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High Yield of Liquid Range Olefins Obtained by Converting
i-Propanol over Zeolite H-ZSM-5

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Abstract: Methanol, ethanol, and *i*-propanol were converted under methanol-to-gasoline (MTH)-like conditions (400 °C, 1−20 bar) over zeolite H-ZSM-5. For methanol and ethanol, the catalyst lifetimes and conversion capacities are comparable, but when *i*-propanol is used as the reactant, the catalyst lifetime is increased dramatically. In fact, the total conversion capacity (calculated as the total amount of alcohol converted before deactivation in $g_{alcohol}/g_{zeolite}$) is more than 25 times higher for *i*-propanol compared to the lower alcohols. Furthermore, when *i*-propanol is used as the reactant, the selectivity toward alkanes and aromatics declines rapidly over time on stream, and at 20 bar of pressure the liquid product mixture consists almost exclusively of $C_4−C_{12}$ alkenes after approximately a third of the full reaction time. This discovery could open a new route to hydrocarbons via *i*-propanol from syn-gas or biobased feedstocks.

Introduction

The methanol-to-hydrocarbons (MTH) reaction was discovered and commercialized more than two decades ago. However, due to the situation on the global oil market, the gasoline synthesis was discontinued.[1,2] Currently, the MTH reaction is receiving renewed attention due to the focus on renewable fuel sources.[3] The level to which this reaction can contribute to a sustainable nonfossil-based energy sector naturally depends on the origin of the methanol.[4] Methanol is traditionally produced from coal or natural gas via syn-gas, but many interesting nonfossil routes for the production of methanol as well as higher alcohols are investigated today.[5] Methods for production of higher alcohols from syn-gas are also under development[6,7] as is the gasification of biomass to syn-gas.[8]

Since the MTH reaction was discovered in the early 1970s and published in 1977,[9] the reaction mechanism has been widely debated.[10] The "hydrocarbon pool mechanism" in which carbonaceous species in the zeolitic pores are part of the catalytic system has become generally accepted. This idea was originally suggested by Mole[11] and Langner,[12] and a decade later Kolboe et al.[13,14] introduced a more general mechanism. Through isotopic labeling experiments Bjørgen et al.[15] uncovered further mechanistic details about the hydrocarbon pool and suggested "the dual cycle mechanism". Recently, mechanistic modeling has also been used to gain insight into the mechanistic details.[16,17]

In the MTH reaction, the zeolite catalyst suffers from deactivation due to coking and frequent regeneration by combustion of the deposited coke is required. It is thus a key research area to improve the catalyst lifetime between regenerations. Another important objective is to suppress the formation of aromatic compounds and shift the selectivity toward the production of olefins (the MTO reaction).[18,19] Numerous approaches have been tried to obtain these goals, most of them dealing with optimization of the catalyst or modifying the reaction conditions.[20−24]

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(1) Stöcker, M. *Microporous Mesoporous Mater.* **1999**, *2*, 9–3.
(2) Topp-Jørgensen, J. *Stud. Surf. Sci. Catal.* **1998**, *36*, 293.
(3) Suntana, A. S.; Vogt, K. A.; Turnblom, E. C.; Upadhye, R. *Appl. Energy* **2009**, *86*, 215.
(4) Vogt, K. A.; Vogt, D. J.; Patel-Weynand, T.; Upadhye, R.; Edlund, D.; Edmonds, R. L.; Gordan, J. C.; Suntana, A. S.; Sigurdardottir, R.; Miller, M.; Roads, P. A.; Andreu, M. G. *Renew. Energ.* **2009**, *34*, 233.
(5) Atsumi, S.; Hanai, T.; Liao, J. C. *Nature.* **2008**, 451.
(6) Iranmahboob, J.; Hill, D. O.; Toghiani, H. *Appl. Catal., A* **2002**, *231*, 99.
(7) Spivey, J. J.; Egbebi, A. *Chem. Soc. Rev.* **2007**, *36*, 1514.
(8) Al Arni, S.; Bosio, B.; Arato, E. *Renew. Energ.* **2010**, *35*, 29.
(9) Chang, C. D.; Silvestri, A. J. *J. Catal.* **1977**, *47*, 249.
(10) Haw, J. F.; Song, W.; Marcus, D. M.; Nicholas, J. B. *Acc. Chem. Res.* **2003**, *36*, 317.
(11) Mole, T.; Whiteside, J. A.; Seddon, D. *J. Catal.* **1983**, *82*, 261.
(12) Langner, B. E. *Appl. Catal.* **1982**, *2*, 289.
(13) Dahl, I. M.; Kolboe, S. *Catal. Lett.* **1993**, *20*, 329.
(14) Dahl, I. M.; Kolboe, S. *J. Catal.* **1994**, *149*, 458.
(15) Bjørgen, M.; Svelle, S.; Joensen, F.; Nerlov, J.; Kolboe, S.; Bonino, F.; Bordiga, S.; Olsbye, U. *J. Catal.* **2007**, *249*, 195.
(16) McCann, D. M.; Lesthaeghe, D.; Kletnieks, P. W.; Guenther, D. R.; Hayman, M. J.; Speybroeck, V. V.; Waroquier, M.; Haw, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 5179.
(17) Svelle, S.; Tuma, C.; Rozanska, X.; Kerber, T.; Sauer, J. *J. Am. Chem. Soc.* **2009**, *131*, 816.
(18) Haw, J. F.; Marcus, D. M. *Nanotechnology in Catalysis*; Plenum Publishers: New York, 2004; Vol. 1, Chapter 13.
(19) Bjørgen, M.; Joensen, F.; Lillerud, K.-P.; Olsbye, U.; Svelle, S. *Catal. Today* **2009**, *142*, 90.
(20) Chen, J. Q.; Bozzano, A.; Glover, B.; Fuglerud, T.; Kvisle, S. *Catal. Today* **2005**, *106*, 103.
(21) Mokrani, T.; Scurrell, M. *Catal. Rev.* **2009**, *51* (1), 145.

Table 1. Feed Rates and Observed Conversion Capacities

|	P (atm)	WHSV (h^{-1})	feed rate $n_{alcohol}$ (mmol/g_{cat}*h)	feed rate n_{carbon} (mmol/g_{cat}*h)	conv. cap. mol$_{carbon}$/$g_{zeolite}$	conv. cap. $g_{alcohol}$/$g_{zeolite}$
methanol	1	8.4	263	263	11	350
ethanol	1	12.1	263	526	22	505
i-propanol	1	15.8	263	789	565	11300

In the literature, many different reactants have been tested under MTH-like reaction conditions. Already in the first article on MTH[9] a number of different oxygen containing reactants (higher alcohols, carbonyl compounds, acids, and esters) were screened in the reaction, all resulting in a mixture of hydrocarbon products. Recently, Gayubo et al.[25,26] did a thorough screening of reactants, including higher alcohols (propanol and butanol) phenols, aldehydes, ketones, and carboxylic acids. In all cases, a mixture of hydrocarbon products containing olefins, paraffins, and aromatics was produced, illustrating that H-ZSM-5 is virtually omnivorous. In an attempt to elucidate mechanistic information, mixtures of methanol and higher alcohols (ethanol, *i*-propanol, and 1-butanol), were reacted over H-ZSM-5 by Tau et al.[27] Through isotopic labeling experiments it was concluded that the carbon atoms from the different alcohols are scrambled and distributed randomly in the products. Lifetime and deactivation of the catalyst however was not addressed in these studies.

Tabak et al. have converted propene and butene to hydrocarbons over ZSM-5.[28] They show that the small alkenes oligomerize and by varying the reaction temperature and pressure they are able to change the reactivity of oligomerization versus cracking and thereby controlling the molecular weight of the products.

In an early study,[29] methanol and ethanol were compared as reactants over H-ZSM-5, and very similar product distributions were obtained. This was confirmed in a recent article from our research group, where the differences in the hydrocarbon pool were also discussed.[30]

Very recently, Gujar et al. studied the conversion of C_1-C_4 alcohols over H-ZSM-5 in a batch reactor. They concluded that the higher alcohols produce more organic liquid than methanol, when allowed to react for the fixed time in the reactor.[31]

Even though several different reactants and cofeeding experiments have been tested in the catalytic conversion over H-ZSM-5, almost no emphasis has been put on the dependence of the reactant on catalyst lifetime and deactivation when using other reactants than methanol or ethanol. In the present study, methanol, ethanol, and *i*-propanol are compared as reactants over H-ZSM-5 and the focus is placed on the beneficial effects
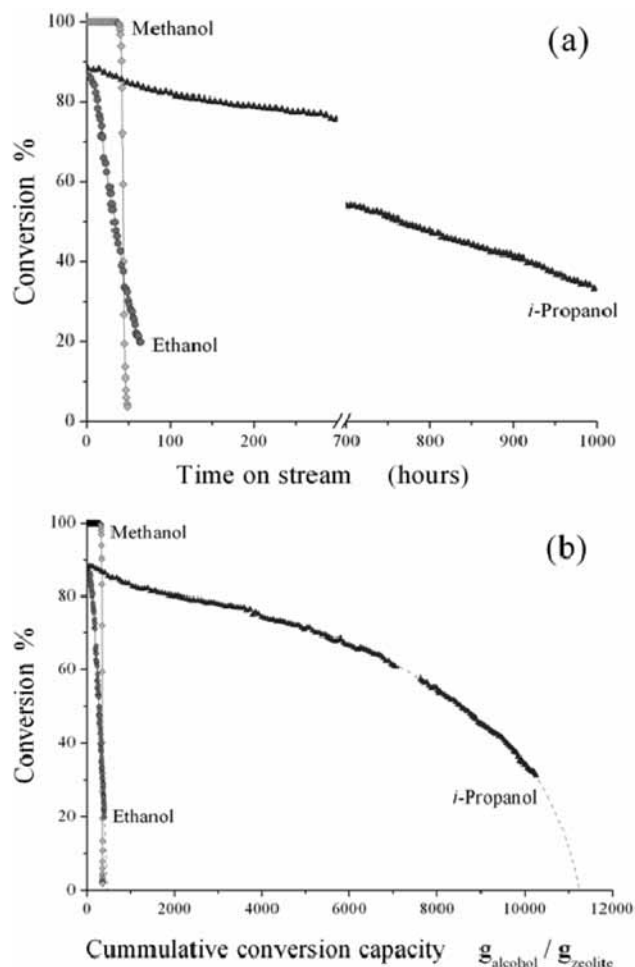
Figure 1. (a) Conversion profiles of methanol, ethanol, and *i*-propanol reacted over H-ZSM-5 at 400 °C. (b) Cumulative conversion capacities in $g_{alcohol}$/$g_{zeolite}$ given as a function of the alcohol conversion.

observed on product selectivity as well as lifetime of the catalyst when feeding *i*-propanol.

Experimental Section

The catalyst used was a commercially available zeolite ZSM-5 (Si/Al = 40) kindly provided by Zeolyst International. The catalytic reactions were performed in a fixed bed reactor at a reaction temperature of 400 °C and a pressure of 1 or 20 bar. In all runs, 300 mg of fractioned (350−500 μm) zeolite catalyst was used. The reactant liquid was introduced by a HPLC pump and evaporated before the catalyst bed. The feed rates of the various alcohols were normalized to introduce an equivalent molar amount of alcohol per unit of time. This resulted in a significantly larger WHSV for the higher alcohols compared to methanol. The feed rates for the different alcohols are listed in Table 1.

For reactions performed at 1 bar, the products were analyzed by an online GC equipped with a flame ionization detector. Helium was used as an inert carrier gas with a flow of 20 mL/min in all nonpressurerized experiments.

When performing the reaction at 20 bar of pressure, the products were condensed at room temperature while still pressurized. The

(22) Bjørgen, M.; Joensen, F.; Holm, M. S.; Olsbye, U.; Lillerud, K. P.; Svelle, S. *Appl. Catal., A* **2008**, *345*, 43.

(23) Christensen, C. H.; Johannsen, K.; Törnqvist, E.; Schmidt, I.; Topsøe, H.; Christensen, C. H. *Catal. Today* **2007**, *128*, 177.

(24) Teketel, S.; Svelle, S.; Lillerud, K. P.; Olsbye, U. *ChemCatChem* **2009**, *1*, 78.

(25) Gayubo, A. G.; Aguayo, A. T.; Atutxa, A.; Aguado, R.; Bilbao, J. *Ind. Eng. Chem. Res.* **2004**, *43*, 2610.

(26) Gayubo, A. G.; Aguayo, A. T.; Atutxa, A.; Aguado, R.; Olazar, M.; Bilbao, J. *Ind. Eng. Chem. Res.* **2004**, *43*, 2619.

(27) Tau, L. M.; Davis, B. H. *Fuel Process. Technol.* **1990**, *26*, 209.

(28) Tabak, S. A.; Krambeck, F. J.; Garwood, W. E. *AIChE J.* **1986**, *64*, 72.

(29) Derouane, E. G.; Nagy, J. B.; Dejaifve, P.; van Hoff, J. H. C.; Spekman, B. P.; Védrine, J. C.; Naccache, C. *J. Catal.* **1978**, *53*, 40.

(30) Johanson, R.; Hruby, S. L.; Rass-Hansen, J.; Christensen, C. H. *Catal. Lett.* **2009**, *127*, 1.

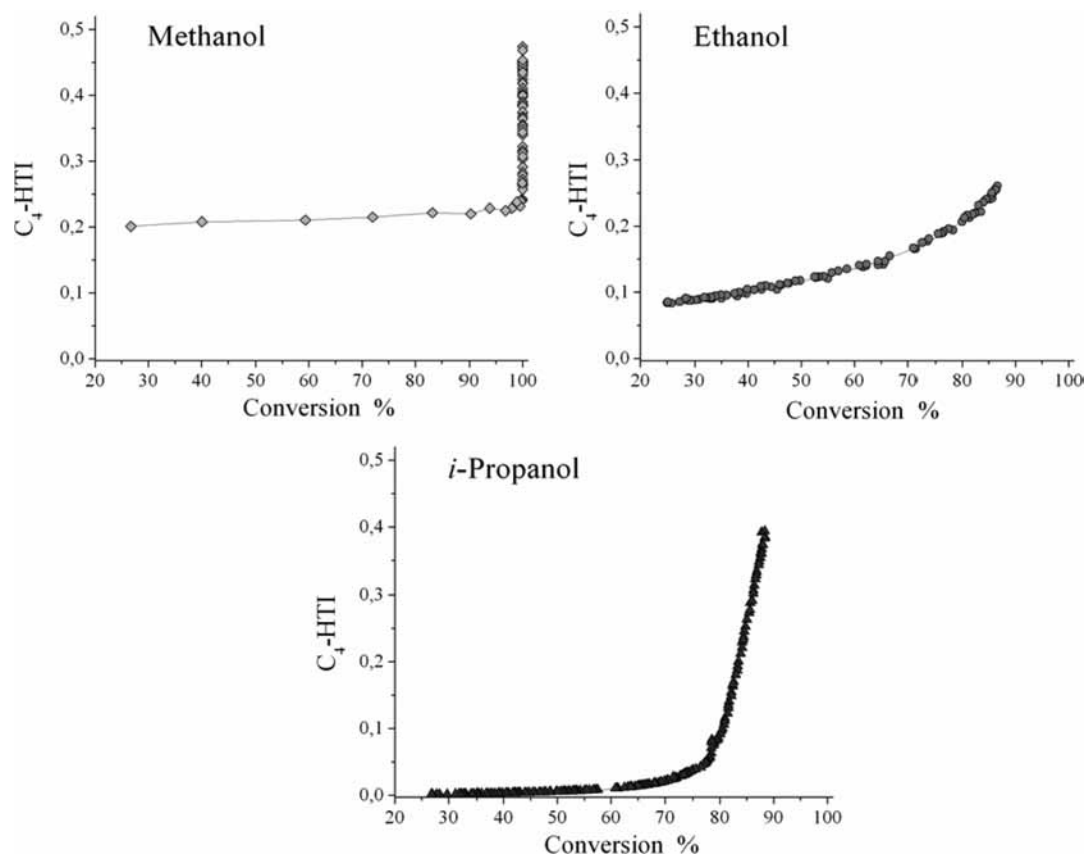(31) Gujar, A. C.; Guda, V. K.; Nolan, M.; Yan, Q.; Toghiani, H.; White, M. G. *Appl. Catal., A* **2009**, *363*, 115.

Figure 2. C_4-HTI plotted as a function of the conversion for the three alcohols tested.

gas phase was continuously monitored by an online GC whereas the liquid products were analyzed by offline GC after decompressing the liquid sample to ambient pressure. Helium was used as the carrier gas with a flow of 40 mL/min in all pressurized experiments.

Results and Discussion

The lifetime of the catalyst (conversion vs time on stream) for the different alcohol feeds is illustrated in Figure 1a. When the conversions of the different alcohols are calculated, the direct dehydration products (dimethyl ether, diethyl ether, ethene, dipropyl ether, and propene, respectively) are considered reactants. These dehydration products are still produced over the completely deactivated catalyst, although dipropyl ether was never formed in significant amounts. Initially, we do not observe full conversion in the cases of ethanol and *i*-propanol. This does not mean that the catalyst is not sufficiently active; the (dehydrated) reactants are simply part of the normal products formed during the reaction.

From Figure 1a it is seen that when methanol or ethanol is fed, the catalyst is deactivated within in a few days, but when *i*-propanol is used, the catalyst is still active (>30% conversion) after more than 1000 h on stream.

In addition, the *molar* feed rates are kept constant for the different alcohols, meaning that the catalyst converts three times the amount of carbon/h when *i*-propanol is fed compared to methanol, see Table 1. If *i*-propanol is fed with a WHSV of 8.4 as in the case of methanol, the deactivation of the catalyst scales accordingly, simply making the reaction times required to reach deactivation impractical.

For conversion of methanol, coke is deposited on the catalyst, and a deactivation zone moves through the catalyst bed, resulting in the sudden drop in conversion when the whole catalyst bed

is deactivated. This sudden drop in conversion is not observed to the same degree for ethanol and especially not for *i*-propanol.

The cumulative conversion capacity is plotted in Figure 1b, and values showing the total amount (calculated on a weight basis) of alcohol converted over the entire lifetime of the catalyst are summarized in Table 1. When propanol is fed, the catalyst is able to convert more than 25 times the amount of alcohol before reaching complete deactivation, compared to the smaller alcohols.

When the catalytic activity in the MTH reaction is described, the "C_4 hydrogen transfer index" (C_4-HTI) is often used.[22] This is defined as the amount of butanes (iso-butane and *n*-butane) divided by the total amount of C_4-compounds and thus gives a good indication of the development of the hydrogen transfer ability of the working catalyst. When the C_4-HTI is high, the catalyst is able to convert alkenes to aromatics and alkanes. The C_4-HTI as a function of conversion for the three alcohols is presented in Figure 2. For methanol the C_4-HTI is quite high (ca. 0.47) in the beginning and drops steadily as the catalyst deactivates to around 0.22, at which point we observe breakthrough of methanol and the catalyst is completely deactivated. For ethanol and *i*-propanol, the initial values are around 0.26 and 0.38, respectively, and they decline with conversion. Interestingly, for *i*-propanol, the C_4-HTI approaches zero already when the conversion is around 60–70%. This means that the catalyst is no longer able to convert alkenes to aromatics and alkanes, and therefore the product mixture consists almost exclusively of alkenes. A decrease in the C_4-HTI is expected during deactivation due to a decrease in the effective acid site

Table 2. Product Selectivities for Conversion of the Three Alcohols Calculated as Carbon Percentages

	methane	ethane	ethene	propane	propene	C_4-butenes	C_4-butanes	C_{5+}(aliphatics)	aromatics
Methanol									
Initially	0.7	0.2	5.3	6.2	11.8	14.7	12.0	28.3	20.8
~80% conv.	2.4	0.1	8.6	1.1	25.4	14.6	4.0	33.5	10.1
~60% conv.	3.0	0.1	10.9	0.8	24.7	13.2	3.5	33.5	10.0
~40% conv.	4.0	0.1	13.8	0.7	24.2	11.8	3.0	31.1	11.0
Ethanol									
Initially	0.1	0.7	−	5.7	20.6	22.9	7.8	27.3	14.5
~80% conv.	0.1	0.9	−	3.9	23.8	25.2	6.1	27.7	12.4
~60% conv.	<0.1	1.0	−	2.2	27.0	27.8	4.3	29.9	7.8
~40% conv.	<0.1	1.1	−	1.3	29.5	28.5	3.0	30.2	6.5
***i*-Propanol**									
Initially	<0.1	0.1	4.4	7.3	−	19.2	12.4	35.5	21.1
~80% conv.	<0.1	<0.1	2.4	2.2	−	37.1	3.7	50.2	4.4
~60% conv.	<0.1	<0.1	0.7	0.8	−	46.7	0.5	50.8	0.5
~40% conv.	<0.1	<0.1	0.4	0.5	−	38.2	0.1	60.8	<0.1

density present in the catalyst bed.[22,32,33] However, as is the case for the presented methanol experiment, the catalyst will normally be completely deactivated before the C_4−HTI approaches zero. In the case of *i*-propanol this is not true, since the catalyst is still able to perform oligomerization and cracking reactions forming a rich mixture of long branched alkenes when the C_4−HTI is approximately zero.

Product selectivities for the three tested alcohols as a function of the conversion are listed in Table 2. We note that the initial product selectivities are quite similar for all the alcohols, as they all produce a significant amount of aromatics. The selectivity toward aromatics compounds (mainly toluene, xylenes and trimethyl benzene isomers) however decreases significantly for *i*-propanol over time. This is naturally expected from the presented low C_4−HTI of the catalyst at intermediate conversions. Again this observation is in strong contrast to the methanol experiment where the catalyst produces aromatic compounds right up to the point of complete deactivation. Another interesting observation when using *i*-propanol as the reactant is, that the production of ethene also decreases over time. This is in good accordance with conclusions drawn by Svelle et al.,[34] suggesting that the production of ethene is mechanistically linked to the production of aromatics; thus, when a smaller amount of aromatics is produced, a smaller amount of ethene is produced. The fact that the concentration of ethene decreases so dramatically also indicates that only a minor fraction (if any) of the produced ethene is formed from cracking of larger alkenes, since the alkene oligomerization/cracking cycle is still very active at this point. This observation is very important since only small amounts of the lower value products methane, ethane, and ethene are produced.

To confirm the above findings under reaction conditions closer to the industrially used and to push the selectivity toward liquid products, similar experiments with methanol, ethanol and *i*-propanol were performed in a pressure setup operated at 20 bar. The condensed liquid products were periodically withdrawn to atmospheric pressure for GC analysis. The rates of formation of liquid products per gram of zeolite are illustrated in Figure 3 for the three alcohols. Again we observe that the lifetime of the catalyst when feeding *i*-propanol is far superior to the other alcohols. Naturally, the rate of liquid product formation is highly

dependent on the WHSV, but in Table 3 the total yields of liquid products before reaching complete deactivation are summarized. Here we see that methanol produces around 160 mL/$g_{zeolite}$ whereas *i*-propanol yields as much as 3550 mL/$g_{zeolite}$.

The dark coloring of the columns in Figure 3(a−c) represents the carbon% present in aromatic compounds. In accordance with the nonpressure experiments *i*-propanol initially produce an aromatic rich liquid but for the latter ~2/3 of the experiment solely C_4−C_{12} alkenes are formed. In Table 3, the total averaged aromatic carbon% of the liquid products is given.

When the reaction is performed at 20 bar, the initial selectivity toward aromatics is higher than at 1 bar, and it declines more rapidly. Furthermore, the lifetime of the catalyst when converting *i*-propanol is around 50% shorter, than at 1 bar. This effect is not observed for methanol and ethanol, where the catalyst shows similar lifetimes at 1 and 20 bar.

Along with the much higher conversion capacity of *i*-propanol, the low aromatic carbon% illustrates the pronounced difference of using *i*-propanol compared to methanol or ethanol as the reactant. GC-MS analysis was used to identify the various compounds formed during the experiment. Figure 4 shows the product distribution in the organic liquid when using *i*-propanol. The sample presented in Figure 4a was obtained after approximately 250 h on stream representing a case from Figure 3c where insignificant amounts of aromatics are formed. Clearly we see that a huge range of different alkene isomers is produced from the reaction. There are no detectable aromatic compounds and only minute traces of alkanes present in the liquid at this point. Alkene contribution ranges from C_4 to C_{12} species. The shape selectivity of the zeolite is clearly affecting the larger products, no bulky products are able to escape the zeolite pores and mainly methylated long chains are present in the products. Interestingly, as the catalyst deactivates further from this point the product distribution changes systematically. In the last hours of operation we observe a pronounced enrichment in the C_6, C_9 and C_{12} alkenes indicating that cracking of the formed alkenes is diminished and we thus mainly observe the direct oligomerization products of propene, see Figure 4b.

Conclusions

It has been shown here that the lifetime and conversion capacity of the zeolite catalyst is increased dramatically when *i*-propanol is used as reactant instead of methanol or ethanol in the catalytic conversion over H-ZSM-5.
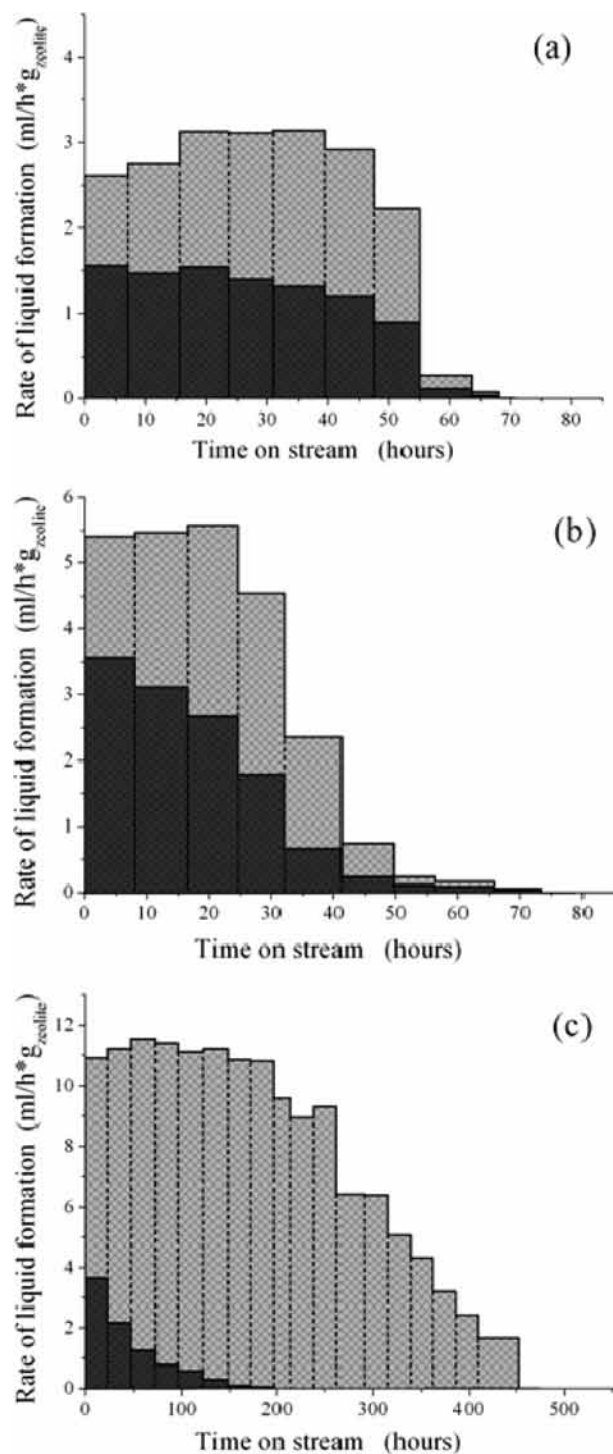
Furthermore, when reacting *i*-propanol the C_4−HTI approaches zero after approximately a third of the full experimental

(32) Janssens, T. V. W. *J. Catal.* **2009**, *264*, 130.
(33) Bjørgen, M.; Kolboe, S. *Appl. Catal., A* **2002**, *225*, 285.
(34) Svelle, S.; Joensen, F.; Nerlov, J.; Olsbye, U.; Lillerud, K. P.; Kolboe, S.; Bjørgen, M. *J. Am. Chem. Soc.* **2006**, *128*, 14770.

Figure 3. Rate of formation of the organic phase from reacting (a) methanol, (b) ethanol, and (c) *i*-propanol over H-ZSM-5 at 400 °C. The dark coloring represents the carbon% present in aromatics.

run time, meaning that the selectivity is almost exclusively shifted toward the production of alkenes, and only minute amounts of aromatics and alkanes are formed. The resulting alkene rich liquid product which is very low in aromatic content

Table 3. Total Yield and Selectivities at 20 bar

	P bar	WHSV gg⁻¹h⁻¹	org. liq. mL/g_cat	total carbon in aromatics
Methanol	20	8.4	160	46.9%
Ethanol	20	12	200	49.9%
i-Propanol	20	16	3550	6.1%
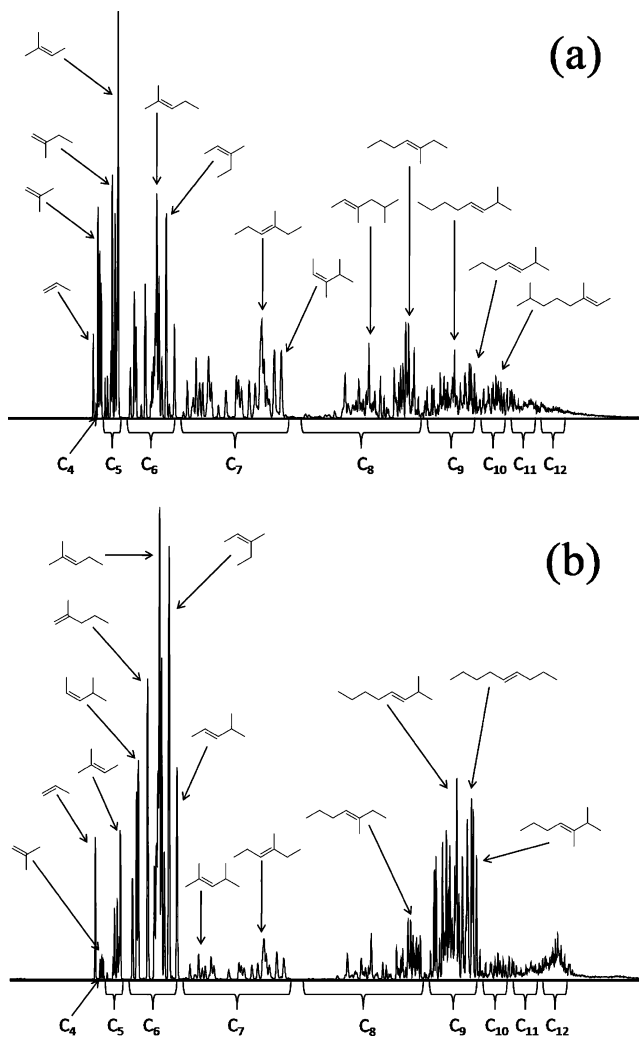
Figure 4. GC-MS analysis of the organic phase feeding *i*-propanol (a) after 250 h on stream and (b) after 425 h on stream. Major compounds are labeled for illustrative reasons.

can serve as an attractive raw material for the chemical industry, or could easily be hydrogenated to produce high quality clean fuel. On the basis of the results presented here, an alternative route from syn-gas or biobased feedstocks to hydrocarbons going via *i*-propanol instead of methanol can be envisaged.