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The Hydrocarbon Pool in Ethanol-to-Gasoline over HZSM-5 Catalysts

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Abstract It is shown that the conversion of ethanol-to-gasoline over an HZSM-5 catalyst yields essentially the same product distribution as for methanol-to-gasoline performed over the same catalyst. Interestingly, there is a significant difference between the identity of the hydrocarbon molecules trapped inside the HZSM-5 catalyst when ethanol is used as a feed instead of methanol. In particular, the hydrocarbon pool contains a significant amount of ethylsubstituted aromatics when ethanol is used as feedstock, but there remains only methyl-substituted aromatics in the product slate.

Keywords Ethanol-to-gasoline · Hydrocarbon pool · ZSM-5

With the current development of new large methanol plants, including a 5000 ton/day plant recently opened in Saudi Arabia [1] and a 1500 ton/day plant under construction in Russia [2], the subsequent expected increases in available methanol and the cost competitiveness due to economics of scale are generating significant potential for the methanol to hydrocarbon (MTH) reaction to become an important industrial process in the coming years. Some existing plants are currently utilizing this route to produce olefins; one of the largest belongs to Viva Methanol Ltd. in Nigeria [3]. MTH or, depending on process conditions, methanol to gasoline (MTG) or methanol to olefins (MTO) can be used to produce liquid fuels for the automotive sector or to make olefins suitable for polymerization. The production of liquid fuels from natural gas via methanol was first commercialized by Mobil in the 1980s with a plant operating in New Zealand with a planned production of 600,000 tons annually. However, at that time the economy for the process was unfavorable due to low fossil fuel costs; consequently, the MTG part of the operation was discontinued in the 1990s. Today, the increasing prices of fossil feedstocks could once again make the MTG process a viable option. The MTG reaction was first discovered by Silvestri and Chang in the 1970s and it is catalyzed by acidic zeolites at temperatures up to 400 °C giving a variety of lower aliphatic hydrocarbons, olefins and aromatics [4]. The product distribution in MTG depends on several factors where, in particular, the topology of the catalyst is of paramount importance. Since its discovery, MTG has been extensively studied and a plausible reaction mechanism has been suggested through the work of several research groups [5, 6]. The basic premise for the proposed mechanism is the hydrocarbon pool model, which suggests that the actual catalytic sites in the zeolite are organic–inorganic hybrids consisting of cyclic organic species contained within the zeolitic framework. These organic species act as the hydrocarbon pool from which the products in the exit gas stem via cracking as shown in a simplified reaction scheme in Scheme 1. The MTG process has been extensively studied by Kolboe et al., who studied the nature and amount of retained material within the catalysts H-beta, [7–9] SAPO-34, [10, 11] and

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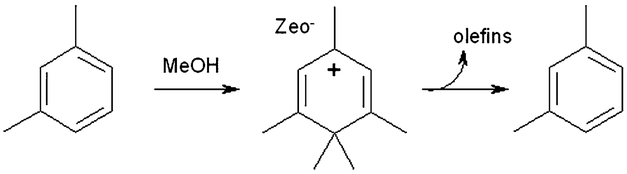

Scheme 1 A simplified scheme showing the principle behind the hydrocarbon pool model in the MTG reaction. Methanol reacts with hydrocarbons trapped inside the zeolite giving a charged organic–inorganic hybrid that then loses a smaller fragment giving back the same or a similar hydrocarbon

H-ZSM-5 [12, 13]. These authors gained considerable insight into the mechanism by determination of retained material in the used catalyst and many aspects of the hydrocarbon pool model stem from their work. The MTG process has a counterpart in the ethanol to gasoline (ETG) process, which gives an almost identical product distribution as the MTG process [14–16]. Since MTG and ETG most likely proceed through similar routes, the study of retained material in the ETG reaction could also provide interesting insight into MTG.

The amount of ethanol currently produced has increased significantly in recent years due to the rising demand for domestic, biorenewable alternatives to petroleum-based fuels and chemicals. There are many potential reactions utilizing ethanol to produce important chemical feedstocks [17] such as steam reforming to hydrogen, [18–20] dehydration to ethylene, [21] oxidation to acetaldehyde, [22] oxidation to acetic acid, [23, 24] and oxidation followed by condensation to butadiene [25]. Some of these aforementioned reactions, namely the processes leading to ethylene and butadiene, have been demonstrated on an industrial scale but have not retained their commercial importance when less expensive routes starting from fossil fuels have been implemented instead. The other processes mentioned above have mostly received attention in the last decade but have not found industrial applications yet. However, this might change in the near future, where commercialization of new (or old) process routes towards renewable chemicals could become industrially important along with the depletion of fossil resources. One of the present important drawbacks of the production of ethanol from biomass is the energy input required for distillation. Except in the case of sugarcane ethanol, where bagasse usually is used for the thermal energy generation, this energy generally comes from fossil resources. New ways of producing fuel grade ethanol like molecular sieves or membranes can decrease this energy input—though not avoid it. Consequently, when developing new reactions aqueous ethanol would be the preferred feedstock to achieve a more favorable energy balance by reducing the required extent of distillation. As a result, processes that do not require fuel-grade ethanol such as the dehydration of ethanol to ethylene and steam reforming to hydrogen are attracting interest [18, 26]. Other researchers have investigated the use of the ethanol to gasoline reaction as an alternative to fuel grade distillation of ethanol [27]. One challenge with the ETG process that can be envisioned when using ethanol as feed is a more rapid catalyst deactivation due to the formation of ethylene, which is a known coke precursor on H-ZSM-5 [28]. This deactivation could perhaps be inhibited by addition of water to the feed, [28, 29] using lightly distilled bio-ethanol as the feed would add additional water to the reaction and slow down deactivation and lower the ethanol feed concentration. Our first effort towards this is to study the mechanism behind ETG through the analysis of retained material in the catalyst after the ethanol to gasoline reaction. This has been done previously for the MTG reaction but to our knowledge no such information exists for the ETG reaction. We are also comparing the ETG and MTG reaction with the same process parameters to increase our understanding of these reactions and to examine possibilities of mixing crude bioethanol with methanol in a combined reaction whereby distillation of ethanol can be avoided.

The catalyst used in this study was H-ZSM-5 (Si/Al = 11.5), supplied by Zeolyst International. The experiments for determining retained material were performed in a continuous flow fixed bed quartz tubular reactor with an inner diameter of 6 mm; the catalyst bed was heated in an oven, the temperature monitored with a thermocouple situated immediately below the catalyst bed. The ethanol was added through a HPLC pump and then evaporated by heating tapes and carried through the catalyst bed with a flow of helium. The stream was then brought to an Agilent 6890 GC equipped with a Varian PoraPlot Q-HT column and a FID where the product distribution was analyzed. The experiments comparing ETG with MTG were performed on a similar setup but using a stainless steel reactor fitted with a condenser to separate gaseous products from condensable products before analysis on a Agilent 6890 GC equipped with a J & W Scientific GS-Gaspro column and a FID where the gaseous products were analyzed.

Experiments were carried out at 450 °C or 400 °C with a WHSV of 9 h^{-1} or 6 h^{-1} respectively. For the retained material study the reactor was heated to 450 °C and after 15, 60 or 120 min, the reactor was immediately moved to another oven where the catalyst was flushed with helium for 5 min at 55 °C to remove small molecules not trapped inside the zeolite pores.

For determining the retained material in the methanol to olefin process we have replicated the method employed by Guisnet et al. [30] in order to gain insight into the ethanol to gasoline reaction. In a closed Teflon vial 100 mg of spent catalyst was dissolved in 3 mL of 20% wt hydrofluoric acid. The mixture was shaken and allowed to stand overnight. When the zeolite was completely dissolved, the retained material was extracted with 1 mL of dichloromethane with added chlorobenzene as an internal standard. The organic phase was filtered and most of the dichloromethane was allowed to evaporate; Arstad et al. [10] have shown that this should not have an effect on the product distribution in the sample. The concentrated samples were then analyzed on an Agilent 6850 GC fitted with a quadruple mass spectrometer detector 5975C.

As it was stated previously, the products achieved from the MTG and the ETG processes are very similar; specifically the gaseous products are the same in both processes as can be seen in Fig. 1. Additionally the condensable products are similar although there are subtle differences between the two processes; Figure 2 gives spectra showing the main liquid products in the ETG and MTG respectively. In the MTG there are small amounts of trimethyl benzene and tetramethyl benzene that are not seen in ETG, in ETG there are instead small amounts of ethyl methyl benzene that is not found in MTG. These differences are not discernible using FID but can be seen when analyzing the samples with mass spectrometry. The similar product distribution for both processes suggests that

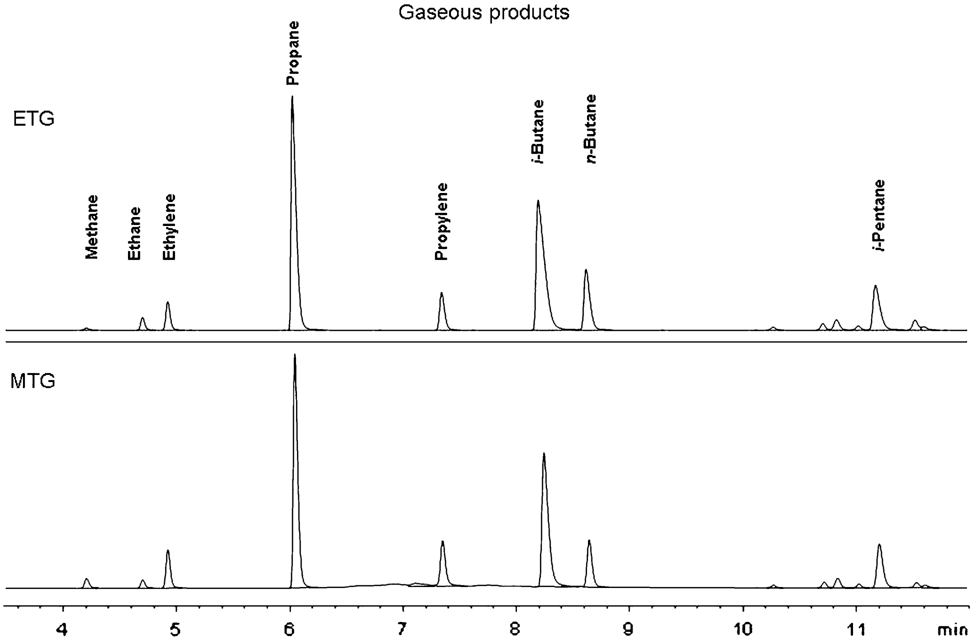

Fig. 1 Comparison of FID spectra of the gaseous products found in ethanol-to-gasoline reaction and methanol-to-gasoline run at 400 °C with a WHSV = 6 h^{-1}. Spectra obtained after 2 h on stream

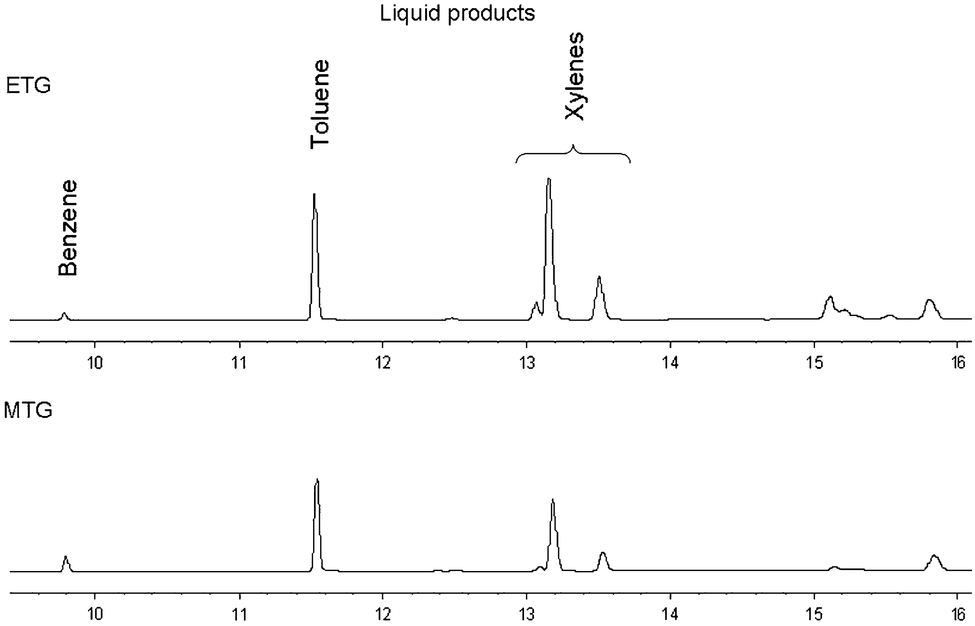

Fig. 2 FID spectra showing the major condensable products in the ethanol-to-gasoline and the methanol-to-gasoline reactions at 400 °C with WHSV = 6 h^{-1}. Spectra is showing the organic phase collected over the first 2 h of reaction

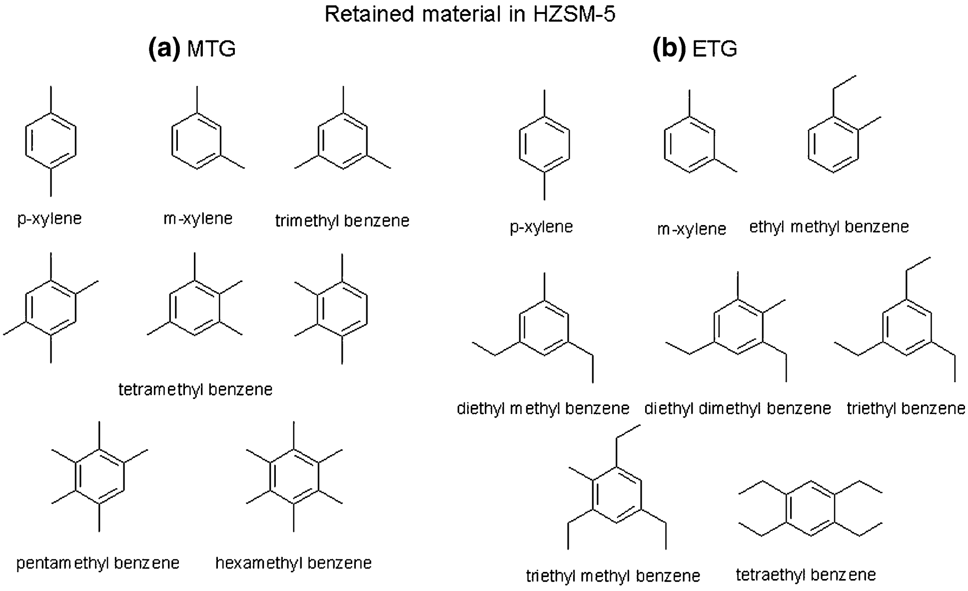

Fig. 3 The major compounds of retained material found within H-ZSM-5 after reaction with either methanol (**a**) or ethanol (**b**). Reactions run at 450 °C with WHSV = 9 h^{-1}. The truly retained compounds are depicted in the last row in the MTG and in the lower two rows in ETG

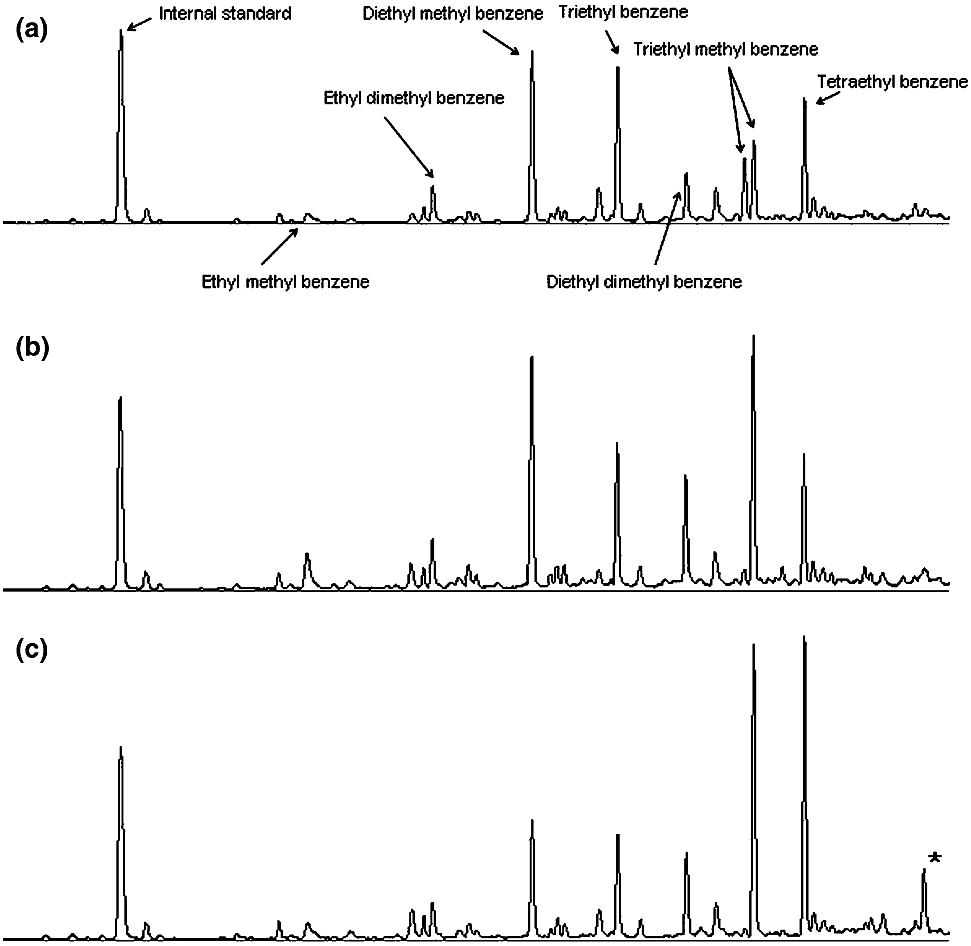

Fig. 4 Total ion chromatogram for the retained material in HZSM-5 after addition of ethanol at 450 °C with a WHSV of 9 h^{-1} for **a** 15 min, **b** 60 min, and **c** 120 min. *Oxidized form of tetraethyl benzene due to the treatment with hydrofluoric acid

the same mechanism is in operation in both of these processes. If the same mechanism is in operation it would also be likely that the same material is retained within the catalyst. Figure 3 shows the most abundant retained material found in HZSM-5 for MTG and ETG respectively. When comparing the material released from the dissolved zeolite from the ETG reaction with the products in the reactor effluent it is apparent that the true retained material consists of tetraethyl benzene, triethyl methyl benzene, triethyl benzene, diethyl dimethyl benzene, and diethyl methyl benzene, see Fig. 3, since these compounds are not present in the reactor effluent. Many of the smaller methyl benzenes such as the xylenes are present in both reactions and are expected to lead to the same products. In the catalyst from the ETG reaction there are several mixed methyl ethyl benzenes that are similar to the methyl benzenes found in MTG but it is surprising that these mixed benzenes give the same product distribution as the hydrocarbon pool containing only methyl benzenes. A more thorough examination of the results from experiments with different reaction times revealed that the amounts of tetraethyl benzene, triethyl methyl benzene, and triethyl benzene were increasing over time whereas the amount of methyl benzenes were approximately the same throughout, as seen in Fig. 4. This implies that the methyl benzenes that are common for both reactions are reacting faster than the ethyl benzenes present in the ETG reaction. Considering that the most reactive species of the hydrocarbon pool are shared between the two processes it is not so surprising that the product distribution is almost the same in both processes, the differences in product distribution should therefore come from those species that are not shared between ETG and MTG. Special attention should be given to the peaks corresponding to triethyl methyl benzene and tetraethyl benzene; these appear to be increasing more than any of the other peaks over time and it is reasonable to believe that these do not participate significantly in the reaction and could be considered as “dead ends” in the reaction network, similar to what Bjørgen et al. found for hexamethyl benzene in HZSM-5 for the MTG reaction [12]. If the triethyl methyl benzene and the tetraethyl benzene are true dead ends, as the time study suggests, they would be left unchanged by a flushing experiment at the reaction temperature, in this paper 450 °C. When flushing the catalyst at 450 °C a substantial decrease in the amount of tetraethyl benzene and triethyl methyl benzene is apparent, but at this time it is not clear why these species are decreasing. This behavior could mean that these species are indeed part of the reaction network, although at a slower rate than the smaller species in the hydrocarbon pool or they could be transformed into coke. When examining the catalysts used in reactions for longer times there are visible traces of the early stages of coke formation, which could be a logical progression from tetraethyl benzene and triethyl benzene. Whether these two species are reacting slowly or are coke precursors is inconsequential to the overall reactivity—either way the product distribution will not depend much on the larger species in the hydrocarbon pool.

The catalyst appears to deactivate faster with the formation of these compounds that potentially block the acidic sites within the zeolitic framework, thereby opening a second route towards deactivation apart from the coke formation on the surface of the zeolite crystals as has been seen by others in reactions with ZSM-5 catalysts [31, 32]. When performing deactivation runs using either ethanol or methanol as the feed it was seen that the ethanol feed gives a faster deactivation than the methanol feed. The deactivation in MTG is seen as a decrease of all products and formation of dimethyl ether, for the ETG reaction the deactivation manifests itself as an increase in the amount of ethylene forming from dehydration of ethanol whereas the other products are decreasing. The faster deactivation could be a consequence of the formation of the larger species found in the retained material in addition to the coke formation due to ethylene that was mentioned previously. From the present study it seems unlikely that ETG process in itself will ever get any commercial value. The process of converting one relatively low-value fuel into a more attractive fuel has to be exceptionally cheap to be economically viable, but the process might give some fundamental insight into the reaction mechanism of the MTG process. Moreover, a combined run where bioethanol is mixed with methanol in a possible MTG plant could find industrial importance.

In conclusion it is reasonable that MTG and ETG give similar product distributions since the products mostly stem from the same retained material via the hydrocarbon pool model, the difference in product distribution seen for the liquid products can be explained by the presence of larger hydrocarbon species found in the zeolite but which are not completely retained. In essence the formation of ethyl benzenes have small effects on the products formed but it could have implications for catalyst activity and deactivation. These issues are however expected to be less critical when a more dilute ethanol-water mixture is used. With the almost identical product distributions for the MTG and ETG experiments it is logical to conclude that one possible way of utilizing bioethanol, without distilling it to fuel grade ethanol, is to mix it with methanol, available from upcoming methanol plants, for a combined run. Thus, methanol mixed with some crude bioethanol can in a combined run be converted to a gasoline product in a METG process or alternatively to olefins (a likely more valuable product) in a METO process by altering the process conditions slightly.

References

1. (2006) Focus Catal 2006(11):5
2. (2007) Chem Week 169(29):22
3. (2008) Focus Catal 2008(3):5
4. Chang CD, Silvestri AJ (1977) J Catal 47:249

5. Haw JF, Song W, Marcus DM, Nicholas JB (2003) Acc Chem Res 36:317
6. Olsbye U, Bjørgen M, Svelle S, Lillerud KP, Kolboe S (2005) Catal Today 106:108
7. Bjørgen M, Kolboe S (2002) Appl Catal A Gen 225:285
8. Mikkelsen Ø, Kolboe S (1999) Microporous Mesoporous Mater 29:173
9. Bjørgen M, Olsbye U, Petersen D, Kolboe S (2004) J Catal 221:1
10. Arstad B, Kolboe S (2001) Catal Letts 71:209
11. Arstad B, Kolboe S (2001) J Am Chem Soc 123:8137
12. Bjørgen M, Svelle S, Joensen F, Nerlov J, Kolboe S, Bonino F, Palumbo L, Bordiga S, Olsbye U (2007) J Catal 249:195
13. Svelle S, Joensen F, Nerlov J, Olsbye U, Lillerud KP, Kolboe S, Bjørgen M (2006) J Am Chem Soc 128:14770
14. Costa E, Uguina A, Aguado J, Hernandez PJ (1985) Ind Eng Chem Process Des Dev 24:239
15. Talukdar AK, Bhattacharyya KG, Sivasanker S (1997) Appl Catal A Gen 148:357
16. Schulz J, Bandermann F (1994) Chem Eng Technol 17:179
17. Rass-Hansen J, Falsig H, Jorgensen B, Christensen CH (2007) J Chem Tech BioTech 82:329
18. Haryanto A, Fernando S, Murali N, Adhikari S (2005) Energy Fuels 19:2098
19. Ni M, Leung DYC, Leung MKH (2007) Int J Hydrogen Energy 32:3238
20. Rass-Hansen J, Christensen CH, Sehested J, Helveg S, Rostrup-Nielsen JR, Dahl S (2007) Green Chem 9:1016
21. Hu YC (1983) Hydrocarb Process 62:113
22. Jorgensen B, Fehrmann R, Christensen CH, Riisager A (2008) Top Catal (submitted)
23. Christensen CH, Jorgensen B, Rass-Hansen J, Egeblad K, Madsen R, Klitgaard SK, Hansen SM, Hansen MR, Andersen HC, Riisager A (2006) Angew Chem Int Ed Engl 45:4648
24. Li X, Iglesia E (2007) Chem Eur J 13:9324
25. Toussaint WJ, Dunn JT, Jackson DR (1947) Ind Eng Chem Res 39:120
26. Le Van Mao R, My Nguyen T, Mclaughlin GP (1989) Appl Catal 48:265
27. Whitcraft DR, Verykios XE, Mutharasan R (1983) Ind Eng Chem Process Des Dev 22:452
28. Aguayo AT, Gayubo AG, Atutxa A, Olazar M, Bilbao J (2002) Ind Eng Chem Res 41:4216
29. Qi GZ, Xie ZK, Yang WM, Zhong SQ, Liu HX, Zhang CF, Chen QL (2007) Fuel Process Technol 88:437
30. Magnoux P, Roger P, Canaff C, Fouche V, Gnep NS, Guisnet M (1987) Stud Surf Sci Catal 34:317
31. Gallezot P, Leclercq C, Guisnet M, Magnoux P (1987) J Catal 114:100
32. Behrsing T, Jaeger H, Sanders JV (1988) Appl Catal 54:289