

The Selective High-Yield Conversion of Methane Using Iodine-Catalyzed Methane Bromination

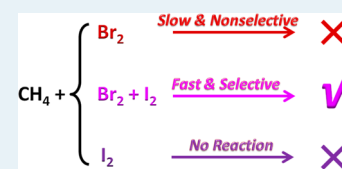
Kunlun Ding, Horia Metiu, and Galen D. Stucky*

Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510, United States

Supporting Information

ABSTRACT: Methyl bromide is used as feed in a process that converts it to gasoline. It is prepared by the gas-phase reaction of CH_4 with Br_2 , a reaction that produces, besides the desired CH_3Br , large amounts of CH_2Br_2 . The latter cokes the catalyst used for gasoline production. The separation of CH_2Br_2 by distillation makes gasoline production too expensive. It is therefore important to increase the selectivity of the bromination reaction. We show that a small amount of I_2 catalyzes the reaction $\text{CH}_2\text{Br}_2 + \text{CH}_4 \rightarrow 2\text{CH}_3\text{Br}$, which leads to higher CH_4 conversion and higher selectivity to CH_3Br . These findings are promising for developing a low-cost integrated bromine–iodine based dual-halogen pathway to convert stranded natural gas into fuels and chemicals.

KEYWORDS: gas-to-liquid, methane bromination, dibromomethane, iodine catalysis



INTRODUCTION

Most natural gas reserves are located far from industrial and population centers, and transportation costs hinder its efficient utilization. Conversion of natural gas into a liquid, at the site of origin, would be an ideal solution for transport to distant places where it can be used.^{1–3} Most stranded gas fields are too small for use in the current gas-to-liquid technology, which is economical only if the plants are of very large size, mainly because of the high energy cost of the production of the synthesis gas intermediate via the reforming reactions (steam reforming and dry reforming).

A low-temperature, high-yield process using a small facility that can be located close to the stranded natural gas source is desirable. In the past few decades, several direct conversion methods have been developed, including thermal and catalytic pyrolysis,^{4,5} oxidative coupling,^{6,7} selective oxidation to methanol,^{8,9} and others.^{10,11} However none is sufficiently economical for commercial use.

The use of halogens in the first step in natural gas conversion has been studied for many years.^{12–18} A typical halogen-based process consists of three steps: methane halogenation, the conversion of methyl halide to higher hydrocarbon or methanol/dimethyl ether, and halogen regeneration.^{16–18} The oxygen- and halogen-based processes for natural gas conversion as well as their energy profiles are illustrated in Figure 1. Compared to the synthesis gas-based GTL process, a halogen process has advantages. First, the whole process can be carried out at rather low temperatures; second, no highly exothermic and endothermic reactions are involved in the process (Figure 1c); third, no oxygen plant is required.

Bromine is the most suitable halogen for methane activation because of higher equilibrium conversion and methyl bromide selectivity and easier regeneration from HBr .¹⁴ Typically, at a temperature of 525 °C and a CH_4/Br_2 ratio of 1, the selective conversion of methane to methyl bromide is 70–80% with the byproducts being primarily dibromomethane and small amounts of tribromomethane.

The formation of polybromomethanes during bromination is a serious problem, if the bromination products are used as feed for a catalytic carbon-coupling reaction to produce higher hydrocarbons,¹⁹ because the polybromomethanes deactivate the catalyst. Separation of these polybromomethanes prior to introduction into the coupling reactor makes the bromine-based methane conversion process more expensive.

The success of halogen-assisted methane activation hinges on the ability to produce CH_3Br with highest selectivity (against CH_2Br_2). In this article we show that the addition of a small amount of I_2 catalyzes the reaction of Br_2 with CH_4 and accelerates the reaction kinetics as equilibrium is approached. Higher methane conversion and methyl bromide selectivity can be achieved at a comparatively short reaction time. Gas-phase I_2 in these experiments satisfies the traditional definition of a catalyst: it participates in the reaction but it is not consumed by it. The idea of using I_2 as a catalyst was suggested by our previous work^{20,21} in which I_2 catalyzed the reaction of CH_2Br_2 with propane to produce CH_3Br and other compounds.

EXPERIMENTAL SECTION

The reactions described here were performed in a glass tube at atmospheric pressure. The configuration of the reaction system is illustrated in Supporting Information, Figure S1. Argon was used as the carrier gas. CH_4 , HBr , and Ar flow rates were controlled by mass flow controllers. I_2 was dissolved in liquid Br_2 or in liquid CH_2Br_2 (depending on the kind of experiment performed) and delivered by syringe pump. The liquid was vaporized in the head space of the reactor. The effluent stream from the reactor was passed through a fritted glass bubbler trap containing an organic solution (10 wt % octadecane in hexadecane) and a 4 M NaOH

Received: November 30, 2012

Revised: February 4, 2013

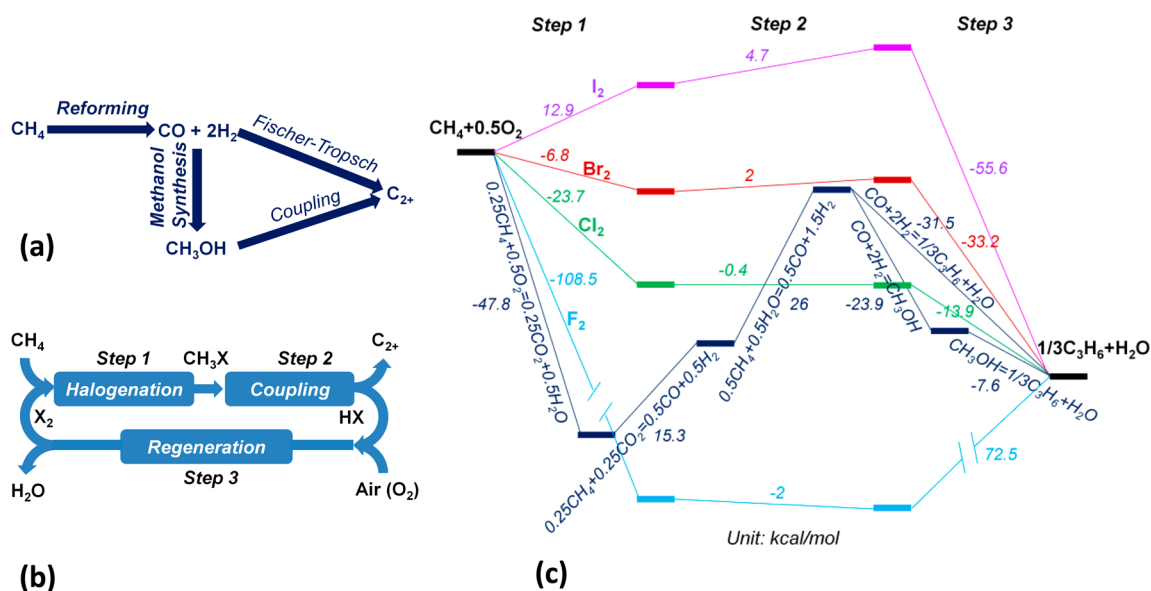


Figure 1. Illustration of the oxygen-based (a) and halogen-based (b) methane upgrading processes for the production of higher hydrocarbons; (c) Energy profiles of the oxygen-based and halogen-based methane upgrading processes at 327 °C. Here we use C_3H_6 as a representative of higher hydrocarbons.

solution. The remaining gaseous product was collected in a gasbag after passing through a final base trap (4 M NaOH solution) to prevent any residual HBr/HI from entering the bag. For most of the experiments, the reactions were run for half an hour with all the products collected. They were analyzed with three GCs, which measured: (1) gaseous halocarbons; (2) gaseous hydrocarbons C_1 – C_6 ; and (3) liquid halocarbons. All the experiments reported here have carbon balances of 95–105%.

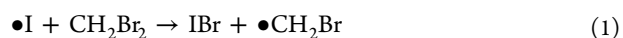
RESULTS AND DISCUSSION

Figure 2a shows the effluent composition as a function of the reaction time. The temperature was held constant at 500 °C, the CH_4/Br_2 ratio was 1/1, and the I_2/Br_2 ratio was 1/9. The solid lines give the effluent composition when I_2 was present, and the dotted lines give the effluent composition in the absence of I_2 . At the earliest time one makes very rapidly CH_3Br , CH_2Br_2 , and $CHBr_3$. Very soon, however, the reproporation reactions $CH_4 + CHBr_3 \rightarrow CH_3Br + CH_2Br_2$ and $CH_2Br_2 + CH_4 \rightarrow 2CH_3Br$ start taking place, which explains the increase in CH_3Br concentration and the decrease in CH_2Br_2 and $CHBr_3$ concentrations. After about five seconds the increase in CH_4 conversion slows down, and the other trends are reversed: the amount of CH_2Br_2 decreases and the amount of CH_3Br increases. In the earlier stage (reaction time < 5 s) the presence of I_2 has no influence on the composition of the products. For reaction time longer than ~5 s the presence of I_2 makes a difference: CH_4 conversion is higher, more CH_3Br is produced, and the amount of CH_2Br_2 is reduced, as compared with the case when I_2 is absent. The graph also shows the equilibrium conversion of CH_4 and equilibrium selectivity to CH_3Br , which are calculated from the thermodynamic data under corresponding reaction conditions (wide temperature range calculation results are given in Supporting Information, Figure S2). The reaction does not reach equilibrium for the reaction times used here. Only trace amount of iodine-containing halocarbons were detected, mainly composed of CH_3I and CH_2BrI . The selectivities of CH_3I and CH_2BrI both reach peak values at short reaction time and then drop (Supporting Information, Figure S3), indicating the

intermediate nature of these compounds. These facts imply that I_2 acts as a catalyst.

The dependence of the effluent composition on temperature is shown in Figure 2b. The data were taken at a reaction time of 8 s, which is a time when there is substantial amount of CH_2Br_2 in the system, at 500 °C (see Figure 2a). The feed composition is the same as in Figure 2a. The presence of I_2 is clearly beneficial (solid lines): CH_4 conversion is slightly higher, the selectivity to CH_3Br is markedly improved, and the amount of CH_2Br_2 is smaller when compared to the performance in the absence of I_2 (dotted lines). Note that in both cases (with I_2 or without it) the amount of unwanted CH_2Br_2 produced is maximum at about ~480 °C and then it drops fairly rapidly as the temperature increases beyond 480 °C. It appears that optimizing with respect to both reaction time and temperature will improve the performance.

Methane bromination is a chain reaction^{22,23} initialized by the formation of Br radicals through the dissociation of Br_2 . The details are described in the work of Kistiakowsky and van Artsdalen,²² and we have collected relevant information on the elementary steps in the chain reaction in the Supporting Information, Table S1. The key mechanistic question for the present work is: what are the main reactions through which catalysis by I_2 takes place? Apparently the reaction kinetics of methane bromination approaching the equilibrium is determined by the reproporation reaction between CH_4 and CH_2Br_2 , which is limited by the activation of the C–Br bond. The energy barriers of Br-abstractions from the C–Br bond by iodine radical are only slightly higher than those by bromine radicals (Supporting Information, Figure S4), while the concentration of iodine radical is much higher than that of bromine radical because of the comparatively lower bond dissociation energies of I–I, Br–I, C–I, and H–I bonds. Therefore, the iodine radical could readily abstract Br from CH_2Br_2 . After a series of cascade reactions, CH_4 and CH_2Br_2 are converted to CH_3Br while the iodine radical is regenerated. Generally speaking, iodine radicals are engaged in the following reactions:



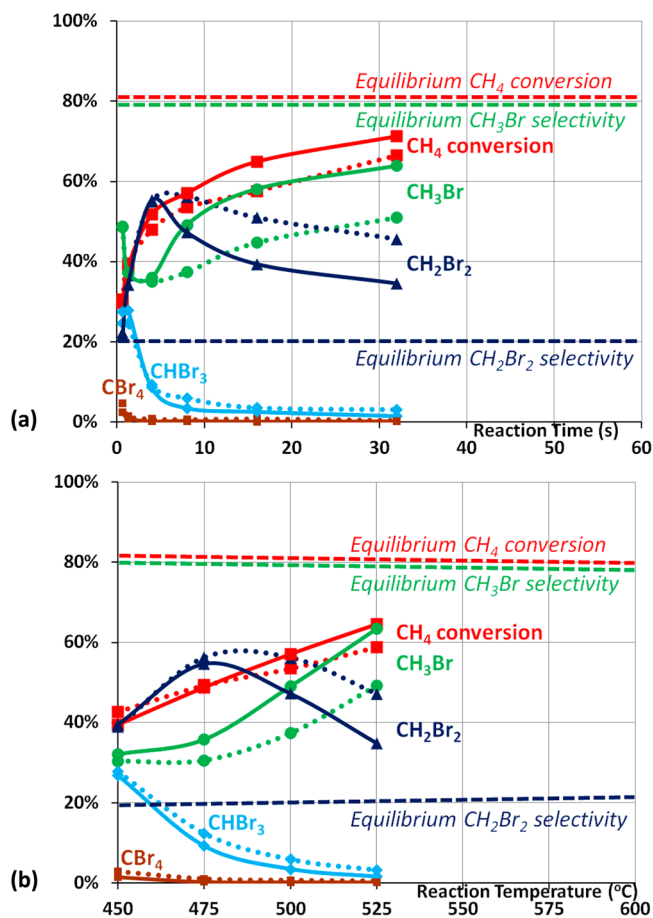
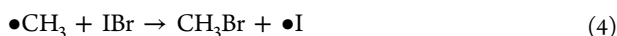
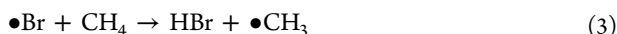
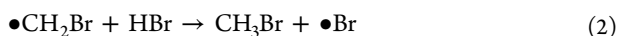


Figure 2. Effluent composition as a function of (a) the reaction time and (b) temperature. (a) The temperature was held constant at 500 °C; (b) The reaction time was 8 s. The CH_4 : Br_2 :Ar mole ratio was 7:7:14; I_2 / Br_2 ratio was 1/9; CH_4 input was 8.2 mmol. The dotted lines are the results obtained in the absence of I_2 ; the solid lines are the results when I_2 was present. Methane conversion is given as percentage of the inflow of methane consumed in the reaction. For the brominated products the percentage is with respect to the total number of moles of brominated compounds.



The sum of these reactions is



Obviously the reactants and the products of the reactions 1–4 are engaged in other reactions, which are detailed in the Supporting Information, Table S1. However, our hypothesis is that these four reactions are the key to understanding the role of I_2 .

An indication that these four reactions do convert CH_4 and CH_2Br_2 into CH_3Br is provided by an experiment in which CH_4 is reacted with CH_2Br_2 in the presence of I_2 . The concentration of the reactants was 47.14% CH_2Br_2 and 52.86% CH_4 . To this we added I_2 such that the I_2 / CH_2Br_2 ratio was 5/95. The temperature was 500 °C and the reaction time 8 s. The products of the reaction are shown as a pie chart in Figure 3. Two reactions take place in the system: one is eq 5, the other is

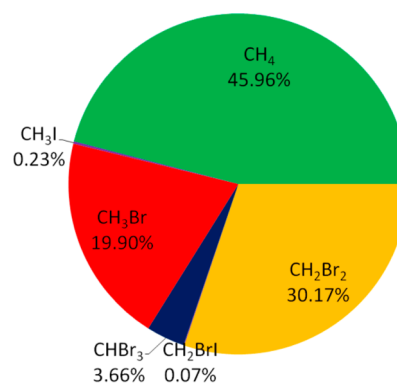
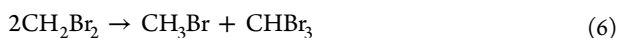


Figure 3. Product distribution in the reaction of CH_4 with CH_2Br_2 in the presence of I_2 . The initial composition was 52.86% CH_4 and 47.14% CH_2Br_2 . To this I_2 was added so that the I_2 / CH_2Br_2 ratio was 5/95. The reaction temperature was 500 °C, and the reaction time was 8 s. Note the very small amount of I-containing compounds.

Note that the effluent contains 0.23% CH_3I and 0.07% CH_2BrI . The concentration of iodine-containing compounds is very small.

Finally, in a separate experiment we have shown that the reaction eq 6 takes place when we run through the reactor CH_2Br_2 and Ar at 500 °C and a reaction time of 8 s.

Kinetic simulations using the “Chemical Kinetics Simulator” (CKS) software were performed to examine the validity of the proposed mechanism. The reactions included in the calculations and their rate constants are listed in the Supporting Information, Table S1. Since most of the rate constants were measured at a temperature lower than 300 °C, we used the Arrhenius equation to calculate the rate constants at 500 °C. Figure 4 shows the simulation results of methane bromination with and without iodine. Clearly the simulation results in Figure 4 are qualitatively similar to the

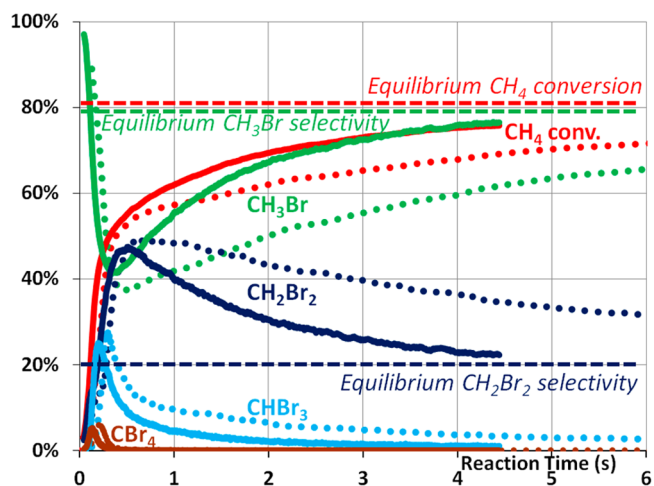


Figure 4. Calculated effluent composition in the reaction of CH_4 with Br_2 as a function of the reaction time when I_2 is present (solid lines) or absent (dotted lines). The conditions are the same as in the measurements reported in Figure 2a.

experimental results shown in Figure 2a. Furthermore, the CKS simulated equilibrium iodine radical concentration is much higher than the bromine radical concentration (Supporting Information, Figure S5). These results agree well with our proposed mechanism.

To test the quality of the kinetic simulations we have also performed kinetic measurements on the reaction of CH_2Br_2 with HBr and show the results in Figure 5a. The results of the simulation

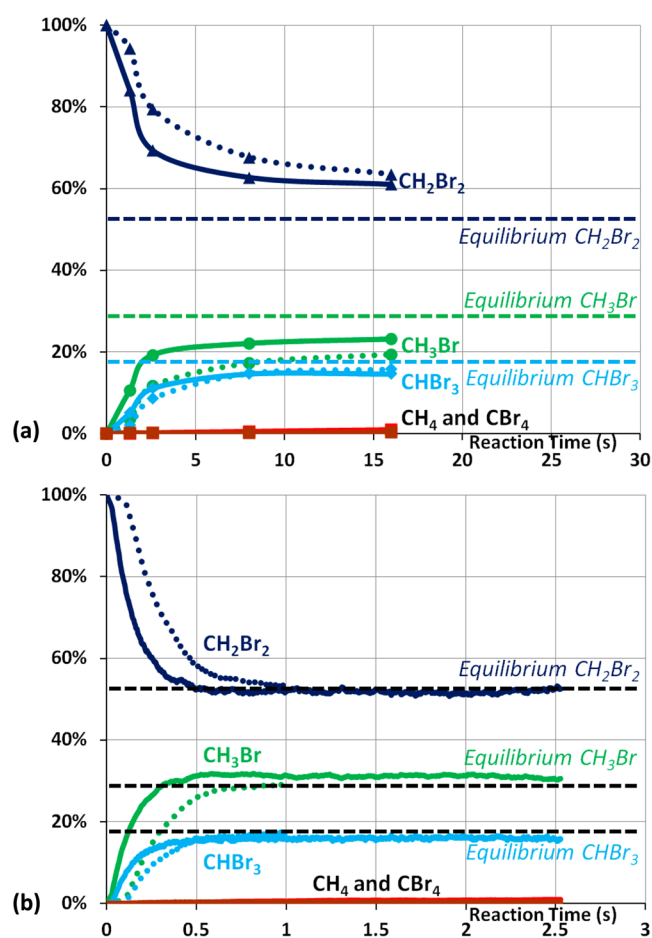


Figure 5. Experimental (a) and calculated (b) effluent concentration in the reaction “ $\text{CH}_2\text{Br}_2 + \text{HBr}$ ” at $T = 500\text{ }^\circ\text{C}$. $\text{CH}_2\text{Br}_2/\text{HBr}$ mole ratio = 1/2. The solid lines show the results when I_2 was present, and the $\text{I}_2/\text{CH}_2\text{Br}_2$ ratio was 5/95; the dotted lines give results obtained in the absence of I_2 .

of the same reaction are shown in Figure 5b. The simulation reproduces well the trends observed in the experiments.

CONCLUSIONS

We have found that a small amount of iodine ($\text{I}_2/\text{Br}_2 = 1/9$) improves the conversion of methane to CH_3Br and the selectivity against formation of CH_2Br_2 . The iodine affects the methane bromination reaction only after the reaction has produced some CH_2Br_2 . The main effect of I_2 is to catalyze the reaction of CH_2Br_2 with CH_4 , to produce CH_3Br . We speculate that the use of iodine, as a catalyst, may be beneficial when selective monobromination is intended. The results, along with our previous work on the iodine catalyzed “ $\text{CH}_2\text{Br}_2 + \text{C}_3\text{H}_8$ ” reaction, provide a general model for developing an integrated bromine–iodine dual-halogen pathway to convert stranded natural gas into fuels and chemicals.

ASSOCIATED CONTENT

Supporting Information

Reactor configuration, equilibrium and selectivity data from experiments, thermodynamic and kinetic information concerning the reaction mechanism. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: stucky@chem.ucsb.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the University of California Discovery Grant Program GCP08-128649, GRT Inc., and the Air Force Office of Scientific Research (FA9550-12-1-0333).

REFERENCES

- (1) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987–1007.
- (2) York, A. P. E.; Xiao, T. C.; Green, M. L. H.; Claridge, J. B. *Catal. Rev. - Sci. Eng.* **2007**, *49*, 511–560.
- (3) Mokrani, T.; Scurrell, M. *Catal. Rev. - Sci. Eng.* **2009**, *51*, 1–145.
- (4) Wang, L. S.; Tao, L. X.; Xie, M. S.; Xu, G. F.; Huang, J. S.; Xu, Y. D. *Catal. Lett.* **1993**, *21*, 35–41.
- (5) Holmen, A.; Olsvik, O.; Rokstad, O. A. *Fuel Process. Technol.* **1995**, *42*, 249–267.
- (6) Keller, G. E.; Bhasin, M. M. *J. Catal.* **1982**, *73*, 9–19.
- (7) Lunsford, J. H. *Angew. Chem., Int. Ed.* **1995**, *34*, 970–980.
- (8) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560–564.
- (9) Tabata, K.; Teng, Y.; Takemoto, T.; Suzuki, E.; Banares, M. A.; Pena, M. A.; Fierro, J. L. G. *Catal. Rev. - Sci. Eng.* **2002**, *44*, 1–58.
- (10) Holmen, A. *Catal. Today* **2009**, *142*, 2–8.
- (11) Alvarez-Galvan, M. C.; Mota, N.; Ojeda, M.; Rojas, S.; Navarro, R. M.; Fierro, J. L. G. *Catal. Today* **2011**, *171*, 15–23.
- (12) Gorin, E. U.S. Patent 2320274, 1943.
- (13) Weissman, M.; Benson, S. W. *Int. J. Chem. Kinet.* **1984**, *16*, 307–333.
- (14) Olah, G. A.; Gupta, B.; Farina, M.; Felberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Melhotra, A. K.; Trivedi, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 7097–7105.
- (15) Noceti, R. P.; Taylor, C. E. U.S. Patent 4769504, 1988.
- (16) Zhou, X. P.; Lorkovic, I. M.; Stucky, G. D.; Ford, P. C.; Sherman, J. H.; Grosso, P. U.S. Patent 6462243, 2002.
- (17) Gadewar, S. B.; Wyrsta, M. D.; Grosso, P.; Zhang, A. H.; McFarland, E. W.; Komon, Z. J. A.; Sherman, J. H. U.S. Patent 7579510, 2009.
- (18) McFarland, E. *Science* **2012**, *338*, 340–342.
- (19) Nilsen, M. H.; Svella, S.; Aravinthan, S.; Olsbye, U. *Appl. Catal., A* **2009**, *367*, 23–31.
- (20) Ding, K. L.; Derk, A. R.; Zhang, A. H.; Hu, Z. P.; Stoimenov, P.; Stucky, G. D.; Metiu, H.; McFarland, E. W. *ACS Catal.* **2012**, *2*, 479–486.
- (21) Ding, K. L.; Zhang, A. H.; Stucky, G. D. *ACS Catal.* **2012**, *2*, 1049–1056.
- (22) Kistiakowsky, G. B.; van Artsdalen, E. R. *J. Chem. Phys.* **1944**, *12*, 469–478.
- (23) Lorkovic, I. M.; Sun, S. L.; Gadewar, S.; Breed, A.; Macala, G. S.; Sardar, A.; Cross, S. E.; Sherman, J. H.; Stucky, G. D.; Ford, P. C. *J. Phys. Chem. A* **2006**, *110*, 8695–8700.