Catalysis Science & Technology

COMMUNICATION



View Article Online View Journal | View Issue

Cite this: Catal. Sci. Technol., 2014, 4, 2891 Received 26th March 2014, Accepted 9th June 2014

DOI: 10.1039/c4cy00376d

www.rsc.org/catalysis

Highly stable boron-modified hierarchical nanocrystalline ZSM-5 zeolite for the methanol to propylene reaction[†]

Zhijie Hu,‡ Hongbin Zhang,‡ Lei Wang, Hongxia Zhang, Yahong Zhang, Hualong Xu, Wei Shen* and Yi Tang*

A highly stable MTP (methanol to propylene) catalyst, boronmodified hierarchical nanocrystalline ZSM-5 zeolite, has been constructed by a facile salt-aided seed-induced route. The cooperative effect of its hierarchical structure and modified acidity gives rise to a significantly stable activity (725 h) even at a high WHSV (weight hourly space velocity) of 4.0 h⁻¹.

With the increasing demand for propylene and the decreasing stores of petroleum in a post-oil society, the methanol to propylene (MTP) process has drawn significant attention in the chemical industry.¹ Over the last two decades, much fundamental research has been conducted to develop effective catalysts with high selectivity and long lifetimes for the MTP process.² Recent studies have demonstrated that ZSM-5 zeolite with a high Si/Al molar ratio is one of the most promising catalysts for the MTP reaction owing to its characteristic MFI topology.³ However, ZSM-5 zeolite still suffers from rapid/ severe deactivation associated with carbon depositions during the acid catalysed reaction process, which would result in the covering of the active sites or the blocking of the micropore channels of the catalyst, especially on the external surface.⁴

In order to solve the problem of rapid/severe deactivation and develop a highly stable catalyst for the MTP reaction, abundant new strategies have been proposed. In terms of pore structure design, hierarchical structured zeolite is an ideal alternative because it possesses the advantages of both mesoporous materials and zeolite crystals with highlyimproved mass transport properties.⁵ Nanocrystalline⁶ and nanosheet⁷ ZSM-5 with short inner diffusion paths have been adopted in several catalytic reactions to reduce the catalyst deactivation caused by pore blockage. Besides, the introduction of mesopores into the zeolite crystal during synthesis or post-synthesis modification, for example by soft templating,⁸ hard templating,⁹ or alkaline treatment,¹⁰ can also slow down the deactivation of the catalysts in MTP due to their improved mass transfer properties and tolerance for a larger amount of coke. The impact of various mesopore types as well as hierarchical porosity in industrial catalysts has been proven in the recent literature.¹¹ Additionally, the modification of acidity and addition of some active components have also been developed with some promising results. For example, phosphorus-modified ZSM-5 has been reported with improved catalytic stability and propylene selectivity.¹² On the approach of boron isomorphous substitution, it is found that the enhanced catalytic stability can be attributed to the increase of weak acid sites.¹³ The introduction of gold nanoparticles into ZSM-5 can considerably stabilize the dehydrogenation intermediates during the coking process to reinforce the catalytic stability.¹⁴ By means of either pore structure engineering or acidity modification, the lifetime of the catalysts can be prolonged from dozens to hundreds of hours at a weight hourly space velocity (WHSV) of around 0.5-2.0 h⁻¹.^{7-10,12-14} However, from a practical point of view, a catalyst with a longer lifetime even at a higher WHSV is still desired, especially via a preparation method which involves simple steps, a high reproducibility and few energyenvironment problems, for large-scale production and industrial applications.11,15

Herein, a highly stable MTP catalyst is designed using the combination of pore structure engineering and acidity modification. This boron-modified hierarchical nanocrystalline ZSM-5 zeolite (denoted as B–N–Z5) catalyst displays intercrystal mesoporosity from oriented self-assembled nanocrystallites and weak acidity from boron-modification. Based on the novel "salt-aided seed-induced route" recently proposed by our laboratory,¹⁶ the one-step synthesis of B–N–Z5 catalyst

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials, and Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433, PR China. E-mail: yitang@fudan.edu.cn,

wshen@fudan.edu.cn; Fax: (+86) 21 65641740

[†] Electronic supplementary information (ESI) available: synthesis procedure, characterization method, catalyst test, SEM and TEM images, ¹¹B and ²⁷Al MAS NMR spectra, TG curves, catalytic performance on MTP, XRD patterns. See DOI: 10.1039/c4cy00376d

[‡] These authors contributed equally to this work.

has the advantages of a fast crystallization process (within 4 h), high yield (>80%), low template consumption (TPABr/SiO₂ = 0.1) and no detectable extra-framework aluminum or boron species. Notably, an ultra-long lifetime (about 725 h) has been realized for this B–N–Z5 catalyst even at a high WHSV of 4.0 h⁻¹. Such an approach may bring new possibilities for developing highly stable MTP reaction catalysts for industrial applications.

A scanning electron microscopy (SEM) image is depicted in Fig. 1a. It clearly shows that the B-N-Z5 sample exhibits a uniformly globular morphology consisting of globules with a diameter of about 500 nm and a very rough external surface. The transmission electron microscopy (TEM) images in Fig. 1b and c show that each of the uniform zeolite microspheres is made up of abundant small nano-crystallite domains with an average diameter of about 20-40 nm. The in situ assembly of these nano-crystallites during the hydrothermal synthesis gives rise to abundant inter-crystallite mesopores amongst these zeolite nano-crystallites. The highresolution TEM (HRTEM) image in Fig. 1d further proves that these small nano-crystallites are highly crystalline and their lattice fringes exhibit the same orientation which even extends over the whole zeolite aggregates, and the inset selected area electron diffraction (SAED) pattern presents a clear single-crystal-like diffraction pattern of ZSM-5 zeolite. This high-crystallinity hierarchical nanocrystalline structure is also evidenced by the N₂ sorption isotherm (Fig. 1e), in which the B-N-Z5 sample shows a type IV isotherm with an



Fig. 1 (a) SEM, (b, c) TEM, (d) HRTEM and SAED images (inset of d), (e) N_2 sorption isotherm, (f) ¹¹B and ²⁷Al MAS NMR spectra of B-N-Z5.

H3 hysteresis loop. The steep increase at low relative pressure $(P/P_0 < 0.2)$ illustrates the perfect microporous structure in this sample while the special hysteresis loop appearing at $P/P_0 = 0.1-0.4$ is associated with the phenomenon of the fluid-to-crystalline phase transition of adsorbed N₂ on the ZSM-5 zeolite with high Si/Al ratio.¹⁷ Moreover, B–N–Z5 has a large hysteresis loop and enhanced adsorption at intermediate and high pressures $(0.4 < P/P_0 < 1)$ arising from nitrogen adsorption on inter-crystallite mesopores formed by the assembly of adjacent nano-crystallites, in agreement with the TEM image in Fig. 1c. In addition, the B–N–Z5 particles possess a high mechanical stability, which is proved by the ultrasound experiment which was conducted for 180 min after calcination (Fig. S1†).

The incorporation of B and its influence on the framework Al in B-N-Z5 are characterized by ¹¹B and ²⁷Al magic-anglespinning nuclear magnetic resonance (MAS NMR) as shown in Fig. 1f. In the ¹¹B MAS NMR spectrum, an intensive and highly symmetric peak is observed at a chemical shift of ca. -3.9 ppm, which is a characteristic peak of tetrahedral B species in the B-MFI framework.¹⁸ There are no peaks at ca. -2.0 or above 5.0 ppm, which correspond to the extra-framework tetrahedral and the various trigonal B species respectively. In the ²⁷Al MAS NMR spectrum, there is only one peak at a chemical shift of ca. 55 ppm, corresponding to the rv-coordinate Al in the framework. No signal at ca. 0 ppm, assigned to vi-coordinate extra-framework Al, is observed, indicating that the Al species in this sample are all *iv*-coordinate framework Al. Therefore, the B species are completely incorporated into the B-N-Z5 zeolite framework and the existence of B does not affect Al incorporation into the zeolite framework during the "salt-aided seed-induced route". The advantages of this method for heteroatom incorporation could also be demonstrated by comparison with the conventional hydrothermal synthesis method reported in our previous work,¹³ where not only extra-framework boron but also extra-framework aluminum species appeared (Fig. S2, ESI†).

To more clearly investigate the effects of the hierarchical structure and boron-modified acidity of B-N-Z5, a conventional ZSM-5 (denoted as C-Z5, Fig. S3a in the ESI,† synthesized according to ref. 13), a hierarchical nanocrystalline ZSM-5 (denoted as N-Z5, Fig. S4 in the ESI,† synthesized according to ref. 16a) and a B-modified conventional ZSM-5 (denoted as B-C-Z5, Fig. S3b and S5 in the ESI,† the best catalyst with boron isomorphous substitution in ref. 13) are adopted as reference samples. Some detailed information on C-Z5, N-Z5 and B-C-Z5 is described in the ESI.† Their compositions and textural properties are summarized in Table 1. Elemental analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES) reveals that all these samples contain a similar Si/Al ratio of ca. 160. Also, B-C-Z5 and B-N-Z5 have a similar boron content. Moreover, all of the samples have a large specific surface area (S_L , ca. 460 m² g⁻¹) and micropore volume (V_{micro} , ca. 0.12 cm³ g⁻¹). N-Z5 and B-N-Z5 possess much larger mesopore volumes (Vmeso, ca. 0.19 cm³ g⁻¹) and external surfaces (S_{ext} , *ca.* 110 m² g⁻¹) than

Table 1 Compositions and textural properties of various samples

Sample	Si/Al ^a	B/Al^a	$S_{\mathrm{L}} \left(\mathrm{m}^2 \mathrm{g}^{-1}\right)$	$S_{\rm ext}^{\ \ b} ({ m m}^2 { m g}^{-1})$	$V_{\rm micro}^{\ \ b} \left({\rm cm}^3 {\rm g}^{-1} \right)$	$V_{\rm meso}^{\ \ c} ({\rm cm}^3 {\rm g}^{-1})$
C–Z5	156	0	435	52	0.12	0.07
N-Z5	152	0	489	122	0.11	0.19
B-C-Z5	160	0.58	452	67	0.12	0.07
B-N-Z5	162	0.62	460	109	0.11	0.18

^{*a*} Determined by ICP-AES. ^{*b*} By the *t*-plot method. ^{*c*} By the BJH method. S_L : Langmuir surface area; S_{ext} : external surface area; V_{micro} : micropore volume; V_{meso} : mesopore volume.

C-Z5 and C-B-Z5 (*ca.* 0.07 cm³ g⁻¹ and 60 m² g⁻¹) due to their hierarchical nanocrystalline structure.

Fig. 2a depicts the powder X-ray diffraction (XRD) patterns of the four ZSM-5 samples. The samples all present the characteristic diffraction peaks for the typical structure of MFI topology at 2θ s of 7.0-9.0 and 23.0-25.0, and no impure or amorphous phase was detected. However, the N-Z5 and B-N-Z5 samples present broader and weaker diffraction peaks, probably due to the submicron size of the N-Z5 and B-N-Z5 particles. The acidities of the samples were characterized by the temperature-programmed desorption of ammonia (NH₃-TPD). Fig. 2b displays the typical profile of s zeolite with two desorption peaks, in which the peak at the low temperature of around 150 °C (peak I) is assigned to the weak acid sites while that at the high temperature of around 330 °C (peak II) is attributed to the strong acid sites. In detail, the amount of strong acid sites in these four samples are close to each other, in good agreement with their similar Si/Al ratio; while the amount weak acid sites for B-C-Z5 and B-N-Z5 increase with B incorporation into the ZSM-5 framework.¹³ Besides, peak I of B-C-Z5 and B-N-Z5 displays an interesting shift to lower temperature probably due to the weaker acidity of B-OH-Si;13 while peak II of N-Z5 and B-N-Z5 has moved to a higher temperature probably due to the seed-induced synthesis method and the resulting special structure.^{16a} This modified acidity due to B incorporation is expected to result in improved catalytic performance in the MTP reaction.

To better study the catalytic stability of the B-N-Z5 for the MTP reaction, comparative tests were performed under approximate industrial conditions (full methanol conversion)⁶⁻¹⁵ but with a more harsh WHSV (4.0 h^{-1} , four times the WHSV of around 1.0 h^{-1} commonly used in the literature^{6-10,12,14}) to accelerate the deactivation of the catalysts. The results show that all the samples present a steady high methanol conversion of nearly 100% (Fig. 3a) and similar olefin and propylene selectivity (Fig. 3b and c). However, their activity would rapidly decay once the methanol conversion begin to decrease (Fig. 3a). The catalyst stability is estimated by using the reaction time for complete methanol conversion at a certain WHSV according to ref. 6-15. The B-N-Z5 catalyst displays the longest lifetime of 725 h (Fig. 3a) compared with C-Z5 (80 h), N-Z5 (120 h) and even B-C-Z5 (320 h). Referring to the textural and acidic properties shown above, the high stability of B-N-Z5 can be attributed to the cooperative effect of its hierarchical structure and boron-modified acidity. In detail, compared with C-Z5 (80 h), the tendency of slowing down the deactivation of N-Z5 (120 h) is derived from its hierarchical nanocrystalline structure, which can shorten the micropore channels to improve the diffusion properties and accommodate more coke deposits.6,7 The enhanced stability of B-C-Z5 (320 h) can be attributed to the increase of weak Brønsted acid sites due to the B-incorporation. The introduction of more weak acid sites is believed to speed up the



Fig. 2 (a) XRD patterns and (b) $\rm NH_3\text{-}TPD$ profiles of C–Z5, N–Z5, B–C–Z5 and B–N–Z5.



Fig. 3 Conversion of methanol (a), selectivity of total olefin (b) and propylene (c) over zeolites C–Z5 (black), N–Z5 (dark cyan), B–C–Z5 (blue) and B–N–Z5 (red). *Reaction conditions*: WHSV = 4.0 h⁻¹, *T* = 733 K, $n(CH_3OH): n(H_2O) = 1:3$, $P_{total} = 1$ atm.

reactions involved in olefin production and suppress the tendency for competitive polycyclic aromatization of the multi-methyl benzene intermediate to coke precursors.13,18,19 Combining both advantages, the B-N-Z5 catalyst successfully realizes the cooperative effect of hierarchical structure and boron-modified acidity, so that it demonstrates a high stability for 725 h at a high WHSV of 4 h^{-1} , much longer than the simple sum of those of N-Z5 with only a hierarchical nanocrystalline structure (120 h) and B-C-Z5 with only boron modified acidity (320 h). Fig. S6[†] further shows the coke deposition on the deactivated catalysts measured by thermogravimetric (TG) analysis. It is found that the amount of coke is in the order $B-N-Z5 > B-C-Z5 > N-Z5 \gg C-Z5$, although the former has the highest stability. It indicates that B-N-Z5 has a strong capability for coke tolerance due to the co-effect of the hierarchical porosity and unique acid distribution with enriched weak acid sites, which ensures the long-term maintenance of the catalytic activity until more coke is finally formed.

The catalytic performance of B-N-Z5 has further been evaluated at an even higher space velocity and with lower water content in the feed after several cycles of catalyst regeneration to deepen the understanding of the properties of B-modified hierarchical catalysts. As shown in Fig. 4, when the WHSV is increased to 10 h⁻¹, the B-N-Z5 still exhibits excellent performance with high methanol conversion (above 80%) after ca. 60 h with 65% olefin and 43% propylene selectivity. After regenerating the catalyst in air (40 mL min⁻¹) at 843 K for 8 h, B-N-Z5 still displays relatively high methanol conversion (above 75%) after *ca.* 40 h at a WHSV of 10 h^{-1} . In order to further study the catalyst stability, a third cycle was been carried out on the second regenerated catalyst at a WHSV of 10 h^{-1} and $n(CH_3OH): n(H_2O) = 1:1$. Interestingly, B-N-Z5 shows high stability with high methanol conversion (above 80%) after 55 h with a lower water ratio in the feed. To shed some light on the role of boron, a B/N-Z5 catalyst was prepared by impregnating a similar amount of boron on



Fig. 4 Conversion of methanol, selectivity of total olefin and propylene over zeolite B–N–Z5. *Reaction conditions*: WHSV = 10 h⁻¹, T = 733 K, $P_{total} = 1$ atm. *Regeneration conditions*: in air (40 mL min⁻¹) at 843 K for 8 hours.

N-Z5. The catalytic performance of B/N-Z5 was also evaluated at a WHSV of 10 h^{-1} (Fig. S7[†]). B/N-Z5 exhibits a much shorter lifetime of only 9 h (methanol conversion above 80%) and lower olefin (<60%) and propylene (34%) selectivity compared with B-N-Z5. Meanwhile, according to the XRD patterns (Fig. S8[†]) of B/N-Z5 before and after the reaction, the appearance of alpha quartz was observed after only 12 h of the reaction, probably due to its lower stability in steam. However, the patterns of B-N-Z5 show almost no alteration. These results imply that the tetrahedral boron incorporated in the zeolite framework is important for catalyst stability. The ¹¹B and ²⁷Al MAS NMR of B-N-Z5 after reaction were further employed to characterize the stability of the B and Al sites towards hydrolysis under the testing conditions. According to the results in Fig. S9,† most of the B and Al species are still w-coordinate species in the framework although some defects or extra-framework B and Al species are observed. Therefore, after regeneration, the catalytic activity can still be maintained to some extent (Fig. 4) under the harsh reaction conditions of WHSV = 10 h^{-1} .

Conclusions

In summary, boron-modified hierarchical nanocrystalline ZSM-5 zeolite (B-N-Z5) could be facilely prepared by a saltaided seed-induced method, which provides a possibility for large-scale production due to the easy synthesis, fast crystallization and low usage of organic templates. The systematic and thorough characterization demonstrates that the typical B-N-Z5 catalyst not only has a rough external surface, abundant intercrystal mesopores and a high crystallinity, but also possesses an increasing amount of weak acid sites arising from the framework incorporation of boron. This B-N-Z5 catalyst has a very long lifetime of 725 h even at a high WHSV of 4.0 h⁻¹ for the MTP reaction, which could be attributed to the unique cooperative effect of the hierarchical nanocrystalline structure and boron-modified acidity in this sample. The results shown here indicate the necessity of the combination of pore structure design and acidity modification for the highly stable MTP catalyst.

Acknowledgements

This work was supported by National Key Basic Research Program of China (2013CB934101), and Science and Technology Commission of Shanghai Municipality (11JC1400400).

Notes and references

 (a) U. Olsbye, S. Svelle, M. Bjorgen, P. Beato, T. V. W. Janssens, F. Joensen, S. Bordiga and K. P. Lillerud, Angew. Chem., Int. Ed., 2012, 51, 5810–5831; (b) M. Stocker, Microporous Mesoporous Mater., 1999, 29, 3–48; (c) D. Lesthaeghe, A. Horre, M. Waroquier, G. B. Marin and V. Van Speybroeck, Chem. – Eur. J., 2009, 15, 10803–10808; (d) U. Olsbye, M. Bjorgen, S. Svelle, K. P. Lillerud and S. Kolboe, Catal. Today, 2005, 106, 108–111; (e) Z. M. Cui, Q. Liu, W. G. Song and L. J. Wan, *Angew. Chem., Int. Ed.*, 2006, 45, 6512–6515; (f) W. Wang, Y. J. Jiang and M. Hunger, *Catal. Today*, 2006, 113, 102–114; (g) W. Wang, A. Buchholz, M. Seiler and M. Hunger, *J. Am. Chem. Soc.*, 2003, 125, 15260–15267.

- 2 (a) Q. Zhu, J. N. Kondo, T. Tatsumi, S. Inagaki, R. Ohnuma, Y. Kubota, Y. Shimodaira, H. Kobayashi and K. Domen, J. Phys. Chem. C, 2007, 111, 5409–5415; (b) A. T. Aguayo, A. G. Gayubo, R. Vivanco, M. Olazar and J. Bilbao, Appl. Catal., A, 2005, 283, 197–207; (c) B. P. C. Hereijgers, F. Bleken, M. H. Nilsen, S. Svelle, K. P. Lillerud, M. Bjorgen, B. M. Weckhuysen and U. Olsbye, J. Catal., 2009, 264, 77–87; (d) M. Bjorgen, S. Svelle, F. Joensen, J. Nerlov, S. Kolboe, F. Bonino, L. Palumbo, S. Bordiga and U. Olsbye, J. Catal., 2007, 249, 195–207; (e) S. Ilias and A. Bhan, ACS Catal., 2013, 3, 18–31.
- 3 (a) J. F. Haw, W. G. Song, D. M. Marcus and J. B. Nicholas, Acc. Chem. Res., 2003, 36, 317–326; (b) J. Z. Li, Y. X. Wei, G. Y. Liu, Y. Qi, P. Tian, B. Li, Y. L. He and Z. M. Liu, Catal. Today, 2011, 171, 221–228; (c) A. G. Gayubo, A. T. Aguayo, M. Olazar, R. Vivanco and J. Bilbao, Chem. Eng. Sci., 2003, 58, 5239–5249.
- 4 H. Schulz, Catal. Today, 2010, 154, 183-194.
- 5 (a) L. H. Chen, X. Y. Li, J. C. Rooke, Y. H. Zhang, X. Y. Yang,
 Y. Tang, F. S. Xiao and B. L. Su, *J. Mater. Chem.*, 2012, 22,
 17381–17403; (b) J. Perez-Ramirez, C. H. Christensen,
 K. Egeblad, C. H. Christensen and J. C. Groen, *Chem. Soc. Rev.*, 2008, 37, 2530–2542.
- 6 M. Firoozi, M. Baghalha and M. Asadi, *Catal. Commun.*, 2009, **10**, 1582–1585.
- 7 (a) M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki and R. Ryoo, *Nature*, 2009, 461, 246–249; (b) S. Hu, J. Shan, Q. Zhang, Y. Wang, Y. S. Liu, Y. J. Gong, Z. J. Wu and T. Dou, *Appl. Catal.*, A, 2012, 445, 215–220.
- 8 J. Kim, M. Choi and R. Ryoo, J. Catal., 2010, 269, 219–228.
- 9 C. Sun, J. M. Du, J. Liu, Y. S. Yang, N. Ren, W. Shen, H. L. Xu and Y. Tang, *Chem. Commun.*, 2010, 46, 2671–2673.

- 10 (a) C. S. Mei, P. Y. Wen, Z. C. Liu, H. X. Liu, Y. D. Wang, W. M. Yang, Z. K. Xie, W. M. Hua and Z. Gao, *J. Catal.*, 2008, 258, 243–249; (b) P. N. R. Vennestrom, M. Grill, M. Kustova, K. Egeblad, L. F. Lundegaard, F. Joensen, C. H. Christensen and P. Beato, *Catal. Today*, 2011, 168, 71–79.
- 11 (a) M. Milina, S. Mitchell, P. Crivelli, D. Cooke and J. Pérez-Ramírez, *Nat. Commun.*, 2014, 3922, DOI: 10.1038/ ncomms4922; (b) S. Mitchell, N. L. Michels, K. Kunze and J. Perez-Ramirez, *Nat. Chem.*, 2012, 4, 825–831.
- J. Liu, C. X. Zhang, Z. H. Shen, W. M. Hua, Y. Tang, W. Shen, Y. H. Yue and H. L. Xu, *Catal. Commun.*, 2009, 10, 1506–1509.
- 13 Y. S. Yang, C. Sun, J. M. Du, Y. H. Yue, W. M. Hua, C. L. Zhang, W. Shen and H. L. Xu, *Catal. Commun.*, 2012, 24, 44-47.
- 14 C. Sun, Y. S. Yang, J. M. Du, F. Qin, Z. P. Liu, W. Shen, H. L. Xu and Y. Tang, *Chem. Commun.*, 2012, 48, 5787-5789.
- 15 R. Chal, C. Gerardin, M. Bulut and S. van Donk, *ChemCatChem*, 2011, 3, 67–81.
- 16 (a) H. B. Zhang, Y. C. Ma, K. S. Song, Y. H. Zhang and Y. Tang, *J. Catal.*, 2013, 302, 115–125; (b) H. B. Zhang, K. S. Song, L. Wang, H. X. Zhang, Y. H. Zhang and Y. Tang, *ChemCatChem*, 2013, 5, 2874–2878.
- 17 J. C. Groen, L. A. A. Peffer and J. Pérez-Ramírez, *Microporous Mesoporous Mater.*, 2003, 60, 1–17.
- 18 R. Millini, G. Perego and G. Bellussi, *Top. Catal.*, 1999, 9, 13–34.
- (a) Q. J. Zhu, J. N. Kondo, T. Yokoi, T. Setoyama, M. Yamaguchi, T. Takewaki, K. Domen and T. Tatsumi, *Phys. Chem. Chem. Phys.*, 2011, 13, 14598–14605; (b)
 Q. J. Zhu, J. N. Kondo, T. Setoyama, M. Yamaguchi, K. Domen and T. Tatsumi, *Chem. Commun.*, 2008, 5164–5166; (c) E. Unneberg and S. Kolboe, *Appl. Catal.*, A, 1995, 124, 345–354; (d) M. Guisnet, L. Costa and F. R. Ribeiro, *J. Mol. Catal. A: Chem.*, 2009, 305, 69–83; (e)
 D. Mores, J. Kornatowski, U. Olsbye and B. M. Weckhuysen, *Chem. - Eur. J.*, 2011, 17, 2874–2884.