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Comment on “Efficient Conversion of Methane to Aromatics by Coupling Methylation Reaction”

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ABSTRACT: Liu et al. recently reported their results on coconversion of methane and methanol at 973 K over a typical methane dehydroaromatization (MDA) catalysts, Mo/HZSM-5.¹ In this work, the authors claimed that adding a small amount of methanol to a methane feed led to more than two times higher methane conversion, substantially higher xylene and toluene selectivities (i.e., combined ca. 80%, nearly an order of magnitude increase as compared to experiments without methanol), and improved catalyst stability to such an extent that no deactivation was observed during 60 h on stream. If reproducible, this result would be a significant achievement, because formation of coke in the MDA reaction has been considered inevitable hitherto. To support their experimental data, Liu et al. carried out a thermodynamic analysis, whose results were in good agreement with their experimental findings.

The purpose of the present commentary is to point out several reproducibility flaws in the work of Liu et al. They concern not only the presented thermodynamic data relevant to coprocessing of methane and methanol but also the experimental observations. Before discussing these two items in detail, we first note that Liu et al. did not discuss several important publications relevant to the influence of oxygenates on the MDA reaction. One of the first studies related to cofeeding oxygen-containing compounds with methane dates back to 1999: Yuan et al. reported that adding a small amount of oxygen to the methane feed (up to O/CH₄ = 0.006) results in slightly improved stability of a 3 wt % Mo/HZSM-5 catalyst.² The main product of coke removal by oxygen was CO, in good agreement with results of our recent study showing that short pulses of oxygen during the MDA reaction decrease the rate of coke deactivation.³ Ichikawa et al. observed that addition of water improves catalyst stability, attributed to steam-reforming of coke species.⁴ The reverse Boudouard reaction of carbonaceous deposits with CO₂ can also improve the stability of MDA catalysts.^{5,6} More recently, in a series of elegant papers, Bhan and co-workers systematically investigated the cofeeding of a range of light oxygenates such as CO₂, water, acetic acid, formic acid, ethanol, methanol, and acetaldehyde with methane.^{7–9} The main insight emanating from this research is that under typical MDA conditions (953 K, 1 bar, Mo/HZSM-5), the oxygenates reform with CH₄ and coke to yield CO and H₂ upstream in a fixed-bed reactor, while the MDA occurs downstream. Furthermore, it was found that the selectivity to aromatic products is independent of the presence of oxygenates in the feed. It should be noted that the O/CH₄ ratio employed by Liu et al. (0.033) is within the range used by Bhan and co-workers (0.012–0.110). Obviously, the large discrepancies in

product selectivity and catalyst stability between these uncited works, and the new results of Liu et al. demand an explanation.

■ THERMODYNAMIC ANALYSIS

As we were surprised by the significant impact of a small amount of methanol on the product distribution, we performed our own thermodynamic analysis. We used the Gibbs reactor model in Aspen Plus to compute mixture composition. This approach allows minimizing the Gibbs free energy of a mixture. Using the same starting composition and thermodynamic conditions as Liu et al., we found very different results. As we expected, the conversion of methane is hardly influenced by the presence of 3.2 vol % methanol in methane. The specific and unusual feature in the 600–1000 K present in the data of Liu et al. could not be reproduced (Figure 1a). Focusing on methanol, our thermodynamic analysis predicts that it can be completely converted over the whole temperature, in complete disagreement with the data of Liu et al. that report methanol conversions of 5% at 600 K and 40% at 820 K (Figure 1b).

The latter results should have been unexpected to anyone working in the field of catalytic conversion of methanol over zeolites, because these acidic materials completely convert methanol to olefins and aromatics at temperatures well below 700 K.^{10,11}

The thermodynamic analysis presented by Liu et al. shows that toluene is favored over benzene in the presence of methanol. Our analysis does not reproduce this result (Figure

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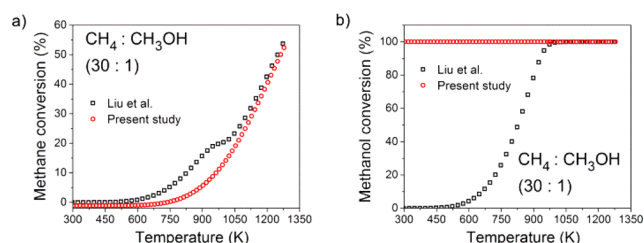


Figure 1. Temperature dependence of (a) methane and (b) methanol conversion in a methane–methanol mixture ($\text{CH}_4/\text{CH}_3\text{OH}$ 30:1). Benzene, toluene, hydrogen, and water were included in the analysis performed by Aspen Plus V8.6.

2) and, as we will show below, in practice benzene is the dominant product in the presence and the absence of methanol.

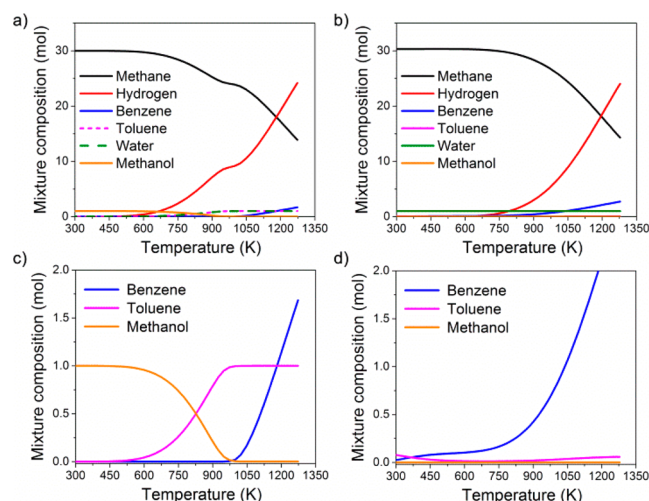


Figure 2. Comparison of thermodynamic calculations performed in this study and by Liu et al. Effect of temperature on the composition of the mixture formed from methane:methanol (30:1). Benzene, toluene, hydrogen, water were included as possible products. (a,c) Liu et al, (b,d) present study. Calculated by Aspen Plus V8.6 software.

Including CO and CO_2 among the possible products—the likely result of methanol decomposition—demonstrates that CO and H_2 are the thermodynamically favored products (Figure 3). This prediction is in good agreement with many experimental reports showing that methanol readily decomposes to CO and H_2 over zeolites, alumina, and other materials at temperatures above 750 K.^{12–17}

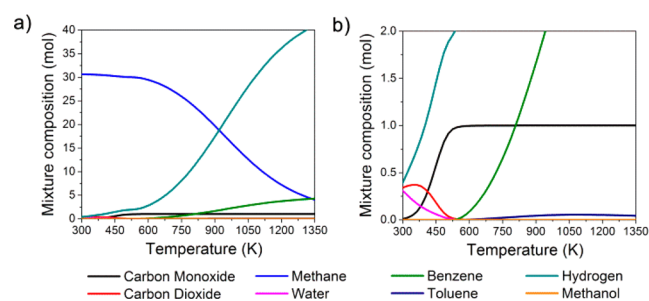
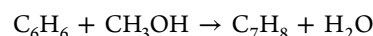
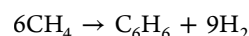


Figure 3. Effect of temperature on the composition of the mixture formed from methane/methanol (30:1). Benzene, toluene, hydrogen, water, CO_2 , and CO were included as possible products. Calculated by Aspen Plus V8.6 software.

Before we leave this discussion, we point out the most likely mistake in the approach taken by Liu et al. As outlined by Reklaitis,¹⁸ the number of independent reactions can be found as the number of species minus the rank of the atomic matrix. For the case discussed in Figures 1 and 2 with 6 species and a rank of 3, there should be 3 independent reactions. However, Liu et al. used only two reactions in their thermodynamic analysis:



Obviously, this leads to erroneous predictions of the product composition, most notably overestimating toluene selectivity and underestimating methanol conversion.

COFEEDING METHANE AND METHANOL

In addition to the thermodynamic analysis, we carried out, in two separate laboratories, catalytic experiments involving cofeeding methanol and methane in the spirit of the work of Liu et al. We used a 6 wt % Mo/HZSM-5 catalyst (Si/Al 40, AkzoNobel) prepared by incipient wetness impregnation of an ammonium heptamolybdate solution. The catalyst and the reaction conditions in our experiments were very close to those used in the work of Liu et al. Other details of catalyst synthesis and catalytic testing can be found elsewhere.^{19,20}

We first investigated the conversion of a feed containing only methanol at 700 °C. In line with thermodynamics, all methanol is converted, and the main carbon-containing products are CO, CH_4 , and CO_2 (total selectivity of >96%) (Figure 4). Other

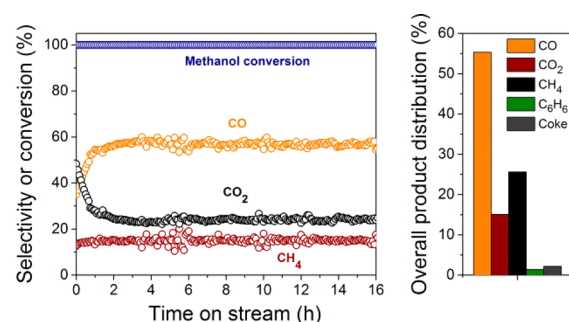


Figure 4. Methanol conversion and product selectivity obtained in a test with pure methanol feed over 6%Mo/HZSM-5. Conditions: 700 °C, 1 bar, methanol GHSV 67 mL/gcat h, methanol delivered by He flow (15 mL/min), 16 h.

products were hydrogen and water and minor amounts of benzene and coke. The formation of CH_4 is ascribed to CO hydrogenation by in situ formed molybdenum carbide,²¹ whereas the formation of CO_2 should be the result of water–gas shift chemistry.

Using a methane feed led to a rapid decrease of the methane conversion with benzene as the predominant product (Figure 5a). Repeating this experiment in the presence of methanol (same composition as employed by Liu et al.) led to a comparable result (Figure 5b). The initial conversion of methane was similar, and although the deactivation rate in the presence of methanol is slightly lower (to be attributed to hydrogen produced from methanol²²), the main aromatic products remained benzene, naphthalene, and coke. In line with the thermodynamic calculations, the yield of toluene and xylenes was very small. It should be noted that Liu et al. did not

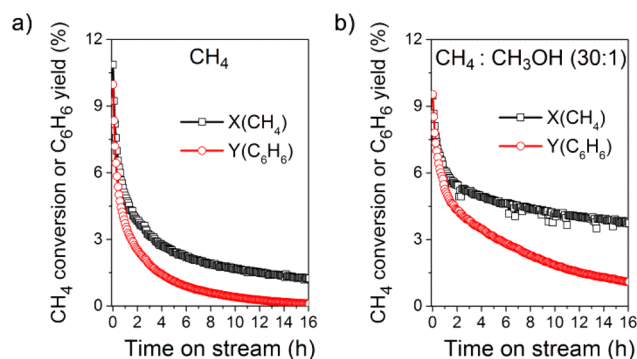


Figure 5. Performance of a 6 wt % Mo/HZSM-5 in methane conversion with (a) and without (b) cofed methanol. Conditions: 700 °C, 1 bar, methane GHSV 2000 mL/g_{cat} h, methanol/methane (30:1), 16 h. Prior measurements the catalysts were held in pure methane at 650 °C for 30 min.

report the formation of CO, while in our case, the CO selectivity was very substantial (Figure 6). Very similar catalytic results were obtained in an independent reaction experiment in the second lab with a 5 wt % Mo/HZSM-5 (Si/Al = 40, Zeolyst) catalyst.

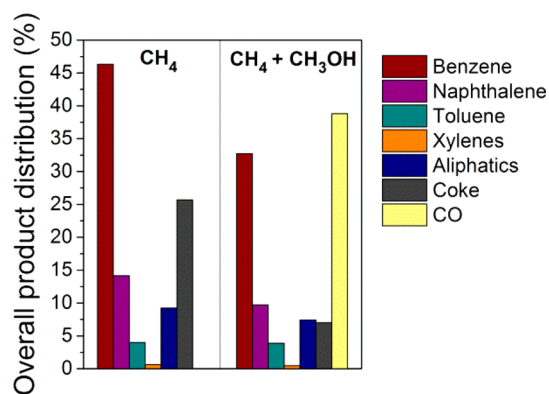


Figure 6. Distribution of products obtained in the catalytic tests.

Overall, our catalytic results correspond very well with thermodynamic data and are in good agreement with previous data available in the literature about cofeeding oxygenates with methane at MDA conditions. Neither the thermodynamic data nor the experimental results reported by Liu et al. could be reproduced in any of our laboratories.

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Notes

The authors declare no competing financial interest.

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