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## Unraveling the Mechanisms of Ketene Generation and Transformation in Syngas-to-Olefins Conversion over ZnCrO<sub>x</sub>|SAPO-34 Catalysts

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Supplementary Information

1 ABSTRACT: Ketene was identified as an intermediate in syngas-2 to-olefins (STO) conversion catalyzed by metal oxide-zeolite 3 composites, which sparked the hot debate on its formation 4 mechanism and catalytic roles. Here we employed large-scale 5 atomic simulations using global neural network potentials to 6 explore the STO reaction pathways, and microkinetic 7 simulations to couple the reaction kinetics in ZnCrO<sub>x</sub> | SAPO-34 8 composite sites. Our results demonstrate that a majority of 9 ketene (86.1%) originates from the methanol carbonylation-to-10 ketene route ( $CH_3OH^* + H^* -> CH_3^* + H_2O -> CH_3^* + CO^* ->$  $11 \text{ CH}_2\text{CO}^* + \text{H}^*$ ) nearby zeolite acidic sites, where methanol is 12 produced through conventional syngas-to-methanol on 13 Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> (0001) surface, while the minority of ketene (13.9%) 14 arises from a direct CHO\*-CO\* coupling (CHO\* + CO\* + H\* -> 15 CHOCO\* + H\* -> CH<sub>2</sub>CO + O\*) on  $Zn_3Cr_3O_8$ . The presence of the 16 ketene pathway significantly alters the catalytic performance 17 in zeolite, as methanol carbonylation to ketene is kinetically 18 more efficient in competing with conventional methanol-to-19 olefins (MTO) and thus predominantly drives the product to 20 ethene. Based on our microkinetic simulation, it is the 21 methanol carbonylation activity in zeolite that dictates the 22 performance of STO catalysts.

#### 23 1. Introduction

Recent years have witnessed significant progresses in the 24 25 one-step syngas-to-olefins (STO) process enabled by OX-ZEO 26 (metal oxide-zeolite) composite catalysts. In this strategy, 27 syngas is first converted to intermediates on metal oxides, 28 which are subsequently transformed into light olefins over 29 zeolites.<sup>1-5</sup> In contrast to a combined prior knowledge on 30 syngas-to-methanol (STM) on oxides and methanol-to-olefins 31 (MTO) in zeolites, the STO process exhibits its own unique 32 features, particularly, the observation of ketene (H<sub>2</sub>C=CO) 33 intermediates<sup>1</sup> and the distinct product distribution—ethene 34 selectivity reaching up to 80%<sup>6</sup> compared to ~50% in typical 35 MTO processes. It was believed that novel reaction pathways 36 must be present in the STO process, which are however, largely 37 elusive due to the lack of experimental characterization 38 techniques and large-scale theoretical calculation methods to 39 explore all likely pathways. How the ketene intermediate is

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40 generated and consumed rank as the top concern in the 41 catalytic process.

Ketene is first observed as an intermediate on the oxide 42 43 part (ZnCrO<sub>x</sub>) of the oxide-zeolite composite by Bao and 44 coworkers<sup>1</sup>, the pioneering group of OX-ZEO catalyst, using 45 synchrotron-based vacuum ultraviolet photoionization mass 46 spectrometry with the unique ionization signal of ketene at m/z 47 = 42. Consequently, they proposed that ketene forms on the 48 ZnCrO<sub>x</sub> surface and subsequently migrates into the zeolite for 49 further transformation. Later, ketene has also been detected 50 within the zeolite framework. Rasmussen et al.7 observed 51 ketene formation in MOR zeolite when deuterated water (D<sub>2</sub>O) 52 was introduced into a co-feeding system of dimethyl ether 53 (DME) and CO, leading to the formation of CH<sub>2</sub>DCOOD. 54 Furthermore, infrared spectroscopy and <sup>13</sup>C solid-state nuclear 55 magnetic resonance spectroscopy have also provided evidence 56 for ketene adsorption within the zeolites through distinct 57 C=C=O vibrational shifts and identified surface acetyl as the 58 ketene hydrogenated derivative.8-13

On the other hand, other non-ketene intermediates, 59 methanol and DME, traditionally regarded 60 mainly, 61 intermediates in STM and MTO catalysis, were also detected in 62 the OX-ZEO catalytic system. At low temperatures (< 600 K), the 63 ZnO-ZrO<sub>2</sub> SSZ-13 composite catalyst predominantly generates 64 methanol and DME, with formate species (HCOO\*) detected 65 from in-situ IR.14 Elevated reaction temperatures promote the  $_{66}$  conversion of these intermediates into C<sub>2-4</sub> olefins, 67 accompanied by a significant decline in methanol/DME 68 selectivity. Chemical trapping-mass spectrometry further 69 confirmed that methoxy (CH<sub>3</sub>O\*) species on the ZnO-ZrO<sub>2</sub> |Zn-70 modified SAPO-34 catalyst migrates to acidic sites in the zeolite, 71 participating in carbon-chain growth. This observation 72 validates methanol as the critical carbon source kinetically.<sup>15</sup>

To elucidate the puzzling observations in experiments, 74 theoretical calculations have been utilized to resolve the 75 reaction network of the OX-ZEO catalytic system. Our previous 76 work<sup>16</sup> investigated the most stable surfaces with varying Zn:Cr 77 ratios of the ZnCrO<sub>x</sub> system using stochastic surface walking 78 (SSW) and global neural network (G-NN). We identified the 79 metastable Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> as the dominant active phase for 80 methanol formation, while the ZnCr<sub>2</sub>O<sub>4</sub> was responsible for the

68 structures.

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1 methane (CH<sub>4</sub>) formation. However, ketene formation was not 2 considered due to their relative high Gibbs energy barriers on 3 oxide catalysts alone. Recently, Lai et al.<sup>17</sup> explored the possible 4 elementary steps for methanol, methane and ketene 5 formation on the highly reduced ZnCr<sub>2</sub>O<sub>4</sub> (110) surface through 6 DFT calculations and microkinetic simulations. They confirmed 7 that CH4 is the primary product but minority ketene and 8 methanol are also produced. When incorporating a 9 hypothetical zeolite conversion reaction with a Gibbs free 10 energy barrier of  $\leq$  1.65 eV, ketene selectivity increases 11 significantly, favoring light olefins formation over CH<sub>4</sub>. 12 Nevertheless, this simplification of the complex reaction 13 network occurring in zeolite as a hypothetical reaction а huge approximation, limiting deep 15 understandings on the quantitative contributions of methanol 16 and ketene routes and also being contradictory with the 17 experimental facts on negligible CH<sub>4</sub> selectivity. In fact, 18 according to a serial of work by Wang et al.<sup>18</sup> on MTO within 19 the SAPO-34 zeolite, ketene formation is also a kinetically 20 feasible via the methanol carbonylation pathway ( $CH_3^* + CO \rightarrow$ 21 CH<sub>3</sub>CO<sup>\*</sup>; CH<sub>3</sub>CO<sup>\*</sup> -> CH<sub>2</sub>CO + H<sup>\*</sup>), which suggests the sole origin 22 of ketene from the oxide part is questionable in the OX-ZEO 23 system. The great complexity of the reaction network 24 highlights the necessity for a systematic investigation to 25 quantitatively determine the contributions of methanol and 26 ketene pathways from both ZnCrO<sub>x</sub> oxide and SAPO-34 zeolite.

Here with the advance of large-scale atomic simulations 28 based on global neural network potential we systematically 29 investigated the STO reaction pathways on ZnCrO<sub>x</sub> |SAPO-34 30 composite catalysts, including the formation of ketene on 31 ZnCrO<sub>x</sub> via CO hydrogenation and on SAPO-34 via methanol 32 carbonylation, as well as the subsequent conversion of ketene 33 to ethene. By integrating with microkinetic simulations, we 34 demonstrated that ketene formation follows a dual-site 35 mechanism, wherein the majority of ketene (86.1%) is 36 generated via the methanol carbonylation-to-ketene route 37 within zeolite, while the minority ketene (13.9%) arises from a 38 direct CHO\*-CO\* coupling on the ZnCrO<sub>x</sub> surfaces. The catalytic 39 consequence of this dual-site mechanism is thus revealed, 40 rationalizing the experimental product distribution.

#### 41 2. Methods

#### 42 2.1 SSW-NN simulation

<sup>43</sup>Our approach for resolving reactions on ZnCrO<sub>x</sub> and SAPO-<sup>44</sup> 34 zeolite is based on the SSW global optimization with G-NN, <sup>45</sup> known as the SSW-NN method, as implemented in the LASP <sup>46</sup> code.<sup>19</sup> The G-NN potential is constructed through iterative <sup>47</sup> self-learning from the plane wave DFT global PES dataset <sup>48</sup> during SSW-NN exploration. The SSW-NN simulation for PES <sup>49</sup> exploration consists of three main steps: generating the global <sup>50</sup> PES dataset using DFT calculations on selected structures <sup>51</sup> obtained from SSW global PES exploration, fitting the G-NN <sup>52</sup> potential, and conducting SSW global PES exploration with the <sup>53</sup> G-NN potential. These steps are repeated iteratively performed <sup>54</sup> until the G-NN potential becomes transferable and sufficiently <sup>55</sup> robust to accurately describe the global PES. The procedure is <sup>56</sup> summarized as follows.

57 The global dataset is initially constructed through iterative 58 self-learning of the global PES. The initial data of the global View Article Online DOI: 10.1039/D5SC01651G 59 dataset comes from the DFT-based SSW simulation with 60 subsequent data progressively accumulated through G-NN-61 based SSW PES exploration. In order to cover all likely 62 compositions of Si-Al-P-C-H-O systems, SSW simulations have 63 been conducted across diverse structural configurations 64 (including bulk, layer and cluster), compositions and atom 65 number per unit cell. Overall, these SSW simulations generate 66 more than 10<sup>7</sup> structures on the PES. The final global dataset, 67 computed from high accuracy DFT calculations, contains 47920

Subsequently, the G-NN potential is constructed using the method as introduced in our previous work.<sup>16,20</sup> To pursue a high accuracy for the PES, we implemented a many-bodyfunction corrected global NN architecture (G-MBNN) and menory 636 power-type structure descriptors for each element to distinguish structures in the global dataset. The sneural network architecture consists of three hidden layers, fo structured as a 636-80-80-80-6 network, containing proximately 386,836 network parameters in total. The final layer with 6 nodes is enveloped into a series of many-body plunctions, which sum to yield the total energy. More details about G-MBNN architecture can be found in our previous layers.

The min-max scaling is utilized to normalize the training adata sets. Hyperbolic tangent activation functions are used for the hidden layers, while a linear transformation is applied to to the output layer of all networks. The limited-memory Broydenfetcher-Goldfarb-Shanno (L-BFGS) method is used to minimize the loss function to match DFT energy, force, and stress. The final energy and force criteria of the root mean square errors for the Si-Al-P-C-H-O G-NN potential are around 4.1 meV/atom on and 0.123 eV/Å respectively. All the low-energy structure and dates from G-NN potential calculations are finally verified by plane wave DFT calculations, and thus the energetic data are ported in this work, unless specifically mentioned, are 4 obtained from DFT.

#### 95 2.2 DFT calculations

All DFT calculations were performed using the plane wave 96 97 VASP code<sup>22</sup>, where the electron-ion interaction was 98 represented by the projector augmented wave 99 pseudopotential.<sup>23,24</sup> The exchange-correlation functional 100 utilized on ZnCrO<sub>x</sub> surface was the spin-polarized GGA-PBE<sup>25</sup> 101 with the local Hubbard term U correction (U = 3.3 eV) for Cr 102 element<sup>26</sup> given that ZnCrO<sub>x</sub> structures generally exhibit a 103 strong correction for Cr atoms; while Bayesian error estimation 104 functional (BEEF) was utilized for the zeolite surface.<sup>27</sup> The 105 kinetic energy cutoff was set to 450 eV. The first Brillouin zone 106 k-point sampling used a  $3 \times 3 \times 1$  gamma-centered mesh grid 107 for the ZnCrO<sub>x</sub> surface and a  $1 \times 1 \times 1$  gamma centered mesh 108 grid for the SAPO-34 zeolite bulk and surface. The energy and 109 force convergence criteria for electron density and structure 110 optimization were set to  $1 \times 10^{-6}$  eV and 0.02 eV Å<sup>-1</sup>, 111 respectively. All transition states (TS) in the Gibbs profile were 112 located using the double-ended surface walking (DESW) 113 method,<sup>28</sup> and the stationary structures were optimized 114 through the SSW method.<sup>29</sup> All those local minima and 115 transition states obtained from SSW-NN sampling were fully re-116 optimized using DFT to obtain the final results.

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Harmonic frequency calculations were conducted using 2 partial Hessian vibrational analysis (PHVA), incorporating all C, 3 H species on both ZnCrO<sub>x</sub> and SAPO-34 surface, as well as the 4 H, O atoms of the acidic site on the zeolite inner surface. Zero-5 point energies (ZPE), enthalpies, entropies, and Gibbs free 6 energies were subsequently derived from harmonic 7 frequencies. The DFT calculations, unless otherwise specified, 8 were performed under typical reaction conditions, with the 9 temperature and CO/H<sub>2</sub> pressure fixed at 673 K and 2.5 MPa, 10 respectively, and a H<sub>2</sub>:CO ratio of 2.5:1.<sup>1</sup>

#### 11 2.3 Microkinetic simulation

<sup>12</sup> The microkinetic analysis was performed using the <sup>13</sup> CATKINAS package developed by Chen et al.<sup>30</sup> The reaction <sup>14</sup> conditions were maintained as reported by Jiao et al.<sup>1</sup> in 2016, <sup>15</sup> namely P(CO) = 7.14 bar and P (H<sub>2</sub>) = 17.86 bar, the total flow <sup>16</sup> rate = 5143 mL g<sup>-1</sup> h<sup>-1</sup>, and the temperature = 673 K.

#### 17 3. Results and discussion

It is known that the Zn:Cr ratio in the oxide component of 19 the ZnCrO<sub>x</sub>|SAPO-34 system significantly affects the catalytic 20 activity and selectivity. Specifically, the the ZnCrO<sub>x</sub>|SAPO-34 21 catalyst with a Zn:Cr ratio of 1:1 achieves about the highest 85 % 22 C<sub>2</sub>-C<sub>4</sub> light olefin selectivity with a CO conversion rate of 58 % 23 at 673 K, while a Zn:Cr ratio of 1:2 leads to a sharp decline in 24 CO conversion to 27 % and light olefin selectivity to 70 %<sup>31</sup>. In 25 this context, we first systematically investigated the impact of 26 different Zn:Cr ratios on the ketene-mediated pathways. Apart 27 from the stoichiometric ZnCr<sub>2</sub>O<sub>4</sub> spinel phase with a Zn:Cr ratio 28 of 1:2, the most stable phase<sup>32</sup> formed after high-temperature 29 calcination, our previous work<sup>16</sup> revealed that ZnCrO<sub>x</sub> with a 30 Zn:Cr ratio of 1:1 has a metastable Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> phase, 31 characterized by its unique [ZnO<sub>6</sub>] structural motif, as 32 confirmed by experimental observations.<sup>33–39</sup> Under reaction 33 conditions, the most stable ZnCr<sub>2</sub>O<sub>4</sub> (111) and Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> (0001) 34 surfaces become reduced, which open the STM pathways.<sup>16</sup> In 35 this work, we explored the reaction profiles of ketene 36 formation on both reduced Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> (0001) and ZnCr<sub>2</sub>O<sub>4</sub> (111) 37 surfaces, where the surface status is based on the phase 38 diagram determined previously. In short, as illustrated in Figure 39 S1, the reduced Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> (0001) surface exposes a two-40 coordinated Zn<sub>2</sub><sub>c</sub> atomic site and two planar [CrO<sub>4</sub>]<sub>pla</sub> sites 41 under typical reductive atmosphere, while the reduced ZnCr<sub>2</sub>O<sub>4</sub> 42 (111) surface exposes two Zn<sub>2</sub><sub>c</sub> atomic sites and two five-43 coordinated pyramidal [CrO<sub>5</sub>]<sub>pyr</sub> sites near the O<sub>V</sub>.<sup>16</sup>

#### 44 3.1 Ketene formation on ZnCrO<sub>x</sub>

By exploring various reaction pathways, we determined 46 that ketene formation mainly follows the CO-> CHO -> CHOCO 47 -> CH<sub>2</sub>CO mechanism on the reduced  $Zn_3Cr_3O_8$  (0001) and 48 ZnCr<sub>2</sub>O<sub>4</sub> (111) surfaces, with the CHO species serving as the key 49 intermediate, as illustrated in Figure 1a. Alternative reaction 50 pathways and local minima, transition state structures of 51 ketene formation are presented in Figure S2, Figure S3 and 52 Figure S4. For comparison, two dominant pathways reported in 53 our previous work<sup>16</sup>, namely methanol and methane synthesis 54 on these two surfaces from syngas, are also shown in Figure S2 55 and Figure S3.

56 **CO to CHO\*** The reaction initiates with the physical adsorption 57 of CO, followed by hydrogenation to form a surface aldehyde 58 group (CHO\*). Our calculations reveal that the  $Zn_3Cr_3O_8$  (0001) 59 and  $ZnCr_2O_4$  (111) surfaces share similar Gibbs free energy



Figure 1 Syngas conversion mechanisms on the  $Zn_3Cr_3O_8$  (0001) and  $ZnCr_2O_4$  (111) surface at 673 K and 2.5 MPa (H<sub>2</sub>/CO = 2.5). (a) Gibbs free energy profiles for the formation pathways of ketene on two  $ZnCrO_x$  surface. The red and blue lines denote ketene formation routes on the  $Zn_3Cr_3O_8$  (0001) and  $ZnCr_2O_4$  (111) surfaces, respectively. (\* indicates surface-adsorbed species). (b) Surface structures of key intermediates on the  $Zn_3Cr_3O_8$  (0001) surface. (c) Surface structures of key intermediates on the  $Zn_3Cr_3O_8$  (0001) surface. (c) Surface structures of key intermediates on the  $Zn_3Cr_3O_8$  (111) surface. The blue, green, red, gray and white spheres represent Zn, Cr, O, C, H atoms, respectively.

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 $_1$  barriers (1.23 eV) and reaction energies (~0.70 eV), consistent  $_2$  with our previous results.  $^{16}$ 

3 **CHO\* to CH<sub>2</sub>CO** Once CHO\* species is formed, distinct 4 conversion behaviors emerge on these two ZnCrO<sub>x</sub> surfaces. On 5 the Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> (0001) surface, the CHO\* preferentially stands on 6 the Zn atom. The CO molecule then occupies the neighboring 7 Cr<sub>2</sub> site while forming an additional C-O bond with adjacent 8 surface O\* species (Figure 1b). This CO adsorption process 9 requires an energy of 0.96 eV to overcome the entropy loss. 10 Following CO adsorption, the CHO\* species can couple with CO 11 to form a tridentate glyoxylic group (CHOCO\*), as illustrated in 12 Figure 1b, with a reaction energy of -1.68 eV and a Gibbs free 13 energy barrier of 0.58 eV. It is noteworthy that this C-C coupling 14 step serves as the rate-determining step with an overall Gibbs 15 free energy barrier of 2.24 eV. The subsequent conversion of 16 CHOCO\* proceeds more readily. It undergoes a further 17 hydrogenation to form the bidentate adsorbed ketene <sup>18</sup> (CH<sub>2</sub>CO<sup>\*</sup>), as shown in Figure 1b, with a Gibbs free energy <sup>19</sup> barrier of 0.56 eV and a reaction energy of 0.40 eV. Finally, the <sup>20</sup> generated ketene desorbs into the gas phase with an energy <sup>21</sup> release of 0.31 eV. The remaining surface O<sup>\*</sup> can be easily <sup>22</sup> reduced by CO and H<sub>2</sub>, as reported in our previous work.<sup>16</sup>

<sup>23</sup> Compared to the reaction on the  $Zn_3Cr_3O_8$  surface, the <sup>24</sup> syngas conversion to ketene on  $ZnCr_2O_4$  exhibits a lower total <sup>25</sup> Gibbs free energy barrier. As shown in Figure 1a (blue line), the <sup>26</sup> major differences between the two catalysts lies in the <sup>27</sup> adsorption energy of CO in the presence of CHO\* species. The <sup>28</sup> ZnCr<sub>2</sub>O<sub>4</sub> surface can adsorb CO with an adsorption energy of <sup>29</sup> 0.60 eV, which is 0.36 eV stronger than that on the Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> <sup>30</sup> surface. Subsequently, the CHO\*-CO\* coupling free energy <sup>31</sup> barrier measures 0.73 eV, resulting in a total Gibbs free energy <sup>32</sup> barrier of 2.01 eV, 0.23 eV lower than that observed on the <sup>33</sup> Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> surface. Further conversion of CHOCO\* to ketene <sup>34</sup> requires only a minimal Gibbs free energy barrier of 0.49 eV.



**Figure 2** Gibbs free energy profiles for C-C coupling pathways on H-SAPO-34 catalysts and surface structures of key intermediates during the C-C coupling pathways on H-SAPO-34 inner surface. Methanol-to-CH<sub>3</sub>\*, CH<sub>3</sub>\* conversion-to-ketene/ethene are plotted in brown, pink and red lines, respectively. Structures of surface-adsorbed and O-adsorbed species are denoted by \*. The Al, Si, P, O, C and H are rendered by purple, yellow, pink, red, gray and white spheres, respectively.

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#### 13.2 Ketene formation on SAPO-34

Next, we explore the ketene formation pathway on zeolite. 2 3 For SAPO-34 zeolite, we selected a medium-strength acid site 4 with an NH<sub>3</sub> temperature-programmed desorption peak at 737 5 K.40 The introduced Si atom in SAPO-34 is located at the corner 6 of the 6- and 8-membered-ring (MR) structure, slightly 7 distorted by the additional H atom (see Supporting Information 8 Figure S5). We found that in SAPO-34 zeolite, ketene formation 9 proceeds through the methanol to CH<sub>3</sub>\* pathway, followed by 10 methoxy carbonylation, as illustrated in Figure 2a. The surface 11 CH<sub>3</sub>\* species is identified to play a central role in both ketene 12 formation and conversion. All the local minima and transition 13 states involving  $CH_3^*$  are shown in Figure S6. The detailed 14 reaction pathways are presented as follows.

15 CH<sub>3</sub>OH to CH<sub>3</sub>\* In the methanol-to-CH<sub>3</sub>\* pathway, CH<sub>3</sub>OH 16 diffuses into the 8-MR cages of H-SAPO-34 and anchors near 17 acidic sites through hydrogen bonding with a length of 1.71 Å, 18 as illustrated in Figure 2. The adsorbed methanol (CH<sub>3</sub>OH\*) is 19 protonated by surface H\* to form hydrogenated methanol 20 ( $CH_3OH_2^*$ ), whose C-O bond length measures 1.49 Å, as shown 21 in Figure 2. This step exhibits a Gibbs free energy barrier of 1.60 22 eV and a reaction free energy of 1.05 eV. Subsequently, 23 CH<sub>3</sub>OH<sub>2</sub>\* undergoes C-O dissociation to generate the key 24 intermediate CH<sub>3</sub>\* and water, with a Gibbs free energy barrier 25 of 0.98 eV and an exothermic energy change of 1.05 eV. The 26 length of the newly formed C-O bond in the key intermediate  $27 \text{ CH}_3^*$  is 1.49 Å, similar to that of the CH<sub>3</sub>OH<sub>2</sub>\* species (see 28 Figure 2). The total Gibbs free energy barrier for CH<sub>3</sub>\* 29 generation is 1.99 eV, consistent with literature reports.<sup>41–43</sup>

#### 30 CH<sub>3</sub>\* to CH<sub>2</sub>CO The further transformation of CH<sub>3</sub>\* to ketene

DOI: 10.1039/D5SC01651G 31 proceeds also suffers a high Gibbs free energy barrier, as 32 illustrated in Figure 2 (pink line). The CO adsorbs near CH<sub>3</sub>\* 33 group with the energy need of 0.58 eV. Subsequently, CH<sub>3</sub>\* 34 combines with CO\* to form an adsorbed acetyl species 35 (CH<sub>3</sub>CO\*) with a C-C bond length of 1.41 Å and a C-O bond 36 length of 1.14 Å (see Figure 2), overcoming a Gibbs free energy 37 barrier of 1.41 eV and requiring an energy input of 0.32 eV. This 38 step is followed by dehydrogenation, which requires 39 overcoming a Gibbs free energy barrier of 0.04 eV, resulting in 40 the formation of CH<sub>2</sub>CO. The C-C bond shortens to 1.33 Å and 41 the C-O bond elongates to 1.17 Å compared to CH<sub>3</sub>CO\*, as 42 shown in Figure 2. The total Gibbs free energy barrier for this 43 pathway is 1.99 eV. It is noteworthy that the reversion of this 44 pathway, i.e. ketene transformation to CH<sub>3</sub>\*, has a total Gibbs 45 free energy barrier of 2.07 eV, being higher than the other 46 pathways reported in Figure 2. This suggests that ketene once 47 produced on ZnCrO<sub>x</sub> surfaces is well likely to diffuse to zeolite.

#### 49 3.3 Ketene conversion on SAPO-34

Once ketene is formed, its further conversion with surface 50 51 CH<sub>3</sub>\* to ethene is more facile, as illustrated by the red line in 52 Figure 2. Initially, ketene adsorbs near the surface CH<sub>3</sub>\* species 53 with an energy requirement of 0.69 eV, as shown in Figure 2. 54 Subsequently, the adsorbed CH<sub>2</sub>CO species undergoes C-C 55 coupling with CH<sub>3</sub>\* to form the propionyl species (CH<sub>3</sub>CH<sub>2</sub>CO\*), 56 with the newly formed C-C bond measuring 1.57 Å while the 57 length of the first C-C bond elongates to 1.43 Å, as illustrated 58 in Figure 2. This step exhibits a moderate Gibbs free energy 59 barrier of 0.97 eV and is exothermic by 0.11 eV. The CH<sub>3</sub>CH<sub>2</sub>CO\* 60 then cleaves the C-H bond in the methyl group to regenerate



Figure 3 Conversion and selectivity results from microkinetic simulations at steady state on ZnCrO<sub>x</sub>, SAPO-34 and **ZnCrO<sub>x</sub>** |SAPO-34 surfaces under different conditions. For ZnCrO<sub>x</sub> and ZnCrO<sub>x</sub> |SAPO-34, the temperature and pressure were maintained at 673 K and 2.5 MPa, with  $H_2/CO = 2.5$ . For SAPO-34, an additional total pressure of methanol and ketene (1.0 MPa) was included in the condition. Two columns in the ZnCrO<sub>x</sub> part show the results from Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> (0001) and ZnCr<sub>2</sub>O<sub>4</sub> (111) surfaces. In the SAPO-34 part, four columns represent varying ratios of CH<sub>3</sub>OH (M) to CH<sub>2</sub>CO (K) in the feed gas is varied across four levels: all methanol, 9:1, 1:1 and all ketene (denoted by the percentage of CH<sub>2</sub>CO). The first two columns in the ZnCrO<sub>x</sub>|SAPO-34 part show results from SAPO-34 composited with the Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> (0001) and ZnCr<sub>2</sub>O<sub>4</sub> (111) surfaces, respectively; the third column demonstrates the assistance of typical MTO results with Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> [SAPO-34; the last column presents experimental results from ref. 1. The red and orange colors in the last two columns represent C<sub>2-4</sub> light olefins and C<sub>1-4</sub> light alkanes, respectively. Conversion is expressed using the common logarithm form of the total CO consumption rate, denoted by squares.

1 the zeolite acid site and form the  $CH_2CH_2CO^*$  species, which 2 spontaneously decomposes through C-C bond cleavage to 3 generate CO and ethylene molecules. This step presents a 4 Gibbs free energy barrier of 1.23 eV and releases substantial 5 energy (1.67 eV). The overall Gibbs free energy barrier for 6 ketene conversion to ethene is 1.82 eV.

#### 7 3.4 Byproduct Pathways: methanol, methane, CO<sub>2</sub>, DME, 8 Ester Formation and methanol, ketene diffusion

9 Apart from ketene pathways, we also considered the 10 formation of other byproducts, including methanol, methane, 11 CO<sub>2</sub>, DME and two esters (methyl acetate and formate acetate) 12 in order to establish a complete reaction network for 13 microkinetic simulations. The exploration of the associate 14 reaction pathways was conducted when it is necessary.

For the formation of methanol and methane, our previous 16 work has demonstrated that the  $Zn_3Cr_3O_8$  (0001) surface serves 17 as the dominant active surface for methanol formation with a 18 Gibbs free energy barrier of 1.69 eV, while the  $ZnCr_2O_4$  (111) 19 surface is responsible for methane formation with a Gibbs free 20 energy barrier of 1.75 eV.

As for CO<sub>2</sub> formation, during the deoxygenation process, 22 the presence of CO leads to the formation of water, which is 23 subsequently catalyzed to CO<sub>2</sub> by ZnCrO<sub>x</sub>. We therefore further 24 examined the water-gas shift (WGS) process on the ZnCrO<sub>x</sub> 25 surface. As illustrated in Figure S7, this process follows the H<sub>2</sub>O 26 -> OH\* -> COOH\* -> CO<sub>2</sub> pathway with a total Gibbs free energy 27 barrier of < 1.30 eV. This indicates the ease of the WGS process, 28 where most H<sub>2</sub>O is expected to be transformed into CO<sub>2</sub>.

For DME formation, it involves the reaction of  $CH_3^*$  with 30 adsorbed  $CH_3OH^*$ , forming protonated dimethyl ether 31 ( $CH_3OHCH_3^*$ ), which then deprotonates to produce DME 32 (Figure S8). This pathway is dynamically favorable, with an



Figure 4 Key reaction pathways pruned from the STO conversion on the  $Zn_3Cr_3O_8|SAPO-34$  catalyst. Species on the surfaces of  $ZnCrO_x$  and SAPO-34 are enclosed in upper and lower frames, respectively. The methanol-mediated pathway is depicted in brown; the ketene formation pathway on  $ZnCrO_x$  and SAPO-34 surfaces are plotted in pink and blue, respectively; the ethene formation and water gas shift pathways are shown in red and purple, respectively.

33 overall Gibbs free energy barrier of 1.49 eV.

<sup>34</sup> For the formation of the two esters, the processes <sup>35</sup> proceed through C-O bond addition of CHO\* and CH<sub>3</sub>CO\* with <sup>36</sup> CH<sub>3</sub>OH, followed by deprotonation, with a total Gibbs free <sup>37</sup> energy barrier of approximately 1.5 eV and a reaction energy <sup>38</sup> of -0.5 eV. Detailed reaction profiles and energy diagrams for <sup>39</sup> these pathways are presented in Figure S8.

<sup>40</sup> To complete the kinetics cycle, we also examined the <sup>41</sup> diffusion kinetics of molecules,  $CH_3OH$  and  $CH_2CO$  in the AlPO-<sup>42</sup> 34 zeolite by utilizing enhanced molecular dynamics via <sup>43</sup> umbrella sampling.<sup>44–46</sup> The diffusion barriers for both <sup>44</sup> methanol and ketene are found to be below 0.6 eV (see Figure <sup>45</sup> S9), indicating that the diffusion of molecules is not rate-<sup>46</sup> determining and will not change the STO reaction mechanism.

#### 47 3.5 Microkinetic simulation of ZnCrO<sub>x</sub> | SAPO-34 catalysts

Our microkinetic simulations were conducted based on 49 the DFT reaction network data using CATKINAS software. Three 50 scenarios were considered:  $ZnCrO_x$  alone, SAPO-34 zeolite 51 alone, and the coupling of  $ZnCrO_x$  and SAPO-34 zeolite 52 composite, each involving 23, 19 and 42 elementary steps in 53 building the microkinetic equations, respectively. In the 54 coupled system, diffusion kinetics were neglected, with each 55 gas molecule assumed to diffuse randomly.

56 First, we assessed the product distribution of ZnCrO<sub>x</sub> in the 57 absence of zeolite and the result on the product distribution is 58 shown in Figure 3 (Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> column). It shows that methanol is 59 predominately formed on the  $Zn_3Cr_3O_8$  (0001) surface, 60 consistent with the previous reports that the main product of  $61 \text{ ZnCrO}_{x}$  with Zn:Cr = 1:1 is methanol.<sup>47</sup> Methane and ketene 62 production remains negligible, with partial pressures at least 63 four orders of magnitude lower than that of methanol (see 64 Figure S10). The CO conversion rate is 1.64 s<sup>-1</sup>, comparable to 65 experimental results.<sup>37,47</sup> For the ZnCr<sub>2</sub>O<sub>4</sub> surface, the product 66 distribution shows a notable difference, with 50 % methane 67 and 50 % CO2 as the primary products. The methane synthesis 68 pathway is both dynamically and thermodynamically more 69 favorable compared to methanol and ketene formation (see 70 Figure S11). The CO conversion rate is 0.28 s<sup>-1</sup>, accounting for 71 one-sixth of that on the Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> surface, consistent with the 72 lower reaction activity of ZnCrO<sub>x</sub> catalyst with Zn:Cr= 1:2.<sup>2,47</sup> In 73 summary, in the absence of zeolite, ketene formation is 74 unattainable, aligning with experimental knowledge that only 75 methane and methanol can be produced on the ZnCrO<sub>x</sub> 76 catalysts.

Next, we investigated the product distribution of SAPO-34 78 in the absence of ZnCrO<sub>x</sub>. Considering that the both ketene and 79 methanol are proposed as the transfer intermediates in the 80 ZnCrO<sub>x</sub> | SAPO-34 system, we directly introduced the ketene 81 and methanol into the feed gas with varying methanol:ketene 82 (M:K) ratios, as shown in all SAPO-34 columns of Figure 3. All 83 the experiments were conducted at the temperature of 673 K, 84 with a syngas pressure of 25.0 bar (H<sub>2</sub>/CO = 2.5), and methanol 85 and ketene pressures of 10.0 bar at varying M:K ratios. When 86 only pure methanol was added to the feed gas, the reaction 87 rate is 0.004 s<sup>-1</sup>, with a product distribution of 34 % ethene, 21 % 88 CH<sub>3</sub>OCH<sub>3</sub> and 45 % H<sub>2</sub>O release. Upon the introduction of 89 ketene into the feed gas, ethene selectivity significantly 90 improves to > 78 % with < 3.0 % CH<sub>3</sub>OCH<sub>3</sub> production when the This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence

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1 M:K ratio is < 9:1. The conversion rate also increases to > 0.01  $2 \text{ s}^{-1}$ . This indicates that the presence of ketene can indeed 3 enhance the ethene selectivity and reaction rate.

4 Finally, we take both ZnCrO<sub>x</sub> and SAPO-34 into 5 consideration with the possible products reaching to eight 6 species, including CO<sub>2</sub>, CH<sub>3</sub>OH, CH<sub>2</sub>CO, CH<sub>4</sub>, CH<sub>2</sub>=CH<sub>2</sub>, 7 CH<sub>3</sub>COOCH<sub>3</sub>, HCOOCH<sub>3</sub> and CH<sub>3</sub>OCH<sub>3</sub>. As illustrated in Figure 3 8 and Figure S12, in the ZnCr<sub>2</sub>O<sub>4</sub> SAPO-34 system, we observed 9 that once CH<sub>4</sub> is generated on ZnCr<sub>2</sub>O<sub>4</sub>, it becomes too stable 10 to convert to any other product, resulting in CH<sub>4</sub> remaining as 11 the final product even with the addition of SAPO-34. In contrast, 12 in the  $Zn_3Cr_3O_8|SAPO-34$  system, we found that the CO 13 conversion rate is 0.025 s<sup>-1</sup> and the main products are  $CO_2$ , 14 ethene and DME with the selectivity of 44.4 %, 33.3 % and 15 22.3 %, respectively, as shown in the Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> SAPO-34 16 column of Figure 3. When considering the DME conversion via 17 the typical MTO process, based on the experimental results 18 indicating that the MTO process normally generates  $\sim$  80 % C<sub>2</sub>-19 C<sub>4</sub> olefins and ~10 % light alkanes (<C<sub>4</sub>),<sup>48</sup> we find that the final 20 product selectivity of CO<sub>2</sub>, light olefin and alkane is 49.9 %, 21 47.8 % and 2.1 %, respectively (Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub>|SAPO-34 with MTO 22 column in Figure 3). This result, not only the evaluated CO 23 conversion rate but also the product distribution, is well 24 consistent with the experimental results for the products of 25 ZnCrO<sub>x</sub>|SAPO-34 system reported by Jiao et al. (see the 26 ZnCrO<sub>x</sub> | SAPO-34 column in Figure 3).<sup>1</sup>

27 Microkinetic simulations allow us to evaluate 28 guantitatively the contribution of each reaction pathway in the 29 Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> SAPO-34 catalyst. As illustrated in Figure 4, we 30 observed that approximately 95.8 % of the CHO\* species 31 undergo stepwise hydrogenation to produce CH<sub>3</sub>OH, while a 32 minor fraction of 4.2% of CHO\* species follows the C-C coupling 33 pathway to form CH<sub>2</sub>CO on the Zn<sub>3</sub>Cr<sub>3</sub>O<sub>8</sub> (0001) surface. The gas 34 mixture of CH<sub>3</sub>OH and a small amount of CH<sub>2</sub>CO then diffuses 35 into the zeolite cages. Within the zeolite framework, all the 36 methanol is converted into methyl groups, of which 46.3 % 37 undergo further carbonylation to form ketene, while the other 38 half remains and couples with the generated ketene to form 39 ethene. Therefore, 86.1 % amount of ketene can be derived 40 from CH<sub>3</sub>OH within the zeolite cage. This in-situ generated 41 ketene within the zeolite, along with the 13.9 % of diffused 42 ketene from the ZnCrO<sub>x</sub> surface, contributes to the production 43 of ethene.

44 We are now at a position to clarify the roles of ketene and 45 methanol as reaction intermediates in the OX-ZEO system. Our 46 results reveal that methanol serves as the primary transport 47 intermediate between metal oxide and zeolite, while ketene 48 acts as the dominant intermediate for ethene formation. This 49 explains why both ketene<sup>1,7–13,18</sup> and methanol<sup>14,15</sup> are 50 observed in experiments. Moreover, the zeolite component 51 actively participates in ketene generation rather than merely 52 receiving it from ZnCrO<sub>x</sub>, with the methanol carbonylation step 53 in zeolite being the rate determining step. Consequently, 54 optimizing activity of the zeolite part should be the correct 55 direction for improving the performance of STO catalysts, 56 which has been validated by recent experimental results 57 showing CO conversion exceeding 80 % through zeolite 58 modification by Ge.<sup>4</sup>

#### 59 4. Conclusions

By using G-NN based large-scale atomic simulations, this 1 work unraveled STO reaction pathways on  $ZnCrO_x|SAPO-34$ 2 composite catalysts with particular focus on ketene generation 3 and transformation pathways, including the formation of 4 ketene on  $ZnCrO_x$  via CO hydrogenation and on SAPO-34 via 5 methanol carbonylation, and the subsequent conversion of 66 ketene to products (ethene) in zeolite. We show that methanol 7 serves as the primary transport intermediate between metal 80 oxides and zeolites, while ketene acts as the dominant 9 intermediate for ethene formation in the OX-ZEO system. Our 70 main findings are highlighted as follows.

On the ZnCrO<sub>x</sub> surface, ketene formation requires a higher 71 72 Gibbs free energy barrier (> 2.0 eV) compared to methanol and 73 methane synthesis (< 1.8 eV), indicating the difficulty of ketene 74 formation when using the  $ZnCrO_x$  catalyst alone. Within the 75 SAPO-34 zeolite, ketene can be formed through the methanol 76 carbonylation pathway with a Gibbs free energy barrier of 1.99 77 eV. The subsequent conversion of ketene to ethylene follows 78 the  $CH_2CO^* \rightarrow CH_3CH_2CO^* \rightarrow CH_2=CH_2$  pathway, requiring a 79 Gibbs free energy barrier of 1.82 eV. Taking both ZnCrO<sub>x</sub> and 80 SAPO-34 into consideration, microkinetic simulations prove 81 that ketene generation follows a dual-site mechanism: the 82 majority of ketene (86.1%) originates from STM on the ZnCrO<sub>x</sub> 83 surface coupled with methanol carbonylation within the zeolite, 84 while the remaining ketene (13.9%) is derived from CHO\*-CO 85 coupling on the ZnCrO<sub>x</sub> surface. The introduction of the ketene 86 pathway into the STO process significantly alters the reaction 87 performance with a higher ethene selectivity, distinct from 88 typical MTO process. The methanol carbonylation step in 89 zeolite is the rate-determining step and thus decides the 90 activity of STO catalysts, implying that the tuning of the zeolite 91 property should be the effective measure to improve the 92 activity of the composite catalyst.

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#### 105 Competing interests

106 The authors declare no competing interests.

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• The data supporting this article have been included as part of the Supplementary Information.