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Letter to the Editor

Comments on "Effect of organic impurities on the hydrocarbon formation via the decomposition of surface methoxy groups on acidic zeolite catalysts" by Y. Jiang, W. Wang, V.R.R. Marthala, J. Huang, B. Sulikowski, M. Hunger

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In this paper [1] Jiang et al. expand on their group's closely related earlier work by Wang et al. [2] regarding the formation of primary hydrocarbon products during methanol-to-olefin catalysis. According to their proposal, "the decomposition of surface methoxy groups results in the formation of primary hydrocarbons on acidic zeolite catalysts" [1]. In our proposal, there is no direct reaction of methanol or dimethyl ether to form primary hydrocarbon species; instead, olefin conversion during the kinetic induction period is dependent on a primordial hydrocarbon pool formed from "trace impurities in the methanol feed, the catalyst, or the carrier gas" [3]. Wang et al. provided the essential explanation for their proposal, claiming that decomposition of surface methoxy groups likely occurs by either carbene or oxonium-ylide routes [2]. In this letter we show that their proposal [1,2] has been contradicted by recent reports from two groups, and further that their paper printed in this issue contains errors in methodology and interpretation. We further note that the intentional addition of acetone or other organic compounds to a methanol feed to create the hydrocarbon pool in MTO catalysts is described in two patents issued to Exxon-Mobil in 2004 [4,5].

Two very recent communications in *Angewandte Chemie* directly dispute Hunger's proposal on the role of surface methoxy groups. On March 6, 2006 Lesthaeghe et al. published their theoretical study [6] of every possible route by which methanol, dimethyl ether, or surface methoxy groups can react directly to form hydrocarbon species. Summarizing their conclusions, Lesthaeghe et al. noted that "we have tied the numerously proposed reaction mechanisms together to find that not a single combination of direct reaction steps can link methanol to ethylene. This theoretical conclusion provides strong additional support for alternative proposals [citing our Ref. [3] and other papers by Haw and Kolboe], which bypass the highly activated concerted steps." Lesthaeghe et al. explicitly showed that the carbene routes (dependent on their step J1) and oxonium ylide routes (dependent on their steps G1 and X1), both invoked by Wang et al. to provide a rationale for their focus on the role of surface methoxy groups in MTO catalysis [2], do not occur, even at a temperature of 720 K.

The second communication was our most recent paper [7], currently web-published. That paper puts to the test the proposal that surface methoxy groups are capable of forming hydrocarbon species directly, providing an experimental complement to the theoretical study of Lesthaeghe et al. Our experiments probed whether or not surface methoxy groups on an acidic MTO catalyst undergo H/D exchange reactions. This is key to testing the supporting claim of Wang et al. that "at reaction temperatures of $T \geqslant 493$ K, these surface methoxy species most probably act as precursors of carbene or ylide intermediates." Wang et al. had an explanation for how this worked: "Most importantly, at reaction temperatures of $T \geqslant 493$ K, the C–H bonds in the surface methoxy groups are weakened, and hydrogen can be readily abstracted by the basic oxygen atoms of the framework." Note that we are quoting from the 2003 paper of Wang et al. [2], because Jiang et al. [1] did not specify the mechanism for their claimed reaction and cited the 2003 paper, which is the clearest elaboration of their proposal for the role of surface methoxy species in direct reactions during the induction period.

Previously [7], we attempted to observe H/D exchange in surface methoxy groups at temperatures as high as 623 K and observed none, even after 2 h in a plug-flow reactor. From that measurement, we were able to set an upper limit on the rate constant for reaction J1 (carbene formation) of $2 \times 10^{-6}\ \text{s}^{-1}$. Furthermore, our experiment showed no detectable C–H bond activation for any species in equilibrium with methanol, dimethyl

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ether, or surface methoxy groups under reaction conditions—conclusive experimental evidence of the claim of Lesthaeghe et al. that neither the oxonium-ylide nor carbene route operates under MTO conditions [6]. We concluded our earlier work [7] by noting that "the present work in combination with [6] and another paper of Waroquier disproves the central claims of [2] that were recently reiterated in [1]."

Jiang et al. [1] studied the conversion of methanol on the methanol-to-olefin catalyst H-SAPO-34 and used their results to comment on our work in methanol-to-olefin catalysis. However, they have not studied methanol-to-olefin catalysis in their work [1,2]. For MTO on H-SAPO-34, conversion is nearly 100% in the temperature range 573–673 K after the induction period and before deactivation, and the yields are typically >80% ethylene and propene, with most of the remainder butenes and aromatic molecules trapped in the catalyst cages. Thus it is highly significant that none of the NMR or UV/vis spectra of Jiang et al. [1] show any signals due to light olefins. Indeed, the UV absorptions for ethylene and propene are in the vacuum UV at energies far above those studied by Jiang et al. What products did they find in their study? In the ^{13}C NMR spectra in Fig. 2, the following findings are apparent: At 593 K, the spectrum shows aromatic hydrocarbons with methyl substituents (ca. 130 and 24 ppm) and light alkanes (15 ppm). After reaction at 673 K, the spectrum shows mostly light alkanes (15 ppm) and intensity from aromatics. The ^{13}C NMR spectra in Fig. 1 (zeolite HY) also contain large signals due to methane (negative chemical shift) and ethane (ca. 7 ppm). This product spectrum is not characteristic of the kinetic induction period of MTO catalysis, in which methanol and dimethyl ether are converted to the primary products ethylene and propene and little or no light alkane is detectable, nor is it characteristic of MTO on a working catalyst. Note that if any MTO products had been found in the Jiang et al. study, then large, sharp, and characteristic ^{13}C resonances would have appeared in the olefin region. This suggests that the lengthy heating and contact times that Jiang et al. used (20 min) resulted in an aged hydrocarbon pool well past that of a working MTO catalyst.

The UV spectra reported by Jiang et al. are entirely consistent with the distribution of aromatic hydrocarbons as the terminal hydrocarbon pool in a deactivated catalyst [8,9]. In the case of H-SAPO-34 (Fig. 2), this terminal pool is known to contain pyrene ($\lambda_{max} = 263, 273, 306, 320$, and 336 nm; ^{13}C $\delta = 125–131$ ppm), phenanthrene ($\lambda_{max} = 252, 275, 282$, and 294 nm; ^{13}C $\delta = 122–132$ ppm), and naphthalene ($\lambda_{max} = 285$ and 311 nm, ^{13}C $\delta = 126–133$ ppm) [10–12]. Remarkably consistent with our interpretation is the fact that the UV spectra of the corresponding products on HY have their greatest intensities at the longer wavelengths, consistent with the larger deactivating coke molecules possible in the larger faujasite supercage, such as perylene ($\lambda_{max} = 251$ and 434 nm; ^{13}C $\delta = 120–135$ ppm) [12,13]. Large coke molecules can also form on the exterior of zeolite particles in deactivated catalyst beds.

All of the results and interpretations of Jiang et al. [1] assume specific and known sample compositions. Their evidence for sample composition is based largely on the ^{1}H NMR spectra included in Supporting Materials. Fig. S3 of Jiang et al. [1] is reproduced in our Comment with all original notations and caption. The most remarkable feature of the spectra in this figure is the authors' identification of one-bond $^{1}H–^{13}C$ coupling constants of 180 Hz for the surface methoxy on H-SAPO-34 and 220 Hz for the same species on HY. For methoxy groups, these coupling constants fall in a narrow range, typically 140–160 Hz. Representative values include 141 Hz for methanol and 140 Hz for dimethyl ether [10], and 160 Hz for surface methoxy on zeolite X [14]. Values in the vicinity reported by Jiang et al. are simply too large for methoxy groups or most other sp^3 systems (exceptions include $CHCl_3$, at 209 Hz) and are more characteristic of sp^2 systems such as formic acid (222 Hz) [10]. The 160-Hz coupling for surface methoxy groups on zeolite X was seen as a clearly resolved splitting in the ^{1}H spectra of Ref. [14]. No such clear splitting is present in the spectra of Jiang et al. [1]. The reported couplings were determined by deconvolution with the coupling constants treated as free parameters in the fit. A 220-Hz coupling for a methoxy group is a very bold claim; a more prosaic and likely interpretation is that a smaller (140- to 160-Hz) coupling is not resolved in the Jiang et al. spectra, and the deconvolution is evidence of multiple chemical species in addition to the methoxy groups. This is consistent with the observation of very different peak separations for the two catalysts. We note that the decoupled spectra in Fig. S2 do not provide any evidence of a 220-Hz coupling constant.

Also troubling are the signals near 2.7 ppm assigned to silanols (SiOH) in these spectra. One of the co-authors of Refs. [1] and [2] has published three previous papers reporting that silanols on H-SAPO-34 have ^{1}H chemical shifts at or very close to 1.5 ppm for nondefected materials: specifically, 1.5 ± 0.3 ppm [15], 1.5 ± 0.1 ppm [16], or 1.6 ppm [17]. A 1.2-ppm discrepancy in a ^{1}H chemical shift is extraordinary. Moreover, replacing acid sites with one hydrogen each by methoxy groups with three hydrogens each necessarily decreases the percent intensity for the SiOH groups. In the case of H-SAPO-34 in Fig. S3, the value should have decreased from 2.6 to 1.2% had 0.6 equivalents of surface methoxy been formed as claimed, but the percentage of silanols reported increased significantly, to 3.7% with methanol-^{13}C and 5.4% with methanol-^{12}C. This is clear evidence of irreproducibility and oversimplification of the chemistry and species actually present. In their Fig. 1, Jiang et al. [1] show a ^{13}C signal at 63.5 ppm that they assign to 2% dimethyl ether. This signal also appears to be present in Fig. 2 as an unlabeled shoulder. Dimethyl ether and methanol are formed by hydrolysis of surface methoxy groups. Under MTO reaction conditions, water, methanol, dimethyl ether, and surface methoxy groups are in equilibrium; dimethyl ether is the mostly weakly adsorbed of these species. Observation of dimethyl ether in these samples implies the presence of water and methanol as well, and these would not be observed in Fig. 1. The presence of water, methanol, and dimethyl ether on the samples suggests a straightforward explanation for the observation of multiple peaks in the ^{1}H spectra and this also accounts Jiang et al.'s [1] other results.

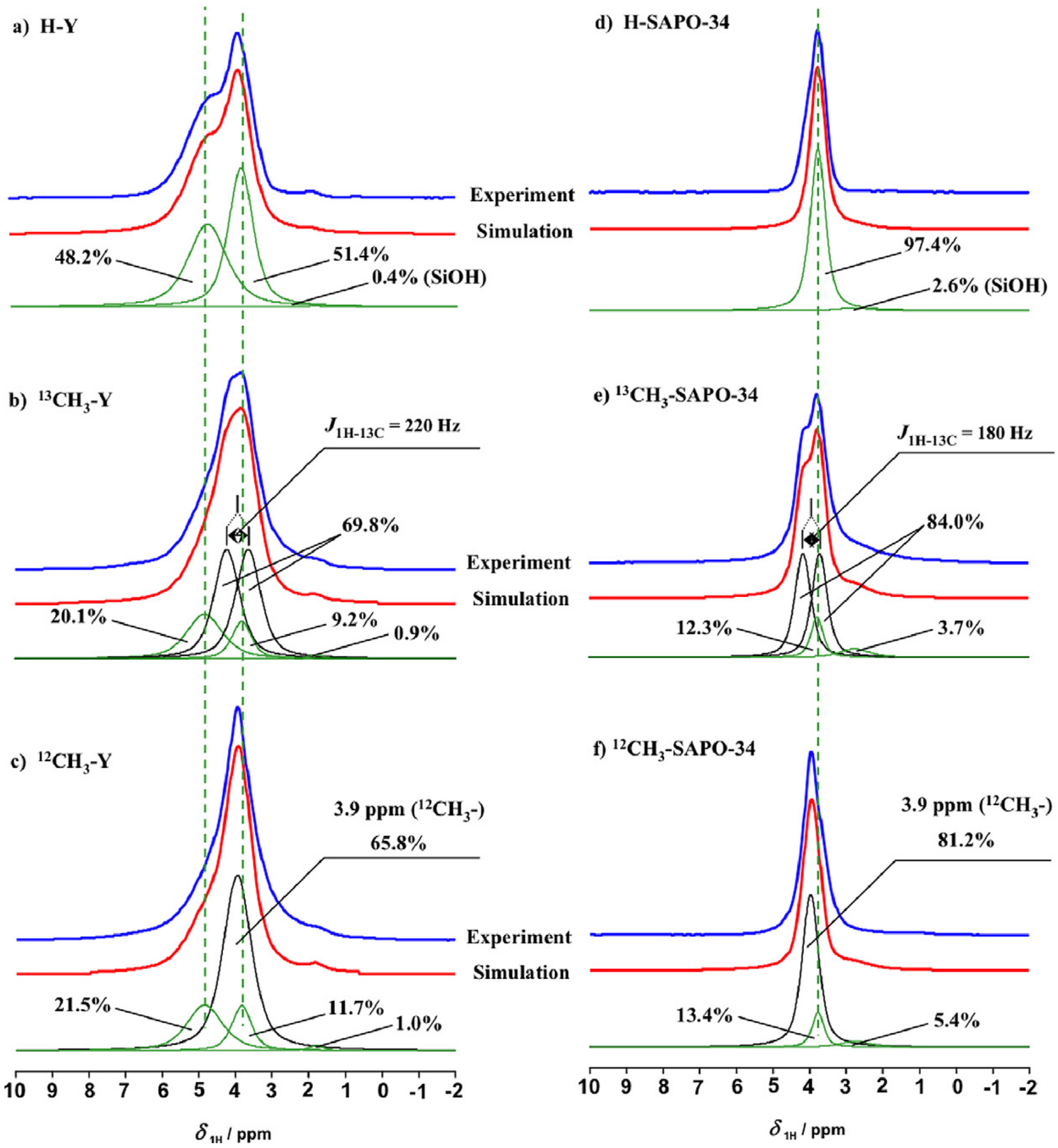

Fig. S3. Deconvolution of the ^{1}H MAS NMR spectra of acidic zeolite H-Y (a), ^{13}C-enriched methylated zeolite Y (^{13}CH$_3$-Y) (b), non-enriched methylated zeolite Y (^{12}CH$_3$-Y) (c), silicoalumino-phosphate H-SAPO-34 (d), ^{13}C-enriched methylated SAPO-34 (^{13}CH$_3$-SAPO-34) (e), and non-enriched methylated SAPO-34 (^{12}CH$_3$-SAPO-34) (f). The quantitative evaluation of the relative intensities is shown for each spectrum.

The debate sparked by Jiang et al. [1] and Wang et al. [2] relates to a reaction that in practice is carried out under flow conditions at ca. 573–773 K. In particular, it pertains to the reaction during a kinetic induction period that lasts a few seconds or tens of seconds under these conditions. The length of this induction period is sensitive to the presence of organic impurities in the methanol feed, catalyst, and carrier gas [3]. Our experimental work has used flow reactors to measure yields and selectivities of volatile products in the time scale of several seconds during the kinetic induction period at 648 K. Recently, we determined the upper limit of the kinetic rate constant for decomposition of surface methoxy groups to carbene to be $2 \times 10^{-6}\ \text{s}^{-1}$ at 648 K [7]. This value is many orders of magnitude too small to support the carbene mechanism favored by Wang et al. [2].

In contrast, Jiang et al. [1] report no product yields, primary or otherwise. They report no selectivities, rate constants, or H/D exchange data [1,2]. They report no spectroscopic evidence of carbene, oxonium ylides, or any other reactive species that could function in a highly energetic direct mechanism such as those they claim. They do not draw a mechanism to explain the direct formation of ethylene from surface methoxy groups before formation of a hydrocarbon pool. What they do report in [1] is spectroscopic measurements on sealed samples prepared by a lengthy sequence of evacuation, heating, sealing, and further heating for no less than 20 min. Their procedure results in thermodynamic products, not the kinetic products of MTO catalysis.

It is important to note that in our work with flow reactors [3,7,18], the *contact times* of reactive olefinic MTO products were only a few seconds in each case, even when we used longer *heating times*. In contrast, in batch reactors [1,2], long *heating times* also necessarily imply long *contact times*. The procedure of Jiang et al. is not designed to, nor is it capable of, probing time scales of several seconds. Their lengthy reaction times in a sealed environment amplify the effects of even the smallest trace impurities through MTO catalysis, which necessarily expands and ages the hydrocarbon pool. Jiang et al. purport to study primary reactivity for methanol-to-olefin catalysis during the kinetic induction period, without studying methanol-to-olefin chemistry or the kinetic induction period. The spectral data presented by Jiang et al. in [1] is evidence only of a hydrocarbon pool aged beyond that of a working MTO catalyst.

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Supplementary material

The online version of this article contains additional supplementary material.

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