The Curious Case of Ketene in Zeolite Chemistry and Catalysis

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Ketenes ($R_2C=C=O$; $R=H$, alkyl, etc.) have been a very popular synthon in the organic synthesis and chemical industry for almost a century.^[1,2] First industrially used for the production of acetic anhydride and cellulose acetate in the 1920s,^[1] since then ketenes have proved themselves as an essential member of the first generation of highly reactive intermediates in organic chemistry, along with carbocations, carbanions, radicals, and carbenes.^[2] Although the *in situ* formation and role of other first-generation intermediates has been comprehensively studied in zeolite chemistry and catalysis (or heterogeneous catalysis in general),^[3] the potential role of ketene has hardly been studied. It is most likely due to the fact that the experimental detection of 'short-lived' ketene is notoriously difficult to achieve. However, over the last two years, it has been postulated that ketenes may play a relevant role in controlling selectivity in important zeolite-catalyzed processes.^[4–12] Contrary, other reports suggested that the formation of ketene is detrimental in zeolite-catalyzed hydrocarbon conversion processes, as it is claimed the presence of it promotes the deactivation of the catalyst *via* formation of coke species.^[8,11,13] As a consequence, an apparent 'conflict' or 'ambiguity' exists regarding the role of ketene in zeolite chemistry, which we believe needs to be resolved. Because mechanistic understanding is instrumental in the development of superior catalytic processes, this highlight article is dedicated to emphasizing the (beneficial or detrimental) significance of this intermediate in zeolite catalysis.

Ketenes were experimentally observed in 2016 by Jiao *et al.* (Figure 1), during the conversion of syngas-to-light olefins using composite catalysts.^[4] The dual component catalyst consisted of a 'spinel' metal oxide ($Zn-CrO_x$) and a mesoporous MSAPO material (Figure 1a), and was reported to produce C_2 - C_4 hydrocarbons (*i.e.*, C_2^o - C_4^o olefins + C_2^o - C_4^o paraffins) with selectivity as high as 94% (including 80% C_2^o - C_4^o) at a CO conversion of 17%.^[4] The authors attributed such high C_2^o - C_4^o selectivity to the formation of a ketene as an intermediate, through the insertion of carbon monoxide, on the partially reduced oxide surface, resulting in the suppression of polymerization of CH_x -species (Figure 1a).^[4,5] The gas-phase presence of ketene was confirmed by highly sensitive synchrotron-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) (Figure 1a, inset). It was proposed that ketenes subsequently diffused from the oxide-phase to the confined acidic pores of the zeolite to produce olefins *via* decarbonylation, in an analogous way to the methanol-to-olefins (MTO) chemistry.^[8] Herein, Jiao *et al.*'s bifunctional catalyst is conceptually an ensemble of a methanol synthesis and a MTO catalyst, instead of a typical Fischer Tropsch (FTS) catalyst.^[4,5] Therefore, more

thermodynamically stable methanol (instead of ketene) could be the key intermediate, as proposed by de Jong.^[5] In order to address this issue, in the follow-up publication, the same group used zeolite MOR (instead of SAPO),^[6] which remarkably gives up to 73% selectivity to ethylene (earlier only ~23%),^[4] at 26% CO conversion (Figure 1b).^[6] This product distribution (A & B in Figure 1b) is remarkably different from the one that would be expected when performing the MTO reaction over MOR (C & F in Figure 1b). Although one could argue that the effect of hydrogen and the high pressures used in the process may be responsible for this high selectivity, these results seem to advocate in favor of ketene (not methanol) as the primary intermediate during the reaction, which simultaneously was theoretically verified by Wang *et al.*^[7] The reason why the oxide component in the bifunctional catalyst prefers to form ketene and not methanol still remains ambiguous and calls for additional research, which should certainly include the use of physically mixed catalysts and double-bed 'non-mixed' reactor configurations.

Figure 1. (a) An illustration of the composite oxide-zeolite catalyzed syngas-to-olefin process, through the involvement of a ketene-intermediate. The formation of ketene essentially inhibits the polymerization of CH_x -entity to circumventing the ASF limits of FTS. Inset: Ketene ($m/z = 42.01$) was detected during an *in situ* study of syngas conversion over $ZnCrO_x$ by SVUV-PIMS. (b) Hydrocarbon distributions over different sites of MOR zeolites at 375 °C. Conversion of syngas over $ZnCrO_x$ -MOR (A, D, G), ketene (B, E, H), and methanol over MOR (C, F, I). The conversion from syngas and ketene is similar, where 8MR sites are accessible (A-C, G-I). Broader product distribution is obtained, where only 12MR sites are accessible (D-F). Reproduced from the references [4-6].

Coming back to the zeolitic component, as pointed out by Wang *et al.*,^[7] the framework bounded ketene species would be reflected in the form of surface acetate species (CH_3CO -zeolite), due to the protonation on the Brønsted acid sites of zeolites. An acetyl group is essentially a physisorbed protonated ketene (*i.e.*, $CH_2=C=O + H$ -zeolite $\rightarrow$ CH_3CO -zeolite) (Figure 2). The rapid equilibrium to acetyl from ketene (*cf.* energy barrier of ≤ 17 kJmol⁻¹ and a large energy gain of >50 kJmol⁻¹) fundamentally toughens its direct experimental detection and triggers the question of whether ketene itself or its derived surface species are the actual reaction intermediates.^[9] Plessow and Studt theoretically proposed that ketenes undergo successive methylation and decarbonylation to form olefins when zeolite H-SSZ-13 is used as MTO catalyst (Figure 2b).^[8] During the MTO process (Figure 2a), it is even more difficult to detect ketene experimentally. A protonated ketene, *i.e.*, surface acetate species would readily be converted to more stable methyl acetate in the presence of methanol (CH_3CO -zeolite + $CH_3OH \rightarrow CH_3CO_2CH_3 + H$ -

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HIGHLIGHT

zeolite).^[8,14] Indeed, both methyl acetate and surface-acetate species have been spectroscopically identified.^[14,15] However, unlike during syngas-to-olefins process, carbon monoxide is hardly reported as a product in MTO chemistry, although it could easily be formed in small amounts as a result of methanol dehydrogenation. In summary, both ketene and surface species most likely derived from ketene have been identified experimentally in MTO like chemistry. Although the formation of these surface species could proceed through other intermediates, however, it is most likely to go through the formation of ketene, considering the fast equilibrium between ketene and surface acetate and the low energy barrier.^[9] Overall, these results call for detailed analysis of minor products during MTO chemistry, including both carbon monoxide and hydrogen.^[8]

The potential formation of olefins from methanol and syngas has a conceptual resemblance to the Monsanto and BP's Cativa processes (*i.e.*, Koch-carbonylation of methanol/ dimethyl ether to form acetic acid/methyl acetate), where similar zeolite-acetate species were identified as intermediates (Figure 2c).^[8,9,11,16] Ketenes were further verified by Rasmussen *et al.*, through the identification of doubly deuterated acetic acid ($\text{CH}_2\text{DCO}_2\text{D}$), when D_2O was co-fed during the carbonylation reaction ($\text{CH}_3\text{CO} + \text{D}_2\text{O} \rightarrow \text{CH}_2\text{DCO}_2\text{D}$) (Figure 2d).^[9] Hence, ketenes are formed independently and are the definitive precursor of acetate/acetyl; otherwise, doubly deuterated acetic acid ($\text{CH}_2\text{DCO}_2\text{D}$) could not be observed during D_2O co-feeding experiments. Due to the highly reactive nature of ketene, it also contributes to catalyst deactivation, through the formation of coke/carbonaceous species within the zeolite-framework.^[8,11,13] Since ketene could enhance the selectivity of ethylene during syngas conversion (Figure 1b),^[4,6] cofeeding of carbon monoxide or ketene might produce more ethylene in MTO (and perhaps trigger a faster deactivation). Such a hypothesis could, for instance, explain the very high ethylene selectivity reported on nickel-containing SAPO-34 catalysts during MTO.^[17] Indeed, we speculate that, in this case, nickel may catalyze the dehydrogenation of methanol to carbon monoxide and hydrogen, resulting in reaction conditions very similar to those present in the case of Jiao *et al.*^[4,6]

Figure 2. (a) An illustration of the olefin cycle and (b) overview of the ketene-based initiation mechanism during the zeolite-catalyzed MTO process. Al-OH: Brønsted acid sites (BAS) of zeolite. (c) The formation route of surface-acetate species from a surface-methoxy species (SMS) and CO during MOR-catalyzed Koch-carbonylation to methyl acetate. Reaction steps: 0. CO in vacuum and SMS; 1. acetyl carbocation and zeolite carbanion; 2. ketene physisorbed onto a BAS; 3. acetyl group on the zeolite. (d) The ratio between the mass-spectrometry signal at $m/z=62$ (doubly deuterated acetic acid) and $m/z=61$ (singly deuterated acetic acid). Reproduced from the references [8-9].

Analogous to MTO and Koch-carbonylation chemistry, the formation of surface-acetate species and its equilibrium with ketene is influential during the zeolite catalyzed Friedel-Crafts acylation of aromatics and furanics.^[12,13,18] However, there is a controversy regarding nature/chemical form of the exact acylating agent and the 'critical role' of ketene during catalysis.^[13,18-20] Herein the contribution from Stockenhuber *et al.* is noteworthy.^[13] They observed zeolite tends to shift the equilibrium to ketene from acylium ion in the presence of an aromatic substrate during the Friedel-Crafts acylation of anisole, whereas the zeolite produces ketene from acylium ion *via* dehydrogenation in the absence of a 'host' aromatic molecule.^[13,21] As the Friedel-Crafts acylation undergoes through a typical electrophilic aromatic substitution mechanism, it is expected that an electrophile/carbocation (*i.e.*, acylium ion) would be the actual acylating agent.^[21] Henceforth, ketene was found to be the deactivating agent in this chemistry and has a negative impact on the catalysis.^[13,21] Therefore, more in-depth investigation is required. For instance, co-feeding of aromatics, in principle, is enough to prevent/deaccelerate the ketene-mediated deactivation during any zeolite-catalyzed hydrocarbon conversion.^[13]

The presence of ketene intermediates has also been verified during zeolite-mediated catalytic fast pyrolysis (CFP),^[10] another promising technology that lacks mechanistic information (Figure 3).^[10,11] Van Bokhoven *et al.* first identified fulvenone ketene is responsible for the formation of phenol during CFP of guaiacol (Figure 3a, b) using imaging photoelectron photoion coincidence spectroscopy (iPEPICO) with synchrotron radiation.^[10] Zeolite promotes demethylation of guaiacol to form catechol, which then hydrolyzed to 6-fulvenone (Figure 3c). The $\text{C}_6\text{H}_4\text{O}$ signal at $m/z=92$ in the photoion mass-selected threshold photoelectron spectra (ms-TPES) supports the existence of fulvenone ketene as a reactive CFP intermediate (Figure 3d).^[10] Finally, ketene undergoes two successive hydrogen transfer reactions to form phenol, which led to benzene, *via* dihydroxylation (Figure 3c). This example gives further evidence that ketene may independently form on a zeolite, without being associated with its corresponding surface species; unlike surface-acetate species during MTO, Koch-carbonylation, and Friedel-Crafts acylation over zeolites.

It has been argued in this highlight article that ketene-based reaction intermediates may be as significant in zeolite-catalyzed hydrocarbon conversions as other members of the first generation of highly reactive intermediates. The reported ability of ketene and its associated surface species to promote the formation of carbon-carbon bonds and enhance product selectivity (*e.g.*, ethylene) makes this intermediate a very interesting one. At the same time, although the detrimental effect of ketene could, in principle, be avoided via doing co-feeding experiments, we expect this article to further stimulate researchers to explore the influence of ketene in zeolite chemistry and catalysis. In this sense, research should be directed into identifying the actual role of ketene, *i.e.*, being either a “simple” precursor in the formation of reactive acetate species and acylium ions or a direct participant in the catalytic cycle. Utilization of this knowledge should lead to the design of more efficient catalytic processes. In view of the current knowledge, we anticipate that cofeeding of additional reactants during, *i.e.*, MTO chemistry, in order to either promote or suppress the formation of ketene should lead to much more selective processes.

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Entry for the Table of Contents

HIGHLIGHT

Ketenes would not be neglected

anymore: Unlike other first generation of highly reactive intermediates (*i.e.*, carbocations, carbanions, radicals, and carbenes), the influential role of ketene has never been adequately acknowledged in zeolite chemistry and catalysis. This highlight article intends to give ketene its due credit on its (both beneficial and detrimental) role during catalysis.

A. D. Chowdhury,* J. Gascon*

Page No. – Page No.

The Curious Case of Ketene in Zeolite Chemistry and Catalysis