on ZSM-5

	Par	ticle Size, nm	
Catalyst (wt%)	TEM	H ₂ -O ₂ Titration	Pt Dispersion
1% Pt	2.9	3.3	28.9
1% Pt-0.1% Bi	3.2	3.4	27.1
1% Pt-0.2% Bi	3.4	3.4	26.3
1% Pt-0.5% Bi	3.7	3.5	25.4
1% Pt-0.8% Bi	3.8	3.6	23.1
1% Pt-1% Bi	4.1	3.8	22.0
1% Bi	3.6	-	-
Used 1% Pt	-	5.9	16.4
Used 1% Pt-0.8% Bi	-	4.1	20.2

Table S2: TEM and H_2 - O_2 Titration Results for Pt-Bi Bimetallic Catalysts Supported on ZSM-5

	Fresh		Used	
Catalyst	Pt %	Bi %	Pt %	Bi %
1%Pt	0.97	-	0.95	-
1% Pt-0.1% Bi	1.01	0.12	0.97	0.11
1% Pt-0.2% Bi	0.99	0.23	0.97	0.19
1% Pt-0.5% Bi	0.98	0.52	0.96	0.48
1% Pt-0.8% Bi	0.96	0.78	0.95	0.77
1% Pt-1% Bi	0.97	0.98	0.94	0.94
1% Bi	-	1.02	-	0.99

Table S3: AES-ICP Element Analysis for Pt-Bi Bimetallic Catalysts Supported on ZSM-5

Catalyst (wt%)	Peak I, °C	Peak II, °C	Accumulated Coke, mg/g_{cat}
Used 1% Pt	440	540	497
Used 1% Pt-0.8% Bi	440	-	27

Table S4: Peak Positions and Coke Amounts from Temperature-Programmed Oxidation (TPO)

Mass, g	1% Pt	1% Pt-0.8% Bi
fresh (m_1)	0.50	0.50
used before TPO (m_2)	0.74	0.53
used after TPO (m_3)	0.52	0.49
m ₂ -m ₁	0.24	0.03
m ₂ -m ₃	0.22	0.04
carbon of methane $-\sum carbon of detectable products$	0.26	0.02

Table S5: Comparison of Various Coke Amount Calculations

Captions for Figures

- S1 TEM Scans of Various ZSM-5 Supported Catalysts: a) 1% Pt, b) 1% Pt-0.2% Bi,c) 1% Pt-0.8% Bi and d) 1% Bi Catalysts
- S2 XRD Patterns for (a) 1% Pt, (b) 1% Pt-0.1% Bi, (c) 1% Pt-0.2% Bi, (d) 1% Pt-0.5% Bi, (e) 1% Pt-0.8% Bi, (f) 1% Pt-1% Bi, (g) 1% Pt-2% Bi, (h) Unsupported ZSM-5, (i) Used 1% Pt and (j) Used 1% Pt-0.8% Bi Catalysts
- S3 Temperature-Programmed Oxidation (TPO) Profiles for (a) Used 1% Pt and (b)Used 1% Pt-0.8% Bi Catalysts
- S4 Effect of Temperature on Equilibrium Methane Conversion to Ethane and Ethylene at 1 atm Methane Partial Pressure
- S5 Effect of Methane Partial Pressure on Equilibrium Methane Conversion to Ethane and Ethylene at 650 $^{\circ}$ C
- S6 Simplified Kinetic Analysis for Conversion in Non-oxidative Coupling of Methane



Figure S1: TEM Scans of Various ZSM-5 Supported Catalysts: a) 1% Pt, b) 1% Pt-0.2% Bi, c) 1% Pt-0.8% Bi and d) 1% Bi Catalysts



Figure S2: XRD Patterns for (a) 1% Pt, (b) 1% Pt-0.1% Bi, (c) 1% Pt-0.2% Bi, (d) 1% Pt-0.5% Bi, (e) 1% Pt-0.8% Bi, (f) 1% Pt-1% Bi, (g) 1% Pt-2% Bi, (h) Unsupported ZSM-5, (i) Used 1% Pt and (j) Used 1% Pt-0.8% Bi Catalysts



Figure S3: Temperature-Programmed Oxidation (TPO) Profiles for (a) Used 1% Pt and (b) Used 1% Pt-0.8% Bi Catalysts



Figure S4: Effect of Temperature on Equilibrium Methane Conversion to Ethane and Ethylene at 1 atm Methane Partial Pressure



Figure S5: Effect of Methane Partial Pressure on Equilibrium Methane Conversion to Ethane and Ethylene at 650 $^\circ$ C



Figure S6: Simplified Kinetic Analysis for Conversion in Non-oxidative Coupling of Methane