A first-principles investigation of gas phase ring opening reaction of furan over HZSM-5 and Ga-substituted ZSM-5

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Gas phase Reactions

To understand the thermodynamic and kinetic feasibilities of various reactions of furan, free energies and activation barriers of selected gas phase reactions are computed using the density functional theory (DFT) based on B3LYP/6-311G(d) level of theory. The computed thermodynamic (free energy, ΔG) and kinetic (energy barrier, ΔG^*) of furan conversion, forming (1) formyl allene, (2) propyne, (3) allene, and (4) ketene are shown in the **Figure S1**. The three-dimensional structures associated with the **Figure S1** are also presented in the supporting information (**Figure S2**, **Figure S3**, and **Figure S4**).



Figure S1. Selected reaction pathways associated with the furan decomposition and their computed energetics at the B3LYP/6-311G(d) level of theory. The computed Gibbs free energies (default numbers, unless noted as the energy barriers (ΔG^*)) at the room temperature (298 K) are shown in eV units. Values in red fonts in parentheses represent the energetics at a higher

temperature, 873 K. Three-dimensional structures of all intermediates are presented in **Figure S2**, **S3**, and **S4** of the supplementary information.

Based on computed thermodynamic and kinetic parameters, the formation of formyl allene, propyne and allene are initiated via an intermediate, β -carbene, while the formation of ketene is initiated via α -carbene (see **Figure S1**). Formyl allene acts as an important intermediates for the further formation of allene and propyne. The computed results show that formation of formyl allene and propyne are the dominant reactions. The rate-determining step is the formation of β carbene ($\Delta G^* = 3.06 \text{ eV}$). In terms of thermodynamics, formation of propyne and CO is preferred (0.55 eV) compared to formation of formyl allene (0.77 eV) due to the gain in entropy. Formation of propyne and CO become dominant when the reaction temperature increases. Computations suggest that the production of allene is the result of isomerization of propyne rather than the direct pyrolysis of furan. Additionally, formation of ketene and acetylene occurs from α -carbene intermediate. Formation of propyne or allene from α -carbene require significant reaction barriers (4.31 and 5.31 eV respectively, **Figure S1**) compared to the β -carbene route (3.06 and 3.51 eV respectively, **Figure S1**). These mechanistic suggestions are consistent with the experimental studies by Urness *et al.*¹ and with the theoretical studies by Sendt *et al.*² and Tian *et al.*³. Supporting information



Figure S2. Computed intermediates and transition state structures associated with the gas phase conversion of furan via α -carbene species. The computed gas phase Gibbs free energies at 298 K (with respect to furan in eV units) using the B3LYP/6-311G(d) level of theory is also shown.

Supporting information



Figure S3. Computed intermediates and transition state structures associated with the gas phase conversion of furan via β -carbene species. The computed gas phase Gibbs free energies at 298 K (with respect to furan in eV units) using the B3LYP/6-311G(d) level of theory is also shown.



Figure S4. Computed reaction intermediates and transition state structures of propyne-allene pathway. The computed gas phase Gibbs free energies at 298 K (with respect to furan in eV units) using the B3LYP/6-311G(d) level of theory is also shown.



Figure S5. Structures of NEB image for 3D -> 3E^{TS} -> 3F.

(Notes: In order to find the transition state structure, the NEB and dimer methods are used. NEB calculation is performed first to obtain the initial guess for the saddle point, which is used as the starting structure for dimer calculations. The 3F shows in the Figure 3 is the most stable structure. When doing the NEB calculation, we use the less stable structure (0.13 eV less stable) for 3F (main manuscript). This calculated energy barrier is lower using the image 08 as final state. We included 7 images for NEB calculations. The image for the reaction step 3D -> 3E^{TS} -> 3F is shown in **Figure R1**. The image 04 is the predicted saddle point, which is further used as the initial guess for dimer calculation. The converged structure from dimer calculation is shown in main text **Figure 3**.)

Reference

1. Urness, K. N.; Guan, Q.; Golan, A.; Daily, J. W.; Nimlos, M. R.; Stanton, J. F.; Ahmed, M.; Ellison, G. B., Pyrolysis of Furan in a Microreactor. *The Journal of chemical physics* **2013**, *139* (12), 124305.

2. Sendt, K.; Bacskay, G. B.; Mackie, J. C., Pyrolysis of furan: Ab initio quantum chemical and kinetic modeling studies. *Journal of Physical Chemistry A* **2000**, *104* (9), 1861-1875.

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