Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 244 (2006) 134–136
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Response to Letter to the Editor

Response to comments on the paper: “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

Yijiao Jiang [a], Wei Wang [a], V.R. Reddy Marthala [a], Jun Huang [a], Bogdan Sulikowski [b], Michael Hunger [a,*]

[a] Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany
[b] Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, Krakow, Poland

Received 30 May 2006; revised 2 August 2006; accepted 3 August 2006

For more than 20 years, the role of surface alkoxy groups in heterogeneous catalysis has been studied and disputed in a controversial manner. In the case of methanol-to-olefin (MTO) conversion on acidic zeolite catalysts, surface methoxy groups are discussed as reactive species responsible for the formation of hydrocarbons, especially during the induction period, when other reaction routes are hindered. In our recently published work [2], the reaction of surface methoxy groups on zeolites H-SAPO-34 and H-Y in the absence and in the presence of organic impurities was studied by combined solid-state NMR and UV/vis spectroscopy. Two routes of methanol conversion on acidic zeolites should be considered. In the first case, the presence of impurities in the feed is at least on the order of a few percent. The second approach, applied in our study [2], uses a very clean methanol, with the level of impurities not exceeding 30 ppm. In the latter case, and on reaching a temperature threshold, conversion of surface methoxy groups on zeolites to hydrocarbons was observed under batch conditions [2].

In our present reply to the comments of Haw et al. [1] on our work [2], we discuss the following topics in detail:

(i) “The lengthy heating and contact times used (20 min) in Ref. [1] (our paper [2]) result in an aged hydrocarbon pool well past that of a working MTO catalyst” [1].
(ii) The ^1H–^{13}C coupling constant of 220 Hz used for the simulation of the ^1H MAS NMR signals of methoxy groups is “simply too large for methoxy groups or most sp^3 systems (exceptions include $CHCl_3$, at 209 Hz) and are more characteristic of sp^2 systems such as formic acid (222 Hz)” [1].
(iii) “Troubling are the signals near 2.7 ppm assigned to silanols (SiOH)” in the ^1H MAS NMR spectra of SAPO-34 [1].
(iv) Two recently published papers of Lesthaeghe et al. [3] and Marcus et al. [4] are disputed.

Topic i. In their comments, Haw et al. [1] criticized the reliability and reproducibility of the method for the preparation of surface methoxy groups and their conversion to hydrocarbons. However, the method that we used in [2] has been well established for the preparation of surface methoxy groups from methanol on acidic zeolites in a number of groups [5–13]. The ^{13}C MAS NMR and ^{13}C CP/MAS spectra of surface methoxy groups prepared via our method [2] are essentially identical to those reported in Refs. [5,7,9,10]. The UV/vis spectra of the methylated catalysts ($^{12}CH_3$-Y, $^{13}CH_3$-Y, $^{12}CH_3$-SAPO-34, and $^{13}CH_3$-SAPO-34) indicate that the surface methoxy groups were prepared before the first hydrocarbon pool compounds could be formed [2].

Haw et al. [1] argued that the contact time of 20 min that we used for the thermal treatment of methoxy groups at 473 to 673 K in [2] would “result in an aged hydrocarbon pool well past that of a working MTO catalyst.” In the work of Song et al. [14], 6 min after pulsing 20 µl methanol onto 300 mg of H-SAPO-34 under flowing He (10 ml s^{-1}) at 673 K, a “nearly 100% conversion of the second methanol pulse” was achieved. This finding was explained by the formation of an active hydrocarbon pool on H-SAPO-34 [14]. In another experiment [15], 30 min after pulsing 200 µl methanol onto 300 mg of H-SAPO-34 under flowing He (10 ml s^{-1}) at 648 K, a “nearly complete

---

[*] Corresponding author.
E-mail address: michael.hunger@itc.uni-stuttgart.de (M. Hunger).

0021-9517/\$ – see front matter
doi:10.1016/j.jcat.2006.08.001

conversion" of methanol was found. Hence, the duration of the heating of the methanol-loaded catalysts to produce a catalytically active hydrocarbon pool was on the same order in [2] as in [14] and [15]. In contrast to [14] and [15], however, in which the loaded catalysts were purged by helium during heating, in [2] thermal treatment of the methylated samples was performed under batch conditions.

Haw et al. [1] further stated 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." Light olefins are reactive on solid acids even at room temperature. Once produced, they undergo fast secondary reactions, such as oligomerization, isomerization, and/or cracking, at reaction temperatures of 473–673 K. Therefore, light olefins can be detected only as volatile products in the gas phase by on-line gas chromatography, not as adsorbed species on acidic zeolites by NMR or UV/vis spectroscopy [16,17]. For example, Song et al. [14] studied the MTO chemistry on H-SAPO-34 catalyst by the pulse-quench technique. Although on-line GC analysis of the gaseous products exiting the H-SAPO-34 catalyst bed showed the formation of ethylene and propylene, no ^{13}C MAS NMR signals due to light olefins adsorbed on the catalyst were observed [14].

Haw et al. [1] also stated that "the UV spectra reported by Jiang et al. are entirely consistent with the distribution of aromatic hydrocarbons well established as the terminal hydrocarbon pool in a deactivated catalyst." The experimental conditions—a large excess of methanol on the catalysts (minimum 300 molecules per acid site) and reaction temperatures of 673–873 K for producing the terminal hydrocarbon pool in a deactivated catalyst, such as in the studies of Fu et al. [18] and Marcus et al. [19]—are significantly different than the treatment conditions used in our work [2] (vide supra). Considering the limited number of methoxy groups present on the catalysts (0.4–0.6 methoxy groups per acid site) and the significantly lower temperatures of 513–673 K used in [2], no terminal hydrocarbon pool species equal to those in [18,19] could be formed. Moreover, the combined NMR-UV/vis spectroscopy, introduced recently by our group [20], allows simultaneous and direct characterization of the hydrocarbon pool formed on working catalysts by the two methods. The ^{13}C MAS NMR spectra recorded simultaneously with the UV/vis spectra [2] show signals of highly alkylated aromatics, which are not typical for a terminal hydrocarbon pool in deactivated catalysts.

Topic ii. In their comments, Haw et al. [1] stated that the evidence for the composition of the organic species formed on the catalysts in [2] "is based largely on the ^{1}H NMR spectra included in Supporting Materials." However, the evidence for the formation of surface methoxy groups is given by ^{13}C MAS and ^{13}C CP/MAS NMR spectroscopy providing signals at 56 ppm for $^{13}CH_3$-Y and $^{13}CH_3$-SAPO-34 [2]. The aim of the application of ^{1}H MAS NMR spectroscopy in our work [2] was to prove *the identical formation* of surface methoxy groups both from ^{13}C-enriched and highly purified nonenriched methanol (see our original text in [2]).

Independent of the unequivocal evidence for the formation of surface methoxy groups delivered by ^{13}C MAS and ^{13}C CP/MAS NMR spectroscopy in [2], Haw et al. [1] questioned the value of J-coupling constant of 220 Hz, which was used to simulate the ^{1}H MAS NMR signal of surface methoxy groups on acidic zeolite H-Y (Fig. S3b in [2]). In contrast to $^{13}CH_3$-SAPO-34 (Fig. S3b in [2]), the high concentration of methoxy groups and residual bridging OH groups in methylated zeolite $^{13}CH_3$-Y results in strong dipolar interactions that cannot be totally averaged out by the MAS technique, thus leading to a significant broadening of the ^{1}H MAS NMR signals. In addition, the surface methoxy groups on zeolite Y are bound to oxygen atoms at different framework positions and in different cages, both causing shift distributions. In our work [2], the best simulation of the ^{1}H MAS NMR signal of methoxy groups on zeolite $^{13}CH_3$-Y was reached with a J(CH) coupling constant of 220 Hz. A simulation with J(CH) = 160 Hz is possible, but requires assuming at least two different doublets. The most important topic is, however, that the splitting of the ^{1}H MAS NMR signal by J(CH) coupling disappears if ^{13}C decoupling is performed (Fig. S2 in [2]). This is additional evidence for the assignment of the ^{1}H MAS NMR signals at 3.9 ppm.

Haw et al. [1] mentioned that the J(CH) coupling constant of 220 Hz is more characteristic of sp^{2} systems such as formic acid. Generally, sp^{2} systems lead to ^{13}C MAS NMR signals at 110–250 ppm and ^{1}H MAS NMR signals at 5–16 ppm, which can be excluded considering the ^{13}C and ^{1}H MAS NMR spectra in [2] (Fig. 1a, left; Fig. 2a, left). Formic acid would give a ^{13}C MAS NMR signal at 165 ppm [21].

Haw et al. [1] stated that "the 160-Hz coupling for surface methoxy groups on zeolite X was seen as a clearly resolved splitting in the ^{1}H spectra of reference 14 (our [22])". Comparing the ^{1}H MAS NMR spectra of methoxy groups in [22] and in our work [2], the different samples and different NMR techniques must be considered. In [22], the methoxy groups were prepared from methyl iodide and on a Na-X zeolite, not by adsorption of methanol on acidic zeolite H-Y. In addition, the ^{1}H MAS NMR spectrum in [22] was recorded with Hahn's spin echo pulse program and at the resonance frequency of 500 MHz.

Topic iii. Due to the high quality of the H-SAPO-34 catalysts used in [2], as confirmed by XRD and solid-state NMR spectroscopy, the ^{1}H MAS NMR signal of isolated SiOH groups at ca. 1.8 ppm is very weak. Only in the strongly zoomed spectrum is this weak signal observed (see Fig. 1). However, an additional broad signal occurs at ca. 2–3 ppm, which is characteristic of hydrogen-bonded SiOH groups [10,23,24]. In the simulation of the ^{1}H MAS NMR spectrum of H-SAPO-34 (Fig. S3d in [2]),

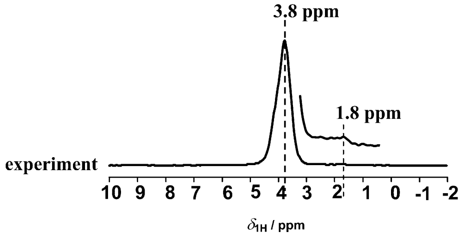

Fig. 1. ^{1}H MAS NMR spectrum of dehydrated H-SAPO-34, shown in the supporting information of Ref. [2] (Fig. S3d) with enlargement of the spectral range between 0.5 and 3.2 ppm.

the signal at 1.8 ppm could be neglected due to its low intensity, whereas a broad signal had to be assumed at ca. 2–3 ppm with an intensity content of 2.6%. After the preparation of methoxy groups on H-SAPO-34 (Figs. S3e and S3f in [2]), a slight increase and low-field shift of the broad signal at ca. 2–3 ppm occurred, which is an indication for the formation of additional SiOH, POH, or AlOH groups (2.7–2.9 ppm [10,23,24]).

Topic iv. Haw et al. [1] cited their experimental work [4] together with the theoretical study of Lesthaeghe et al. [3] to dispute our proposal that thermal treatment of surface methoxy groups on acidic zeolite catalysts leads to the formation of hydrocarbons typical for hydrocarbon pool species in the MTO process [25].

In 1997, Sinclair and Catlow [26] showed by DFT calculations that "acid-catalyzed deprotonation of methyl groups during the methanol-to-gasoline conversion can occur to produce surface-stabilized carbenes with a calculated activation barrier of 215–232 kJ mol^{-1}. The calculated barriers are in reasonable agreement with recent experimental findings indicating that methyl group deprotonation may be the rate-determining step during methanol conversion." Lesthaeghe et al. [3] described in their theoretical study that "an altogether different ylide, incorporated into the framework, can be formed by deprotonation of a framework-bound methyl group (J1). This step was found to be highly activated" (242 kJ mol^{-1}) in comparison with reaction routes, where the contribution of other organic compounds, such as impurities, was assumed. In [2], however, a number of experiments were performed in the absence of impurities with highly purified methanol (impurities < 30 ppm [2]), and, thus the conditions were not comparable with those assumed in the work of Lesthaeghe et al. [3].

The results of H/D exchange experiments recently published by Marcus et al. [4] contradict those reported by a number of other groups [27–30]. For example, Novakova et al. [27] studied the H/D exchange during the methanol reaction on acidic zeolite H-ZSM-5 by mass spectrometry. At reaction temperatures above 670 K, "the cleavage of C–H bonds in methoxy groups and rapid deuterium exchange between intermediates and hydroxyl groups" were found by analyzing the H/D distribution in the obtained hydrocarbons. The experimental approach used by Novakova et al. [27] was similar to that of Marcus et al. [4], but without adsorption water and investigation of the products of the subsequent reaction. Ono and Mori [28] reported IR evidence for the formation of surface methoxy groups on zeolite H-ZSM-5 from CD_3OH and showed that at 512 K, the "desorption of methoxy species is accompanied with the cleavage of C–D bonds."

Marcus et al. [4] did not exclude the formation of hydrocarbons. They mentioned that "the use of highly purified reagents strongly suppressed the formation" of these compounds [4]. It would be important to know whether the analysis of the H/D distribution in these hydrocarbons leads to similar isotope distributions to those found by Novakova et al. [27]. After thermal treatment of the methylated zeolite catalyst, Marcus et al. [4] performed adsorption of water and analyzed the H/D distribution in the products of the reaction between water molecules and remaining surface methoxy groups. However, this approach leads to a selective study of the H/D distribution in methoxy groups, which did not experience a cleavage of C–H bonds. On the other hand, methoxy groups formed on acidic zeolite catalysts are organic surface compounds. There must be a temperature threshold leading to a decomposition of these organic surface species. But the reactions of surface methoxy groups on acidic zeolites occurring above this temperature threshold were not studied in [4].

In summary, the comments of Haw et al. [1,2] and our reply indicate that the debate on the formation of hydrocarbons during methanol-to-olefin conversion on acidic zeolite catalysts remains open and merits further investigation and discussion.

References

[1] J.F. Haw, D.M. Marcus, P.W. Kletnieks, J. Catal., in press.

[2] Y. Jiang, W. Wang, V.R.R. Marthala, J. Huang, B. Sulikowski, M. Hunger, J. Catal. 238 (2006) 21.

[3] D. Lesthaeghe, V. van Speybroeck, G.B. Marin, M. Waroquier, Angew. Chem. Int. Ed. 45 (2006) 1714.

[4] D.M. Marcus, K.A. McLachlan, M.A. Wildman, J.O. Ehresmann, P.W. Kletnieks, J.F. Haw, Angew. Chem. Int. Ed. 45 (2006), in press, doi:10.1002/anie.200504372.

[5] I.I. Ivanova, E.B. Pomakhina, A.I. Rebrov, M. Hunger, Y.G. Kolyagin, J. Weitkamp, J. Catal. 203 (2001) 375.

[6] C.E. Bronnimann, G.E. Maciel, J. Am. Chem. Soc. 108 (1986) 7154.

[7] V. Bosáček, J. Phys. Chem. 97 (1993) 10,732.

[8] L. van Wuellen, H. Koller, M. Kalwei, Phys. Chem. Chem. Phys. 4 (2002) 1665.

[9] F. Salehirad, M.W. Anderson, J. Catal. 164 (1996) 301.

[10] F. Salehirad, M.W. Anderson, J. Catal. 177 (1998) 189.

[11] P. Salvador, J. Fripiat, J. Phys. Chem. 79 (1975) 1842.

[12] F. Wakabayashi, J.N. Kondo, C. Hirose, K. Domen, in: M.M.J. Treacy, B.K. Marcus, M.E. Bisher, J.B. Higgins (Eds.), Proceedings of the 12th International Zeolite Conference, Materials Research Society, Warrendale, 1999, p. 2577.

[13] J. Datka, J. Rakoczy, G. Zadrozna, in: M.M.J. Treacy, B.K. Marcus, M.E. Bisher, J.B. Higgins (Eds.), Proceedings of the 12th International Zeolite Conference, Materials Research Society, Warrendale, 1999, p. 2601.

[14] W. Song, J.F. Haw, J.B. Nicholas, C.S. Heneghan, J. Am. Chem. Soc. 122 (2000) 10,726.

[15] W. Song, D.M. Marcus, H. Fu, J.O. Ehresmann, J.F. Haw, J. Am. Chem. Soc. 124 (2002) 3844.

[16] (a) J.F. Haw, B.R. Richardson, I.S. Oshiro, N.D. Lazo, J.A. Speed, J. Am. Chem. Soc. 111 (1989) 2052;
(b) E.J. Munson, A.A. Kheir, N.D. Lazo, J.F. Haw, J. Phys. Chem. 96 (1992) 7740.

[17] M.W. Anderson, B. Sulikowski, P.J. Barrie, J. Klinowski, J. Phys. Chem. 94 (1990) 2730.

[18] H. Fu, W. Song, J.F. Haw, Catal. Lett. 76 (2001) 89.

[19] D.M. Marcus, W. Song, L.L. Ng, J.F. Haw, Langmuir 18 (2002) 8386.

[20] M. Hunger, W. Wang, Chem. Commun. (2004) 584.

[21] E.J. Munson, N.D. Lazo, M.E. Moellenhoff, J.F. Haw, J. Am. Chem. Soc. 113 (1991) 2783.

[22] V. Bosáček, H. Ernst, D. Freude, T. Mildner, Zeolites 18 (1997) 196.

[23] V.M. Mastikhin, I.L. Mudrakovsky, A.V. Nosov, Prog. Nucl. Magn. Reson. Spectrosc. 23 (1991) 259.

[24] C.E. Bronnimann, R.C. Zeigler, G.E. Maciel, J. Am. Chem. Soc. 110 (1988) 2023.

[25] W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc. 125 (2003) 15260.

[26] P.E. Sinclair, C.R.A. Catlow, J. Phys. Chem. B 101 (1997) 4787.

[27] J. Nováková, L. Kubelková, Z. Dolejšek, J. Catal. 97 (1986) 277.

[28] Y. Ono, T. Mori, J. Chem. Soc. Faraday Trans. 1 77 (1981) 2209.

[29] G. Perot, F.X. Cormerais, M. Guisnet, J. Mol. Catal. 17 (1982) 255.

[30] G. Perot, F.X. Cormerais, M. Guisnet, J. Chem. Res. S 2 (1982) 58.