Catal Lett (2007) 118:123–128
DOI 10.1007/s10562-007-9166-x

Activities of MFI-Supported Rhenium Catalysts for the Aromatization of Methane: Effect of Cationic Form of the Inorganic Carrier

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Received: 7 September 2006 / Accepted: 12 June 2007 / Published online: 28 July 2007

Abstract MFI type inorganic carrier was used in two different cationic forms, hydrogen and calcium respectively. MFI-supported molybdenum and rhenium catalysts were prepared. The activities of the catalysts were compared for the aromatization reaction of methane. Higher activity values were attained with the catalysts supported on HZSM-5. Aromatics were also observed with the catalysts supported on CaZSM-5, despite their deficiency in acid sites. Highly dispersed rhenium is expected to be formed with the use of the inorganic carrier in calcium form. On the other hand, lower reaction rates were observed with rhenium supported on CaZSM-5, in spite of the improved dispersion of the active rhenium species on this catalyst. This was interpreted in terms of the critical role of the acid sites in the conversion of methane to aromatics, compared to the improved dispersion of the active metal.

Keywords Molybdenum · Rhenium · MFI · Acidity · Methane · Aromatics

1 Introduction

Conversion of methane into useful chemicals has been and still is a subject of worldwide renewed efforts. Several routes have been explored over the previous two decades. In addition to methane conversion into syngas which is of real industrial significance, more ambitious routes such as direct conversion into oxygenates [1–4], methanation of olefins [5], oxidative coupling of methane [6–9] and conversion of methane into benzene and hydrogen were explored [10–28].

The latest developments were concerned with the latter reaction carried out in the presence of various transition metal oxide-loaded inorganic carriers. Mainly molybdenum- and rhenium-based active components deposited over HZSM-5 were thoroughly investigated [22–28].

In the case of molybdenum-based catalysts, the activation procedure was scrutinized and it was generally agreed that whatever the nature of the precursor, molybdenum was converted, in the presence of methane, under the reaction conditions, into molybdenum carbide [12, 13, 24]. It was generally accepted that the reaction proceeded via the formation of C_2H_2 or C_2H_4 over the molybdenum carbide species. Further cyclization and aromatization of acetylene

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or ethylene would occur over the acid sites [10, 29, 30]. If it is assumed that dimolybdenum carbide is the active precursor for methane conversion into a C_2 primary compound (ethylene or acetylene), one might speculate, in agreement with Lunsford et al. [13], Iglesia et al. [31] and our recent study [32] that, methane decomposition into carbon and hydrogen would convert the overactive dimolybdenum carbide into the truly active carbide capable of generating C–C bonds upon interaction with methane.

Rhenium as the active transtion metal ion was first studied by Ichikawa et al. [25, 26]. They found that the aromatization of methane on the Re/HZSM-5 catalysts proceeds at rates of product formation comparable to the reference data on Mo/HZSM-5, which has been thought to be a unique catalyst for the aromatization reaction of methane. In contrast to the molybdenum carbide as the active species for the aromatization of methane to benzene and naphthalene, the metallic rhenium on HZSM-5 was proposed as the active species.

In an effort to see the possible effect of the acidity of the inorganic carrier, calcium and hydrogen forms of MFI were used as support for rhenium and molybdenum catalysts. The activities of the catalysts were compared for the aromatization of methane.

2 Experimental

An HZSM-5 sample with a Si/Al ratio of 28, a gift from Sud-Chemie (Germany), was used in the experiments. About 5 g of HZSM-5 was ion-exchanged with 250 mL of saturated $Ca(NO_3)_2$ solution. After ion-exchange with Ca^{2+}, the zeolite was separated by centrifugation and thoroughly washed with deionized water. These treatments were repeated for three times to assure full ion-exchange. The resulting zeolite in calcium form had only a few residual acid sites as apparent from the results of the pyridine adsorption study (weak IR band at about 1547 cm^{-1}) carried out using infrared spectroscopy (Fig. 1).

Wet impregnation method was used to prepare the catalysts. For HZSM-5-supported molybdenum catalyst, ammonium molybdate ($(NH_4)_2MoO_4$, Touzart & Matignon) was dissolved in a minimum volume of water and the zeolite was added to the solution so as to achieve a nominal molybdenum content of 4% by weight. Chemical analysis confirmed the molybdenum content to be 3.85%. The slurry was subsequently dried at 80 °C. CaZSM-5-supported molybdenum catalyst was prepared in a similar manner and the molybdenum content of the sample was confirmed by chemical analysis as 3.9%.

Similarly, MFI-supported rhenium catalysts were prepared with two different cationic forms of ZSM-5 zeolite (Ca and H). Ammonium perrhenate (NH_4ReO_4, Aldrich 99+%) was used as the rhenium salt. Ammonium perrhenate was dissolved in a minimum volume of water, and either HZSM-5 (Si/Al = 28, Sud Chemie, Germany) or CaZSM-5, prepared from HZSM-5 as described above, was added to the solution so as to achieve a nominal rhenium content of 4% by weight. The slurry was subsequently dried at 80 °C. Chemical analyses confirmed the rhenium contents to be 3.95 and 3.90%, for HZSM-5 and CaZSM-5, respectively.

In experiments with MFI-supported molybdenum catalysts, a 200 mg sample of the dry powder was placed in a U shaped quartz reactor with 14 mm inner diameter. The catalyst was first activated in dry air at 650 °C and then purged by argon flow (Air Liquide UP) at the same temperature, for 30 min. The catalyst was then subjected overnight to a 730:30 H_2:CH_4 mixture (total atmospheric pressure) at 700 °C, to achieve carburization of the supported/exchanged Mo species.

In experiments with MFI-supported rhenium catalysts, a 200 mg sample of the dry powder was placed in a U shaped quartz reactor with 14 mm inner diameter and was first activated by dry air at 500 °C and then cooled to 200 °C under argon atmosphere. At 200 °C, H_2 was flown over the catalyst bed for 0.5 h to reduce the rhenium precursor to metallic rhenium. The catalyst bed was then heated to 300 °C and kept at that temperature for 3 h under H_2 flow. After treatment with H_2 flow, the bed was subsequently heated to 700 ° C under H_2 atmosphere.

The activated catalysts were reacted with a 44:716 CH_4:Ar mixture under a flow rate of 20 L/h at 700 °C. Products were analyzed in line using three gas chromatographs, two of them equipped with F.I. Detectors and columns packed with unibeads 35 to analyze aliphatics and with bentone to analyze aromatics. The third chromatograph, equipped with a thermal conductivity cell detector and a column packed with carbosieve S, was devoted to the analysis of CO, CO_2, and mainly H_2.

CH_4 conversion to hydrocarbon products $(X_{CH_4\,\mathrm{to\,HC}})$ was calculated from the partial pressures of the hydrocarbons formed based on the measured GC responses, reaction stoichiometries, and the differential reactor assumption, as $P_{CH_4\,\mathrm{to\,HC}}/P_{CH_4,\mathrm{inlet}}$.

Selectivity to any hydrocarbon product was defined as the ratio of the CH_4 converted to that product to the total CH_4 converted to hydrocarbon products.

3 Results and Discussion

For the aromatization reaction of methane under non-oxidative conditions, CaZSM-5-supported molybdenum and rhenium catalysts showed much lower activity values compared to the ones obtained with HZSM-5-supported

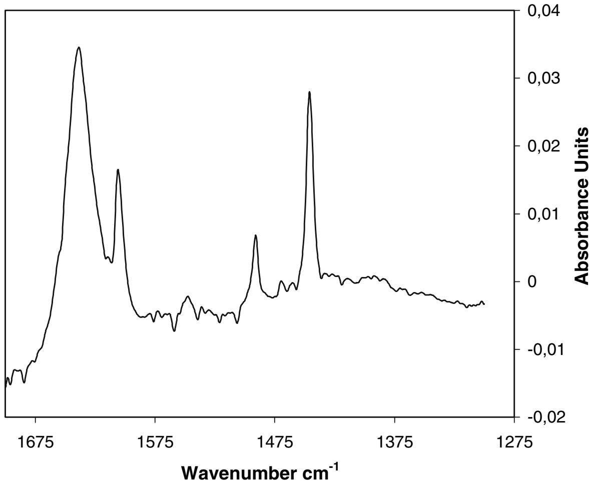

Fig. 1 Pyridine adsorption study on CaZSM-5 by infrared spectroscopy. Absorbance versus wavenumber in cm^{-1}

molybdenum and rhenium catalysts, as can be seen from Figs. 2 and 3. Calcium form of the inorganic carrier, which was determined to be deficient in acid sites, was specifically chosen so as to investigate the effect of the acidity of the inorganic carrier. Acid sites of the inorganic support are accepted [13, 29, 30, 33, 34] to be functional for the cyclization and aromatization of ethylene/acetylene, formed on Mo_2C via C–C bond activation, according to the bifuntional mechanism. Yet, it is worthwhile to point out that although the catalyst samples in calcium form were much less active, they still could function in this study, to form benzene and naphthalene as seen in Fig. 4 and Table 1. Since the zeolite carrier was in the calcium form, there was practically no available acid site left to carry out the cyclization and aromatization of C_2's to benzene and naphthalene. The performance of the catalysts supported on CaZSM-5 confirms the claim of Ha et al. that aromatics could form thermally via the cyclization of polyene, such as hexadiene [33].

It is also interesting to note that higher initial activity values were attained with MFI-supported rhenium samples (Figs. 2 and 3). On the other hand, all samples deactivated in a similar manner irrespective of the active metal. Metallic rhenium species, formed during the activation of the catalyst with H_2, seem to be the active site for the aromatization of methane, as suggested by Ichikawa et al. [25, 26].

In Figs. 4 and 5, the selectivities versus time on stream for CaZSM-5 and HZSM-5-supported molybdenum catalysts are shown, respectively. As can be seen from the figures, higher ethylene selectivities were observed at very early times on stream. After an abrupt decrease, ethylene selectivities started increasing gradually. On the other hand, the periods of time on stream needed to achieve the maximum conversion values were 6 and 12 min for HZSM-5-and CaZSM-5-supported molybdenum catalysts, respectively. This may be an indication of the role of acidity in converting Mo_2C into the active molybdenum carbide species [13, 31, 32], which was almost totally absent in the case of the CaZSM-5 support. By contrast, no difference was observed between the values of time on

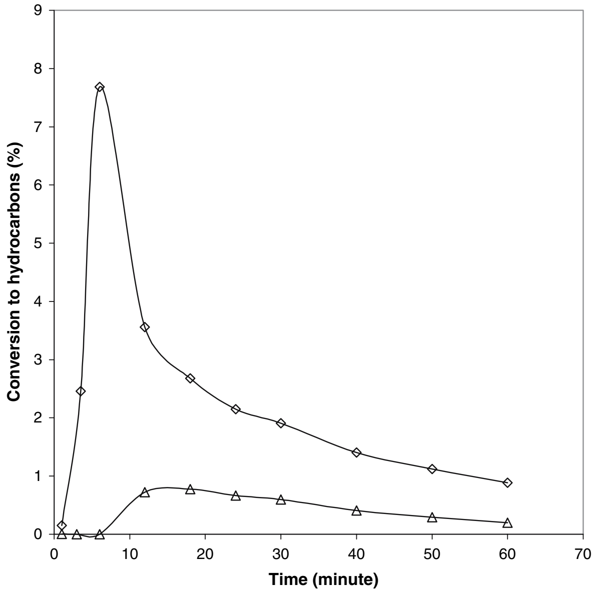

Fig. 2 Variation of the conversion to hydrocarbons with time on stream for (◇) HZSM-5-supported molybdenum catalyst; (Δ) CaZSM-5-supported molybdenum catalyst

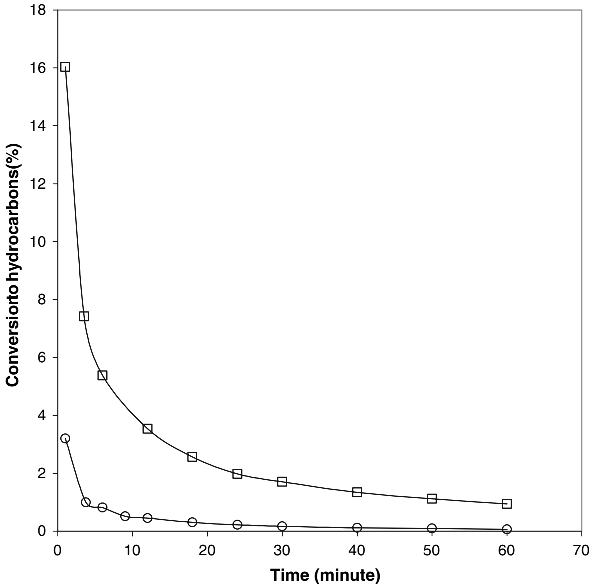

Fig. 3 Variation of the conversion to hydrocarbons with time on stream for (□) HZSM-5-supported rhenium catalyst; (○) CaZSM-5-supported rhenium catalyst

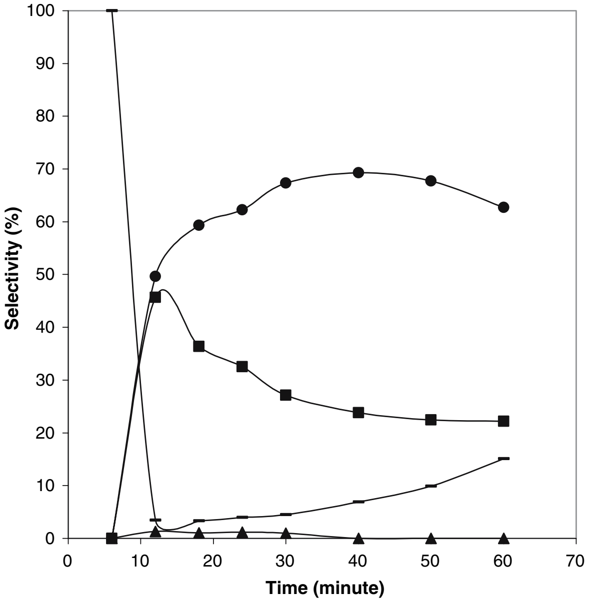

Fig. 4 Variation of the selectivity (%) with time on stream for CaZSM-5-supported molybdenum catalyst; (■) Benzene (▲) Toluene (•) Naphthalene (–) Ethylene

stream required to reach the maximum conversion in the case of rhenium catalysts supported on HZSM-5 and CaZSM-5, for which the active sites are rhenium metal particles.

In Ca-exchanged ZSM-5, calcium is expected to be attached to the zeolite at exchange sites in the probable form of Zeolite–O–Ca–OH. Upon introducing ammonium perrhenate, rhenium is expected to be ion exchanged and attached to the framework according to the reaction given below, resulting in highly dispersed metal precursors:

$$Ze - O - Ca - OH + NH_4ReO_4 \rightarrow$$
$$Ze - O - Ca - ReO_4 + NH_4OH$$

The set of data concerning the selectivities is at variance with most published data in that the selectivity to naphthalene is higher than that to benzene, initially in the case of CaZSM-5 supported molybdenum and HZSM-5 supported rhenium as seen in Figs. 4 and 6. It is common knowledge that the lower aliphatics and benzene are the kinetically favoured products whereas naphthalene and higher polynuclear aromatics are the thermodynamically

Table 1 The selectivity values with time on stream for CaZSM-5-supported rhenium catalyst

Time (min)	Selectivity % for ethylene	Selectivity % for benzene	Selectivity % for acetylene	Selectivity % for naphthalene
1	4.5	95.4	0	0
6	11.4	88.2	0.5	0
12	14.8	84.7	0.4	0
18	18.9	81.0	0	0
24	23.2	76.8	0	0
30	26.2	73.8	0	0
40	34.2	65.8	0	0
50	38.4	61.6	0	0
60	49.5	50.5	0	0

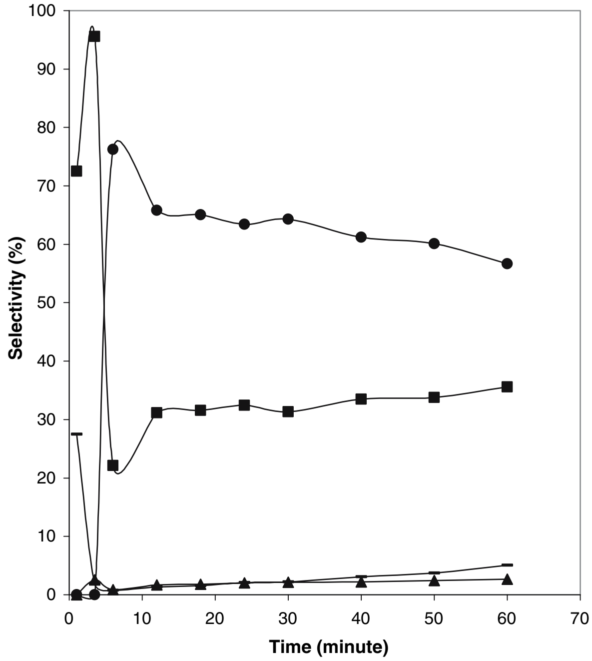

Fig. 5 Variation of the selectivity (%) with time on stream for HZSM-5-supported molybdenum catalyst; (■) Benzene (▲) Toluene (•) Naphthalene (–) Ethylene

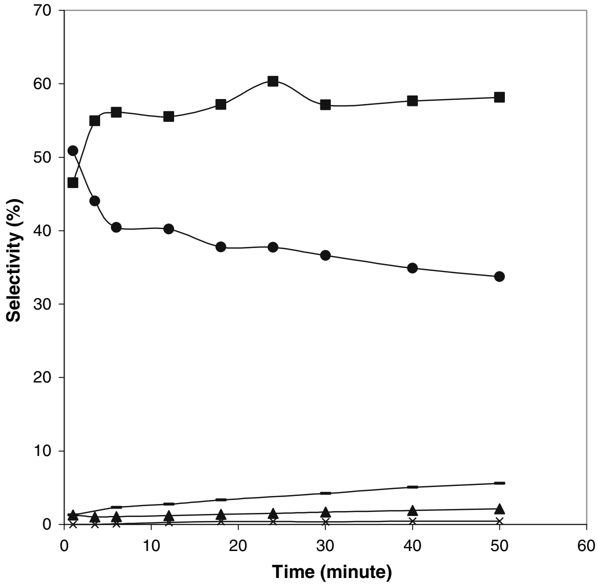

Fig. 6 Variation of the selectivity (%) with time on stream for HZSM-5-supported rhenium catalyst; (■) Benzene (▲) Toluene (•) Naphthalene (–) Ethylene (x) Acetylene

favoured ones. It is also admitted that the selectivity to naphthalene is primarily governed in the case of porous catalysts by the space limitation to the formation of this bulky molecule and or by the diffusion limitations to its escape once formed. This is why it was generally observed that naphthalene selectivity grew as a sequential product then receded because of decreasing effective pore diameter or decrease of available space needed to the formation of this bulky molecule due to increasing deposit of carbonaceous materials at the active sites or at the pore entrance.

Table 1 shows the selectivity values with time on stream for CaZSM-5-supported rhenium catalyst. The zero selectivity to naphthalene in the case of CaZSM-5 supported rhenium is an illustration of the above. As explained earlier, the anchoring of the perrhenate precursor to the zeolite internal exchange sites (see equation) makes it very probable that upon the mild reduction conditions used here most if not all rhenium particles are located at the internal cavities. The restricted available space by the very presence of metallic rhenium may not permit the formation of naphthalene. (Note that not even toluene, whose escape from the pores should not be of a problem was observed). By contrast, the impregnation of the HZSM-5 zeolite by the ammonium perrhenate and further activation may not provide for a similar anchoring of the rhenium precursor inside the internal porosity. Rather an external deposit should be obtained leading most probably to a preferential location of the rhenium particles at the external surface, providing space for naphthalene formation and easy escape, resulting in the observed high selectivity to this product (Fig. 6).

Similarly, the impregnation of CaZSM-5 by the ammonium molybdate precursor may barely lead, as is the case for HZSM-5, to the exchange of MoOx dimers, rather to the deposit of molybdenum species layers at the external surface. It is therefore expected that the selectivity to naphthalene should be quite higher than when Mo species are located at exchange sites. The selectivity values obtained for molybdenum catalysts supported on CaZSM-5 and HZSM-5, are reported in Figs. 4 and 5, respectively. The initial selectivity to naphthalene is indeed higher on CaZSM-5 than on HZSM-5 supported molybdenum. The fact that only the initial selectivity to benzene is higher than that to naphthalene in the case of the latter catalyst may be indicative in a preferential surface formation of the active molybdenum carbide species in spite of the initial internal location of the molybdenum precursor presumably due to the severe reduction procedure.

It is well known that the highly dispersed metal precursors favour highly dispersed metal particles, hence it is reasonable to expect that rhenium attached to the framework may result in higher dispersion. Although rhenium is expected to be highly dispersed in CaZSM-5, the limited acid function results in lower conversion values. The reaction seems to proceed according to the bifunctional mechanism in which H^+ acid sites of the inorganic carrier convert C_2's into benzene more easily and hence improve the catalytic performance. This result is in line with the report of Ha et al. [33] pointing to the possibility of acid site catalyzed cyclization and aromatization of ethylene/acetylene proceeding faster than the possible thermally occurring cylization reactions.

4 Conclusion

HZSM-5-supported molybdenum and rhenium catalysts are more active for the aromatization of methane compared to those supported on CaZSM-5. As evident from the formation of aromatics, the reaction also proceeds, but to a lower extent on CaMFI-supported molybdenum and rhenium catalysts, which were shown to have only residual acidity. Although highly dispersed rhenium is expected to form over CaZSM-5, lower conversion values obtained with CaZSM-5-supported rhenium catalyst in this study underline the importance of acid sites on the formation of aromatics, in line with the commonly accepted bifunctional mechanism.

Acknowledgment A. Sarıoğlan acknowledges the funding provided by TUBITAK MRC via the World Bank Program, which covered all his expenses during his stay at Institut de Recherches sur la Catalyse-France.

References

1. Koenig G (1982) D.O.S. 3 101 024
2. Onsager OT, Lodeng R, Soraker P, Anundskaas A, Helleborg B (1989) Catal Today 4:355
3. Otsuka K, Hatano MJ (1987) J Catal 108:252
4. Banares MA, Pawelee B, Fierro JLG (1992) Zeolites 12:882
5. Scurrell MS (1987) Appl Catal 34:109
6. Keller GE, Bhasin MM (1982) J Catal 73:9
7. Ito T, Lunsford JH (1982) Nature 314:9
8. Ito T, Wang JX, Lin CH, Lunsford JH (1985) J Am Chem Soc 107:5062
9. Wang L, Tao L, Xie M, Xu G, Huang J, Xu Y (1993) Catal Lett 21:35
10. Xu Y, Liu S, Wang L, Xie M, Guo X (1995) Catal Lett 30:135
11. Solymosi F, Erdohelyi A, Szoke A (1995) Catal Lett 32:43
12. Wang D, Lunsford JH, Rosynek MP (1996) Top Catal 3:289
13. Wang D, Lunsford JH, Rosynek MP (1997) J Catal 169:347
14. Solymosi F, Cserenyi J, Szoke A, Bansagi T, Oszko A (1997) J Catal 165:150
15. Weckhuysen BM, Wang D, Rosynek MP, Lunsford JH (1998) J Catal 175:338
16. Liu S, Dong Q, Ohnishi R, Ichikawa M (1998) Chem Commun 1217
17. Mériaudeau P, Tiep LV, Ha VTT, Naccache C, Szabo G (1999) J Mol Cat 144:469
18. Mériaudeau P, Ha VTT, Tiep LV (2000) Catal Lett 64:49

19. Liu S, Wang L, Ohnishi R, Ichikawa M (1999) J Catal 181:175
20. Borry RM, Kim HY, Huffsmith A, Reimer JA, Iglesia E (1999) J Phys Chem B 103:5787
21. Ding W, Meitzner GD, Iglesia E (2002) J Catal 206:14
22. Zhang W, Ma D, Han X, Liu X, Bao X, Guo X, Wang X (1999) J Catal 188:393
23. Ma D, Shu Y, Cheng M, Xu Y, Bao W (2000) J Catal 194:105
24. Ding W, Li S, Meitzner GD, Iglesia E (2001) J Phys Chem B 105:506
25. Wang L, Ohnishi R, Ichikawa M (1999) Catal Lett 62:29
26. Wang L, Ohnishi R, Ichikawa M (2000) J Catal 190:276
27. Lee JS, Oyama ST, Boudart M (1987) J Catal 106:125
28. Sarioglan A, Erdem-Senatalar A, Savasci OT, Ben Taarit Y (2004) J Catal 226:210
29. Shu Y, Xu Y, Wong ST, Wang L, Guo X (1997) J Catal 170:11
30. Borry RW III, Lu EC, Ho Kim Y, Iglesia E (1998) Stud Surf Sci Catal 119:403
31. Kim YH, Borry RW, Iglesia E (2000) Micropor Mesapor Mater 35–36:495
32. Sarioglan A, Erdem-Senatalar A, Savasci OT, Ben Taarit Y (2004) J Catal 228:114
33. Ha VTT, Tiep LV, Meriaudeau P, Naccache C (2002) J Mol Catal A: Chem 181 (1–2):283
34. Tang S, Chen Y, Lin J, Tan KL (2001) Catal Commun 2:31