A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Title: Shape-Selective Zeolites Promote Ethylene Formation from Syngas via a Ketene Intermediate

Authors: Feng jiao, Xiulian Pan, Ke Gong, Yuxiang Chen, Gen Li, and Xinhe Bao

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201801397
Angew. Chem. 10.1002/ange.201801397

Link to VoR: http://dx.doi.org/10.1002/anie.201801397
http://dx.doi.org/10.1002/ange.201801397

WILEY-VCH

Angewandte Chemie International Edition

10.1002/anie.201801397

WILEY-VCH

COMMUNICATION

Shape-Selective Zeolites Promote Ethylene Formation from Syngas via a Ketene Intermediate

Feng Jiao,‡ Xiulian Pan,‡* Ke Gong, Yuxiang Chen, Gen Li, Xinhe Bao*

Abstract: Syngas conversion via Fischer-Tropsch synthesis (FTS) is characterized by a wide distribution of hydrocarbon products ranging from one to a few ten carbon atoms. We report here that selectivity can be effectively steered toward ethylene employing the oxide-zeolite (OX-ZEO) catalyst concept with $ZnCrO_x$-mordenite (MOR). The selectivity of ethylene alone among hydrocarbons reaches as high as 73% at 26% CO conversion, in stark contrast to a maximum 30% predicted for C_2 hydrocarbons by the Anderson-Schultz-Flory (ASF) model in FTS. Ethylene selectivity is also significantly higher than those obtained in any other direct syngas conversion or the multi-step via methanol-to-olefin process. Selective site blocking experiments reveal that this highly selective pathway is realized over the catalytic sites within the 8-membered ring (8MR) side pockets of MOR via ketene as an intermediate. The 12MR channels are not at all selective for ethylene. This study provides substantive evidence for a new type of syngas chemistry with ketene as the key reaction intermediate that enables extraordinary ethylene selectivity within the OX-ZEO catalyst framework.

Ethylene ($C_2^=$) is an important basic building block for production of a wide range of plastics, solvents and cosmetics. Its worldwide demand exceeds that of most other organic compounds. Ethylene is traditionally produced by steam cracking of naphtha. Alternatively, it can be synthesized by C–C coupling of C_1 molecules e.g. via the methanol-to-olefins (MTO) process or directly from CO via Fischer-Tropsch synthesis (FTS). The multi-step via MTO technology gives mixed olefins ($C_2^=$-$C_4^=$) as products and its selectivity is as high as 80-90%, but that of $C_2^=$ is usually only 40-50%. The $C_2^=$ selectivity can be increased up to 60% using small cavity zeolites but at the expense of a much shorter catalyst lifetime.[1] In comparison, direct conversion of syngas to ethylene is attractive because it involves fewer operation units. This has been under extensive study for over 50 years with efforts mainly focusing on modification of Fe- and Co-based FTS catalysts.[2] Despite of significant progress recently,[2c, 2e, 3] the $C_2^=$ selectivity remains low and the highest C_2 selectivity (including $C_2^=$ and ethane C_2^o) is predicted to be 30% by the ASF model (Figure S1).

A previous study demonstrated that a selectivity of ethane as high as 83% can be obtained by applying ZSM-5 impregnated with Cr, Zn, and Al, but no ethylene was detected which is obviously a much more valuable C_2 product.[4] A series of bifunctional catalysts were reported giving C_2-C_4 paraffins as products but no ethylene.[5] Arakawa et al. reported an ethylene selectivity of 45% together with 33% CH_4 at CO conversion of 6% by sequential conversion within two catalyst beds, i.e. a Rh-based catalyst and H-silicate.[6]

We recently reported that partially reducible oxides such as $ZnCrO_x$ and MnO_x in combination with a mesoporous SAPO-34 (MSAPO) zeolite can separate CO activation and C-C coupling onto two active sites.[3a, 7] This OX-ZEO catalyst concept has enabled synthesis of mixed light olefins directly from syngas with a selectivity of 80% among hydrocarbons at CO conversion of 17%.[3a] Thereafter, Cheng et al. reported a selectivity of 70% to mixed light olefins over a similar oxide-zeolite combination at CO conversion of 10%.[3b] However, in that study,[3a] the ethylene selectivity was only 23%. More importantly, the chemistry leading to the "surprisingly high selectivity"[8] to light olefins remains controversial, particularly the actual intermediates being either methanol or ketene.[3, 9]

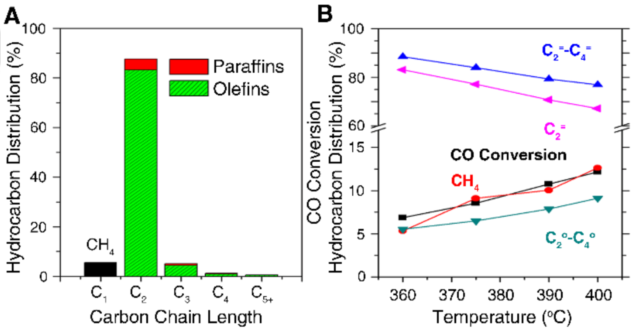


Figure 1. Syngas conversion over the composite catalyst $ZnCrO_x$-MOR#1. (A) Hydrocarbon distribution at 360 ℃; (B) Performance at different temperatures. Reaction conditions: $ZnCrO_x$/MOR#1 = 1/1 (mass ratio), H_2/CO = 2.5/1 (vol.), 2.5 MPa and space velocity = 1857 ml/g_{cat}·h.

Here we report evidence for ketene as the key intermediate in a highly selective reaction pathway toward ethylene, which becomes accessible by employing mordenite zeolite (MOR) in the OX-ZEO concept. Figure 1A shows that the composite $ZnCrO_x$-MOR#1 with a 1:1 mass ratio catalyzes syngas conversion to hydrocarbons at 360 ℃, H_2/CO = 2.5/1 and 2.5 MPa. Remarkably, the selectivity of ethylene alone (excluding CO_2) reaches as high as 83%, which is much higher than the 23% obtained over $ZnCrO_x$-MSAPO (Figure S2).[3a] Such an ethylene selectivity is unprecedented in any other direct syngas

---

[*] F. Jiao, Prof. Dr. X. Pan, K. Gong, Y. Chen, G. Li, Prof. Dr. X. Bao
State Key Laboratory of Catalysis, National Laboratory for Clean Energy, 2011-Collaborative Innovation Center of Chemistry for Energy Materials
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
457 Zhongshan Road, Dalian 116023
E-mail: panxl@dicp.ac.cn
xhbao@dicp.ac.cn

F. Jiao, K. Gong, Y. Chen, G. Li
University of Chinese Academy of Sciences, Beijing 100049

‡ These authors contributed equally.

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

conversion processes[2, 10] and also higher than that of MTO processes reported so far.[1, 11] Furthermore, the selectivity of the byproduct CH_4 is only 5%. Figure 1B shows that CO conversion increases with the temperature and reaches 11% at 390 ℃ while $C_2^=$ selectivity still remains at 71%. As proposed previously,[3a] the OX-ZEO concept affords a bifunctionality, where CO is activated over oxides, and subsequent C-C coupling is effectuated by zeolites. Still, the extraordinary selectivity toward ethylene over $ZnCrO_x$-MOR is surprising considering the predominant unidirectional 12MR channels of MOR (7.0 × 6.5 Å), which has been widely employed in reactions involving long chain hydrocarbons such as isomerization and hydrocarbon cracking.[12] Yet, MOR possesses another smaller channel formed by elliptical 8MR (5.7 × 2.6 Å) windows running in parallel as the 12MR channels, which are interconnected by the 8MR openings (with an aperture of 4.8 × 3.4 Å), so called side pockets (Figure S2).[13] The properties of Brønsted acid sites, from which the catalytic activities usually originate, differ strongly in these channels due to their specific local environments. The infrared (IR) spectra in Figure S3 show characteristic antisymmetric stretch modes of these sites in the range of 3550-3650 cm^{-1}.[13-14] The 3582-3590 cm^{-1} band is attributed to the OH sites within the 8MR side pockets (denoted as LF band), while the bands at 3600-3610 cm^{-1} (HF band) and 3617-3625 cm^{-1} (TF band) belong to the OH groups vibrating in the 12MR channels.[13-14] Many studies have demonstrated that the H^+ species in the 8MR pockets can be preferentially exchanged by Na^+.[13, 14c, 14d] Figure S3 shows that the LF band progressively attenuates with increasing Na^+ concentration and eventually disappears while the TF and HF bands are retained. It validates that the 8MR sites can be selectively shielded in this way (Table S1).

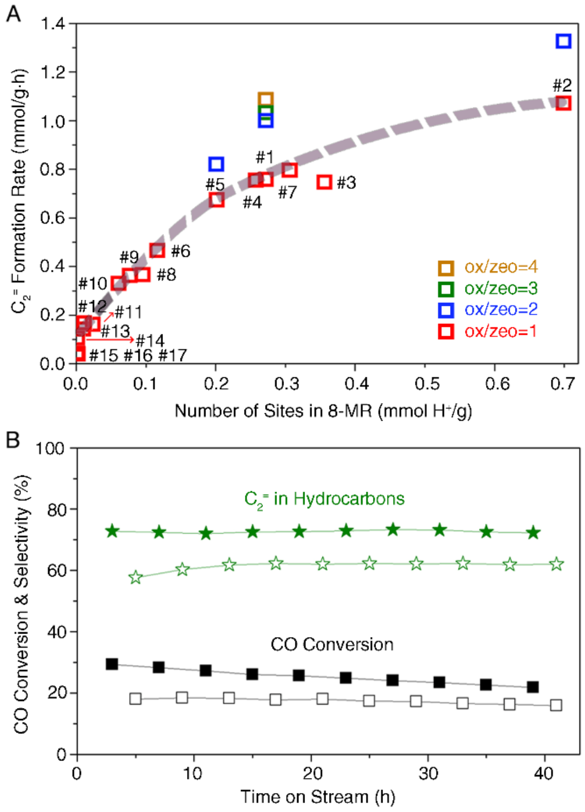


Figure 2. **Formation rate of ethylene in syngas conversion.** (A) As a function of the number of the 8MR acid sites over composite catalysts $ZnCrO_x$-MOR#n (with n representing the sample number from 1 to 17) at 375 ℃; (B) $ZnCrO_x$-MOR#2-py, with MOR#2-py denoting pyridine modified MOR#2 (filled symbols) in comparison to the unmodified MOR#2 (open symbols) at 360 ℃. Reaction conditions: H_2/CO = 1, 2.5 MPa, 1857 ml/g_{cat}·h .

Figure 2A demonstrates that the rate of ethylene formation (expressed in mmol $C_2^=$ per gram catalyst per hour) increases monotonically with the number of H^+ sites in the 8MR pockets. They are almost linearly correlated in the range of 0–0.20 mmol H^+/g_{cat} (Figure S4A). Above 0.20 mmol H^+/g_{cat}, $C_2^=$ formation slows down due to the mismatched activities in the tandem catalysis: the intermediates generated over the oxide are insufficient for the subsequent C-C coupling over MOR. When more active sites are provided by increasing the mass ratio of, e.g. $ZnCrO_x$/MOR#1, from 1/1 up to 4/1, $C_2^=$ formation rate is enhanced from 0.76 to 1.09 mmol $C_2^=/(g_{cat}\cdot h)$. Similar enhancement is observed for $ZnCrO_x$-MOR#2 and $ZnCrO_x$-MOR#5. In contrast, there is no clear correlation of the $C_2^=$ formation activity with the number of H^+ sites within the 12MR channels (Figure S4B). These results indicate that the acid sites within the 8MR are likely the active sites for ethylene formation. This is further corroborated by the sample MOR#14 whose 8MR acid sites are largely shielded by Na^+ leaving only the 12MR H^+ sites available. In combination with $ZnCrO_x$, this composite gives a wide distribution of hydrocarbons in syngas conversion (Figure S5), indicating that the 12MR sites are not selective for ethylene formation.

Further experiments with the 12MR acid sites selectively shielded point in the same direction. For example, 29% acidic sites of MOR#2 are located within the 12MR channel, which can be selectively shielded by pyridine (MOR#2-py, Figure S6) because this molecule is too large to enter the 8MR channels.[14a, 14b] Thus only the 8MR H^+ sites are accessible for the reaction with this MOR#2-py. As a result, $C_2^=$ selectivity increases to 73% compared to 62% over the unmodified MOR#2 (at reaction time of ~20 h, Figure 2B). Interestingly, the overall CO conversion is also enhanced from 18% to 26%, which, however, is not understood yet. These results clearly demonstrate that the reaction proceeds along different pathways over the 8MR and 12MR sites, thus leading to significantly different product distributions.

Our previous study suggested that syngas conversion via methanol may not be the dominating pathway over $ZnCrO_x$-MSAPO but ketene likely plays an important role.[3a] Ketene was also ever suggested to be an important intermediate in several syngas conversion processes.[15] Theoretical modelling by Wang et al. demonstrated that ketene can be effectively converted to light olefins within the pores of SAPO-34,[9] but methanol was also proposed to be the key intermediate in other studies.[3b] In order to assess the likelihood of ketene and methanol as the intermediates in the selective conversion of syngas to ethylene over $ZnCrO_x$-MOR catalysts, we fed both directly as educts to MOR zeolites and studied their adsorption and conversion since adsorption is the first step of the reaction. Solid state NMR using ^{129}Xe as a probe molecule (Figure 3A) shows that ^{129}Xe adsorbs in both the 8MR and 12MR channels giving two signals at 245-208 and 176-162 ppm, respectively.[16] The intensity ratio reflects the relative concentration of ^{129}Xe in these two channels. When MOR is first exposed to ketene followed by ^{129}Xe, the intensity ratio of the 8MR ^{129}Xe signal to that of 12MR diminishes

10.1002/anie.201801397

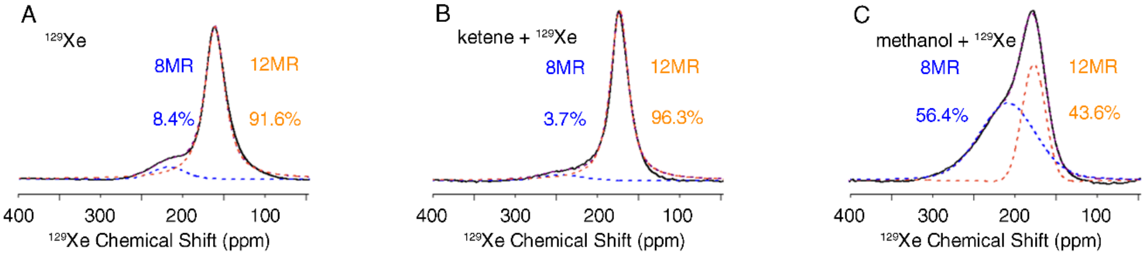


Figure 3. **^{129}Xe NMR spectra of the preferential adsorption of ketene and methanol in different channels of MOR.** (A) Exposure to ^{129}Xe; (B) Exposure to ketene followed by ^{129}Xe and (C) Exposure to methanol followed by ^{129}Xe.

obviously (Figure 3B) compared to the spectrum in Figure 3A. It indicates that more ketene molecules have entered and occupied the 8MR than the 12MR channels. In contrast, exposure to methanol and then ^{129}Xe results in a significantly lowered intensity ratio of the 12MR signal to that of the 8MR one (Figure 3C), suggesting that more methanol molecules have occupied the 12MR channels than the 8MR side pockets. These results demonstrate that ketene is more favored to adsorb over the 8MR sites whereas methanol prefers the 12MR sites. The DFT calculations presented by Boronat et al. also showed that the 12MR sites were much more favored for methanol adsorption, as the adsorption energies were 6-12 kcal/mol higher than those over the 8MR sites.[17] In addition, those authors showed that the T4-O44 position in the 12MR channel (corresponding to HF O10 in this study) exhibited a lowest reaction energy for the process of $\text{Z-H} + \text{CH}_3\text{OH} \rightarrow \text{Z-CH}_3 + \text{H}_2\text{O}$.[17] Furthermore, Rasmussen et al. predicted that ketene adsorbed stronger over the 8MR sites than that over the 12-MR ones.[18] Thus, ketene conversion may be facilitated over the 8MR sites whereas methanol conversion may be more favored over the 12MR sites.

Figure 4 shows the product distribution profiles of ketene and methanol conversion over MOR zeolites in comparison to syngas conversion over the corresponding composite catalysts. One sees that syngas conversion over ZnCrO$_x$-MOR#2-py (Figure 4A) gives a similar product distribution profile as that of ketene conversion over MOR#2-py (Figure 4B), where only the 8MR sites are accessible. But in ketene conversion the ethylene selectivity is higher (reaching 89%). Such a high selectivity toward ethylene is retained under different space velocities of ketene and reaction temperatures (Figure S7). In contrast, methanol conversion over MOR#2-py gives a much widerproduct distribution with C$_3$ hydrocarbons being the most dominant (selectivity 48%) and C$_2$ only 31% (Figure 4C). In comparison, over MOR#14 with the 8MR sites blocked and only the 12MR sites being accessible, ketene is converted non-selectively to a wider range of hydrocarbons (Figure 4E), again similar to syngas conversion over ZnCrO$_x$-MOR#14 (Figure 4D). Interestingly, for methanol conversion these blocked 8MR sites do not impede its conversion as the initial conversion reaches almost 100% (Figure S8). However, it produces mainly higher hydrocarbons with C$_{3+}$ selectivity 86% and C$_2$ only 12% (Figure 4F). In addition, it deactivates fairly fast within 75 min, consistent with previous (D)MTO studies.[19] The relative distribution of

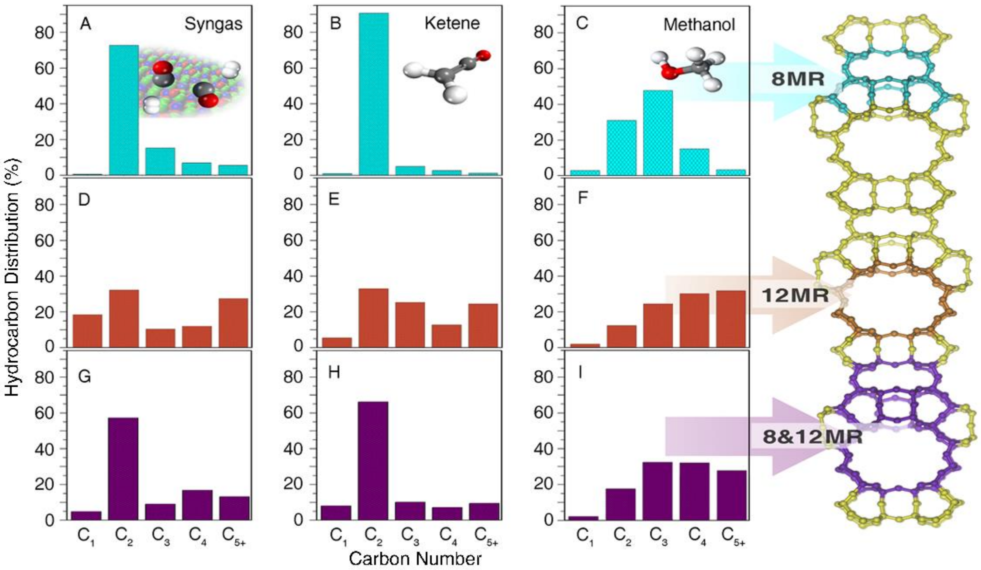


Figure 4. Hydrocarbon distributions in the conversion of syngas, ketene and methanol over different sites of MOR zeolites at 375 ℃. (A), (B) and (C) MOR#2-py with only the 8MR acid sites accessible; (D), (E) and (F) MOR#14 with only the 12MR acid sites accessible; (G), (H) and (I) MOR#3 with both the 8MR and 12MR acid sites available; (A), (D) and (G) syngas over ZnCrO$_x$-MOR; (B), (E) and (H) ketene conversion over MOR; (C), (F) and (I) methanol conversion over MOR.

$C_3^{=}/C_2^{=}$ also agrees with the previously reported MTO catalyzed by other zeolites.[1, 20] Furthermore, a previous syngas conversion study combining a methanol synthesis catalyst (Pd/SiO_2) and MOR also showed favored formation of longer aliphatic hydrocarbons (C_{3+}) and aromatics.[21] Note that varying methanol partial pressures (0.05 – 5.0 kPa), space velocities (0.03 – 5.27 $g_{CH3OH}/g_{zeolite}\cdot h$) and reaction temperatures, methanol conversion changes between 80-100% and the hydrocarbon product distribution changes slightly but remains non-selective, with C_2 no more than 36%, no matter over MOR#2-py, MOR#14 or MOR#3 (Figure S8 and S9). It suggests that methanol can be convered to hydrocarbons by MOR but non-selectively even though formation of methanol from syngas is detected over metal oxides (Figure S5) whereas ketene can be highly selectively converted to ethylene over the 8MR sites. When both the 8MR and 12MR sites are accessible (MOR#3), syngas is also converted preferably to C_2 hydrocarbons with a similar distribution profile (Figure 4G) as ketene conversion but a lower C_2 selectivity (Figure 4H), whereas methanol conversion (Figure 4I) resembles that by the 12MR sites with C_2 selectivity lower than 20% (Figure 4F). Furthermore, hydrocarbon distribution is also very wide when feeding dimethyl ether (DME) together with syngas to these three MOR zeolites, which is dominated by C_{3+} and the highest C_2 selectivity among hydrocarbons is only 38% (Figure S10 and Table S2). These results support that highly selective syngas-to-ethylene conversion proceeds more likely via ketene as an intermediate over the MOR 8MR sites rather than methanol or DME over the 8MR or 12MR sites.

The above results demonstrate that by combining partially reduced $ZnCrO_x$ with the confined active sites of the MOR 8MR side pockets, syngas conversion is steered along a new reaction pathway via ketene as an intermediate leading to an extraordinary ethylene selectivity as high as 73% at a CO conversion 26%. This opens up a new avenue for development of syngas-to-ethylene technology. Furthermore, it demonstrates the versatility of the bifunctional OX-ZEO catalyst concept, which turns syngas conversion into a tandem catalysis. Consequently, the product selectivity can be controlled by shape selective zeolites. This provides an effective strategy to tackle the selectivity challenge of syngas chemistry, which has been under study for almost a century.

Acknowledgements

This work was supported by the Ministry of Science and Technology of China (No. 2016YFA0202803), the National Natural Science Foundation of China (Grant No. 91645204, 21425312 and 21621063).

Conflict of interest

The authors declare no conflict of interest.

Keywords: heterogeneous catalysis • syngas conversion • zeolites • ethylene • shape selective

[1] a) J. Z. Li, Y. X. Wei, J. R. Chen, S. T. Xu, P. Tian, X. F. Yang, B. Li, J. B. Wang, Z. M. Liu, *ACS Catal.* **2015**, *5*, 661-665; b) N. H. Ahn, S. Seo, S. B. Hong, *Catal. Sci. Technol.* **2016**, *6*, 2725-2734.

[2] a) R. A. Dictor, A. T. Bell, *J. Catal.* **1986**, *97*, 121-136; b) T. Riedel, M. Claeys, H. Schulz, G. Schaub, S.-S. Nam, K.-W. Jun, M.-J. Choi, G. Kishan, K.-W. Lee, *Appl. Catal. A Gen.* **1999**, *186*, 201-213; c) H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan, K. P. de Jong, *Science* **2012**, *335*, 835-838; d) G. Melaet, W. T. Ralston, C. S. Li, S. Alayoglu, K. An, N. Musselwhite, B. Kalkan, G. A. Somorjai, *J. Am. Chem. Soc.* **2014**, *136*, 2260-2263; e) L. Zhong, F. Yu, Y. An, Y. Zhao, Y. Sun, Z. Li, T. Lin, Y. Lin, X. Qi, Y. Dai, L. Gu, J. Hu, S. Jin, Q. Shen, H. Wang, *Nature* **2016**, *538*, 84-87; f) C. L. Xie, C. Chen, Y. Yu, J. Su, Y. F. Li, G. A. Somorjai, P. D. Yang, *Nano Lett.* **2017**, *17*, 3798-3802.

[3] a) F. Jiao, J. Li, X. Pan, J. Xiao, H. Li, H. Ma, M. Wei, Y. Pan, Z. Zhou, M. Li, S. Miao, J. Li, Y. Zhu, D. Xiao, T. He, J. Yang, F. Qi, Q. Fu, X. Bao, *Science* **2016**, *351*, 1065-1068; b) K. Cheng, B. Gu, X. Liu, J. Kang, Q. Zhang, Y. Wang, *Angew. Chem. Int. Ed.* **2016**, *55*, 4725-4728.

[4] C. D. Chang, J. N. Miale, R. F. Socha, *J. Catal.* **1984**, *90*, 84-87.

[5] a) K. Fujimoto, H. Saima, H. O. Tominaga, *J. Catal.* **1985**, *94*, 16-23; b) C. Li, K. Fujimoto, *Catal. Sci. Technol.* **2015**, *5*, 4501-4510; c) Q. W. Zhang, X. H. Li, K. Asami, S. Asaoka, K. Fujimoto, *Fuel Process. Technol.* **2004**, *85*, 1139-1150; d) Y. Chen, Y. Xu, D.-g. Cheng, Y. Chen, F. Chen, X. Lu, Y. Huang, S. Ni, *J. Chem. Technol. Biotechnol.* **2015**, *90*, 415-422.

[6] H. Arakawa, Y. Kiyozumi, K. Suzuki, K. Takeuchi, T. Matsuzaki, Y. Sugi, T. Fukushima, S. Matsushita, *Chem. Lett.* **1986**, 1341-1342.

[7] Y. F. Zhu, X. L. Pan, F. Jiao, J. Li, J. H. Yang, M. Z. Ding, Y. Han, Z. Liu, X. H. Bao, *ACS Catal.* **2017**, *7*, 2800-2804.

[8] K. P. de Jong, *Science* **2016**, *351*, 1030-1031.

[9] C. M. Wang, Y. D. Wang, Z. K. Xie, *Catal. Sci. Technol.* **2016**, *6*, 6644-6649.

[10] a) X. Chen, D. Deng, X. Pan, Y. Hu, X. Bao, *Chem. Commun.* **2015**, *51*, 217-220; b) A. M. Hilmen, E. Bergene, O. A. Lindvag, D. Schanke, S. Eri, A. Holmen, *Catal. Today* **2001**, *69*, 227-232.

[11] a) Z. Liu, C. Sun, G. Wang, Q. Wang, G. Cai, *Fuel Process. Technol.* **2000**, *62*, 161-172; b) U. Olsbye, S. Svelle, M. Bjorgen, P. Beato, T. V. Janssens, F. Joensen, S. Bordiga, K. P. Lillerud, *Angew. Chem. Int. Ed.* **2012**, *51*, 5810-5831; c) D. Chen, K. Moljord, A. Holmen, *Micro.Meso.Mater.* **2012**, *164*, 239-250.

[12] a) K. J. Chao, H. C. Wu, L. J. Leu, *Appl. Catal. A Gen.* **1996**, *143*, 223-243; b) A. Chica, A. Corma, *J. Catal.* **1999**, *187*, 167-176; c) O. Bortnovsky, P. Sazama, B. Wichterlova, *Appl. Catal. A Gen.* **2005**, *287*, 203-213.

[13] N. Cherkasov, T. Vazhnova, D. B. Lukyanov, *Vib. Spectrosc.* **2016**, *83*, 170-179.

[14] a) M. Maache, A. Janin, J. C. Lavalley, E. Benazzi, *Zeolites* **1995**, *15*, 507-516; b) J. Datka, B. Gil, A. Kubacka, *Zeolites* **1996**, *17*, 428-433; c) A. Bhan, A. D. Allian, G. J. Sunley, D. J. Law, E. Iglesia, *J. Am. Chem. Soc.* **2007**, *129*, 4919-4924; d) V. A. Veefkind, M. L. Smidt, J. A. Lercher, *Appl. Catal. A Gen.* **2000**, *194*, 319-332.

[15] a) P. M. Loggenberg, L. Carlton, R. G. Copperthwaite, G. J. Hutchings, *Journal Of the Chemical Society-Chemical Communications* **1987**, 541-543; b) H. Y. Wang, J. P. Liu, J. K. Fu, Q. R. Cai, *Acta Physico-Chimica Sinica* **1991**, *7*, 681-687; c) D. B. Cao, F. Q. Zhang, Y. W. Li, J. G. Wang, H. J. Jiao, *J. Phys. Chem. B* **2005**, *109*, 10922-10935; d) A. Andersen, S. M.

WILEY-VCH
10.1002/anie.201801397

Kathmann, M. A. Lilga, K. O. Albrecht, R. T. Hallen, D. H. Mei, *Catal. Commun.* **2014**, *52*, 92-97; e) M. Akita, Y. Morooka, *J. Synth. Org. Chem. Jpn.* **1992**, *50*, 726-736.

[16] J. A. Ripmeester, *J. Magn. Reson.* **1984**, *56*, 247-253.

[17] M. Boronat, C. Martinez-Sanchez, D. Law, A. Corma, *J. Am. Chem. Soc.* **2008**, *130*, 16316-16323.

[18] D. B. Rasmussen, J. M. Christensen, B. Temel, F. Studt, P. G. Moses, J. Rossmeisl, A. Riisager, A. D. Jensen, *Angew. Chem. Int. Ed.* **2015**, *54*, 7261-7264.

[19] J. W. Park, S. J. Kim, M. Seo, S. Y. Kim, Y. Sugi, G. Seo, *Appl. Catal. A Gen.* **2008**, *349*, 76-85.

[20] S. Wang, Y. Y. Chen, Z. H. Wei, Z. F. Qin, H. Ma, M. Dong, J. F. Li, W. B. Fan, J. G. Wang, *J. Phys. Chem. C* **2015**, *119*, 28482-28498.

[21] K. Fujimoto, Y. Kudo, H. O. Tominaga, *J. Catal.* **1984**, *87*, 136-143.

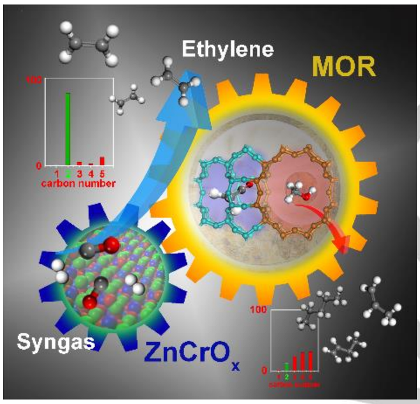
10.1002/anie.201801397

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Ethylene blessed by the 8MR side pockets of MOR: Syngas conversion can be effectively steered toward ethylene via ketene intermediates by the 8MR side pockets of MOR employing the ZnCrO$_x$-MOR composite. The selectivity of ethylene alone reaches 73% at CO conversion of 26%. In comparison, the 12MR sites of MOR may favor methanol as intermediates but lead to a remarkably different product distribution dominated by longer chain hydrocarbons.



Feng Jiao,‡ Xiulian Pan,‡ Ke Gong, Yuxiang Chen, Gen Li, Xinhe Bao**

Page No. – Page No.

Shape-Selective Zeolites Promote Ethylene Formation from Syngas via a Ketene Intermediate