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CrHZSM-5 zeolites – Highly efficient catalysts for catalytic cracking of isobutane to produce light olefins

Jiangyin Lu, Zhen Zhao,* Chunming Xu, Aijun Duan, and Pu Zhang

Faculty of Chemical Science and Engineering, State Key Laboratory of Heavy Oil Processing, China University of Petroleum,
18#, Fuxue Road, Chang Ping District, Beijing 102249, China

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The CrHZSM-5 catalysts with trace amount of Cr were firstly used for catalytic cracking of isobutane, and the effect of Cr-loading on the catalytic performances of CrHZSM-5 catalysts for the cracking of isobutane was also studied. The results suggested that when the loading of Cr in the CrHZSM-5 catalysts was less than 0.038 mmol/g Cr, especially at Cr loading of 0.004 mmol/g, both the reactivity of isobutane cracking and the selectivity to light olefins of CrHZSM-5 samples were greatly enhanced compared with the unpromoted HZSM-5, and very high yields of olefins(C_2+C_3) and ethylene were obtained. For instance, the yield of olefins(C_2+C_3) and ethylene reached 56.1% and 30.8%, respectively, at 625 °C when 0.004 mmol/g Cr was loaded on HZSM-5 sample.

KEY WORDS: CrHZSM-5 zeolite; catalytic cracking; isobutane; light olefins.

1. Introduction

At present, ethylene is primarily produced by steam cracking, and propylene is the main byproduct in this process, accounting for over 90% of total propylene output. The method of steam cracking for producing ethylene and propylene cannot satisfy a fast growing demand for them today. The new methods to produce propylene including the catalytic cracking of C4 olefins [1–2] or C4 alkanes feedstocks [3–6], Oxidative dehydrogenation of propane, and catalytic cracking of heavy oil are indispensable and significant to be studied and developed.

Nowadays, the turnout of C_4 fraction is about 150–200 million tons every year in the world. It is predicted that the C_4 fraction will be another valuable petrochemical material that could be well utilized after ethylene and propylene. C_4 fraction is mainly produced from catalytic cracking and steam pyrolysis. The utilization of C4 in chemical industry was mainly olefins, and C4 alkanes were primarily used as fuel. Isobutane was one of the main components of C4 alkanes which is often used for alkylation reaction to produce high octane number gasoline[7,8], and dehydrogenation to produce isobutene [9–11].

ZSM-5 zeolite has been extensively studied as the active catalyst for a variety of reactions owing to its reactivity and special pore structure [12–14]. Alfons *et al.* [3,4] reported the kinetic and product distribution pattern of isobutane pyrolysis. Ararwal *et al.* [15] investigated the catalytic cracking of isobutane and methylcyclohextane over USY zeolite, and discriminated reaction steps with kinetic significance, introduced model parameter, and undertook interrelated kinetic calculation. Sun *et al.* [16] reported the isobutane catalytic cracking over HZSM-5 under low pressure and dehydrogenation kinetics.

In this paper, isobutane was used as feedstock to investigate its catalytic cracking property over CrHZSM-5 to produce light olefins. Very high reactivity and selectivity for catalytic cracking of isobutane was obtained over CrHZSM-5 catalysts with trace amount of Cr. For example, the yields of olefins(C_2+C_3) and ethylene reached 56.1% and 30.8%, respectively, at 625 °C.

2. Experimental

The HZSM-5 zeolite was manufactured by Qi Lu Petrochemical Corporation Catalysts factory (Si:Al mole rate = 32). The zeolite was impregnated by certain concentration $Cr(NO_3)_3 \cdot 9H_2O$ solution with an incipient-wetness impregnation method. The loading amounts of Cr were 0.00, 0.004, 0.010, 0.019, 0.038, 0.077, 0.154 and 0.231 mmol/g, respectively. The impregnation period lasted for half an hour at the temperature range of 30–40°C and then dried at 120 °C and finally calcined at 700 °C in air atmosphere for 4 h. After finishing the preparation of this series of catalysts, they were marked as 0#, 1#, 2#, 3#, 4#, 5#, 6# and 7# according to the different concentrations of Cr correspondingly.

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*To whom correspondence should be addressed.
E-mail: zhenzhao@cup.edu.cn

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In a fixed-bed flow reactor the catalytic reaction was carried out by passing a gaseous isobutane (2 mL min^{-1}, 99.9%) in a N_2 flow at a total flow rate 40 mL min^{-1} over 200 mg catalyst (total pressure: 1 atm). The products were analyzed on-line using a gas chromatograph (SP3420) equipped with a 50 m PONA capillary column and FID detector [5].

Acidic amounts of the zeolite were measured by NH_3–TPD (Temperature-programmed desorption of ammonia) method. 0.2 g samples with the sizes of 40–80 mesh were pretreated at 500 °C for 2 h, cooled to 120 °C and adsorbed NH_3 for 30 min, then temperature-programmed desorption started at a rate of 15 °C/min from 120 to 800 °C. The signal was monitored with a TCD detector. In order to obtain the total acid amount, the desorbed ammonia was absorbed by HCl solution (0.01 mol/L) and then titrated by NaOH solution (0.01 mol/L), finally the acidic amount and density of the zeolite were calculated. According to the temperature of the desorption peak and the relative intensity of acid sites of the samples was analyzed, and the acid amount of the acid sites with different intensities by peak areas were calculated.

UV–Vis absorption spectra of the samples were measured with a spectrophotometer (Hitachi U-4100) equipped with the integration sphere diffuse reflectance attachment.

3. Results and discussion

The effect of loading amount of Cr(III) on the reactivity and selectivity of CrHZSM-5 catalysts for the cracking of isobutane are shown in table 1.

The results in table 1 indicate that the reactivity of the catalysts for catalytic cracking changed obviously with the loading amount of Cr(III). For the CrHZSM-5 samples with the loading amount of Cr (III) below 0.038 mmol/g Cr, the reactivities of CrHZSM-5 samples were higher than that of 0#, HZSM-5 sample. The highest catalytic cracking reactivity was obtained over 1# sample, and the reactivity of catalytic cracking slowly decreased with the further increasing of Cr-loading amount. In the same temperature range, the loading amount of Cr had also large effect on the selectivity of the product. The selectivity to aromatic hydrocarbon and butene smoothly increased with rising the loading amount of Cr(III), while the selectivity to methane, ethylene, propane and olefins(C_2+C_3) slowly decreased with the increasing loading amount of Cr(III).

The product yields of ethylene, proylene and olefins(C_2+C_3) in the catalytic cracking isobutane over CrHZSM-5 catalysts are shown in figure 1.

It can be seen from figure 1 that the yields of ethylene and olefins(C_2+C_3) over 1#$\sim$4#CrHZSM-5 samples were apparently higher than those of 0#, the unmodified HZSM-5 sample, which were all more than 24.9% and 51.8% at 625 °C, respectively. Especially at 625 °C, over 1# CrHZSM-5 samples, the yields of olefins(C_2+C_3) and ethylene could reach 56.1%, 30.8%, respectively, which were much higher than those of 0#, HZSM-5 sample.

Compared with unmodified HZSM-5 zeolite, the olefins of propylene and ethylene of 1#$\sim$4# could keep high yields at the temperatures of 600 and 625 °C, and the yield of butene obviously decreased. These results demonstrate that a small amount of Cr played an important role of modification, not only did it enhance

Table 1
The reactivity and the selectivity (%) of CrHZSM-5 for the cracking of isobutane to produce light olefins

Catalysts	Temperature (°C)	Conversion (%)	Selectivity (%)							
			Methane	Ethane	Propane	Ethylene	Propylene	Butene	Arene	Olefins(C_2+C_3)
0#	600	93.4	13.4	0.4	2.7	19.5	30.6	12.7	10.1	50.1
White	625	98.8	12.8	0.4	2.2	21.6	25.4	9.2	14.7	47.0
1#	600	97.0	15.0	0.8	3.5	27.1	29.3	7.6	14.3	56.4
White	625	99.7	15.4	1.0	2.9	30.9	25.4	4.7	19.2	56.3
2#	600	96.5	14.5	0.9	3.3	25.0	28.5	7.7	14.0	53.5
White	625	99.6	15.2	1.1	2.5	28.2	24.9	4.7	20.0	53.1
3#	600	96.5	14.0	1.0	3.2	24.3	28.6	8.1	16.8	52.9
Lightyellow	625	99.6	14.7	1.3	2.4	27.4	24.8	4.8	21.6	52.2
4#	600	94.0	13.4	1.1	2.8	22.1	30.3	9.7	15.1	52.4
Light green	625	98.9	14.1	1.4	2.3	25.2	27.2	6.6	20.3	52.4
5#	600	92.4	13.7	1.4	2.5	20.4	29.3	10.4	18.4	49.7
Light green	625	98.0	14.2	1.7	2.2	22.6	26.0	7.1	23.4	48.6
6#	600	93.3	14.0	1.3	2.3	20.3	29.1	10.2	18.1	49.4
Green	625	98.4	14.7	1.5	1.8	22.9	26.3	7.0	23.1	49.2
7#	600	94.3	13.1	1.1	2.3	19.7	27.6	9.6	17.3	47.3
Green	625	98.7	13.6	1.3	1.8	22.4	25.0	6.5	24.5	47.4

Note: The butene was mainly i-butene, 2-butene (including *trans*-butene and *sis*-butene), the arene included benzene and toluene, the selectivity of olefins included ethylene and propylene without butene and dibutene.

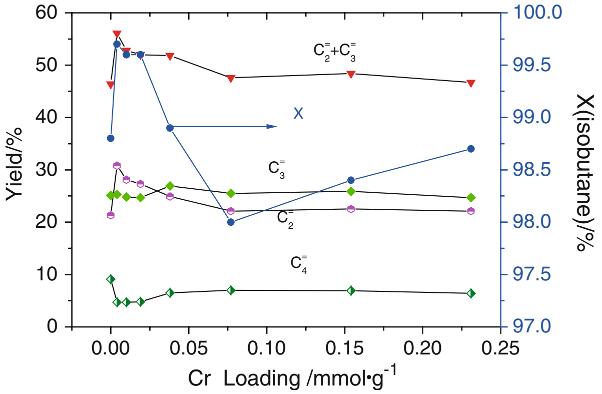

Figure 1. The olefin yields in catalytic cracking isobutane over CrHZSM-5(at 625 °C).

the reactivity for the catalytic cracking of isobutane, but also increased the selectivity of olefins, especially the selectivities to ethylene.

In order to study the nature of catalytic cracking of isobutane over CrHZSM-5 zeolite samples and exclude the effect of pyrolysis of isobutane, a comparative study of isobutane pyrolysis was also made. The product yield of isobutane pyrolysis as a function of reaction temperature is showed in figure 2.

It can be seen from figure 2 that isobutane did not undertake pyrolysis below 575 °C. When the temperature was at 625 °C, the conversion of isobutane was about 2%. It demonstrates that although obvious pyrolysis could occur at 625 °C, the catalytic cracking is still major reaction. Besides ethylene, propylene, butene, dibutene and a small amount of ethane, methane are the main products of the pyrolysis reaction. At 850 °C (conversion nearly 100%), the yield of methane could reach 30.2%.

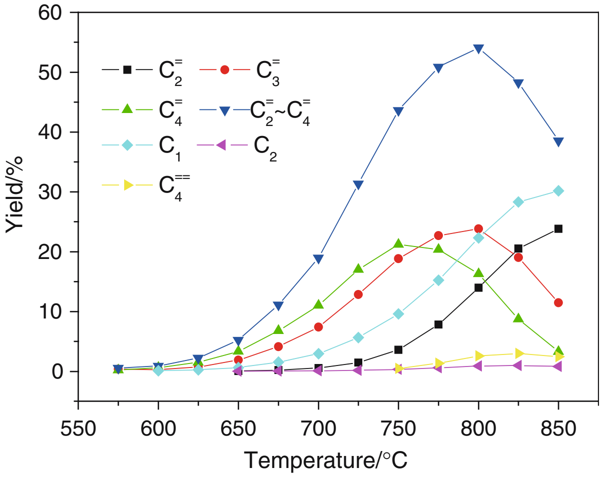

Figure 2. Product yield of isobutane pyrolysis as a function of reaction temperature.

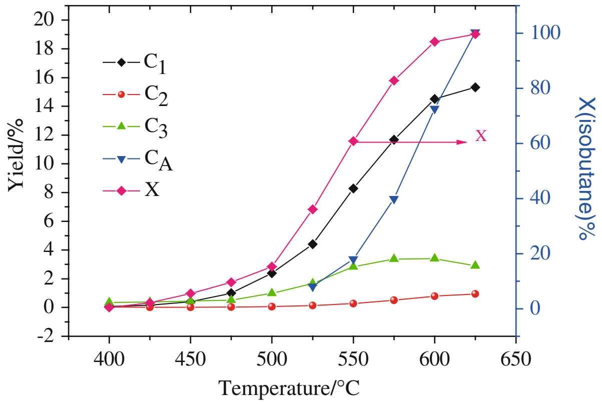

Figure 3. The yields of alkanes and aromatic hydrocarbon over 1#CrHZSM-5 catalyst as a function of reaction temperature.

In addition, a small amount of alkyne, complex olefin, coke and carbon deposition could be formed, these products were all the results of dehydrogenation and cracking of isobutene at high temperatures.

As 1#CrHZSM-5 sample gave good reactivity and high light olefins yields, it was chosen to investigate the effect of reaction temperature on the catalytic performance for catalytic cracking of isobutane.

The reaction started from 400 °C and followed temperature-programmed heating at a rate of 3 °C/min to study the isobutane catalytic cracking reaction over CrHZSM-5 molecular sieve. The effects of reaction temperature on the yields of alkanes including aromatic hydrocarbon and olefins are shown in figures 3 and 4.

From figure 3 the yields of methane and aromatic hydrocarbon dramatically increased when temperature rose from 500 to 550 °C, while the yield of propane increased slowly and that of ethane remained very low. At 625 °C, the yield of aromatic hydrocarbon was 19.2%, methane was 15.3%, propane and ethane were 2.9% and 1.0%, respectively.

It can be seen from figure 4 that the yields of olefins($C_2 + C_3$), and propylene rapidly increased with the increasing of reaction temperature. They reached the maximum value of 56.1% at 625 °C and 28.4% at 600 °C, respectively. The yield of ethylene was 30.8% at 625 °C and the maximum value of the yield of butene was 8.8% at 575 °C.

The isobutane mainly undertook catalytic cracking rather than pyrolysis (see figure 2) when the reaction temperatures were lower than 575 °C. Therefore, the cracking of isobutane over 1# CrHZSM-5 catalyst at the temperature below 575 °C could be classified into catalytic cracking reaction. When the reaction temperatures were higher than 575 °C, the catalytic cracking and pyrolysis reactions coexist, and the higher the temperature is, the higher extent of pyrolysis is. It can also be observed that the yields of methane, ethylene and aromatic hydrocarbon increased with the rising of reaction temperature, while the yields of propane, propylene and

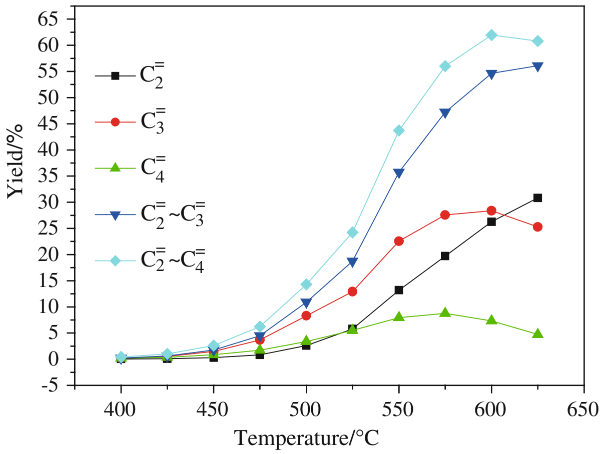

Figure 4. The yields of olefins over 1#CrHZSM-5 catalyst as a function of reaction temperature.

butene increased at first and then decreased, and they reached the maximum value at about 600 °C.

It is well known that the acidity of the catalysts plays an important role in the catalytic cracking of hydrocarbon. The effect of Cr addition on the acidity of HZSM-5 catalysts was evaluated by means of NH_3–TPD (Table 2). The results, as shown in figure 5, indicate that the acidic amount of the catalysts firstly increased quickly and then slowly increased with increasing of loading amount of Cr(III). In the meantime, the strength of strong acid of 1# ~ 4# CrHZSM-5 samples obviously reduced. The weak acidic amount of 1# ~ 4# CrHZSM-5 samples are evidently increased compared with that of 0#, which maybe related to its high reactivity and high selectivity. It is obvious that suitable acidic amount and density are favorable high reactivity and high yield of CrHZSM-5 samples.

Figure 6. show UV–Vis spectra of calcined CrHZSM-5 catalysts. It was found previously [17–19] that there may be three species inside calcined CrHZSM-5 catalysts: framework Cr(III), extraframework Cr(III), and extraframework Cr(VI).

The spectra of calcined CrHZSM-5 catalysts are dominated by two intense bands around 259 and 350 nm. These bands are usually assigned as $O^{2-} \rightarrow$ Cr(VI) charge transfers of a monochromate species [18–20]. This kind of loaded Cr(VI) dispersed on the HZSM-5 zeolite surface. The molecular structure of the anchored Cr(VI) from monochromate to dichromate or to polychromate have been proposed. Chromium(VI) oxide compounds prefer tetrahedral coordination both in aqueous solution and in a crystalline lattice [21]. A band around 450 nm which is the characteristic of Cr(VI) polychromate is not observed [20] for the samples with Cr loading of 0.004 mmol/g. These results indicate that Cr(VI) monochromate($CrO_4{}^{2-}$) predominates on the HZSM-5 samples with trace amount of Cr.

With the increasing of Cr loading on the HZSM-5 zeolites, besides the two absorption bands at 259 and 350 nm, a shoulder absorption band at around 460 nm appeared [22], and its intensity increased with the further increasing in Cr loading and a complete absorption band at 460 nm was observed when Cr-loading is equal to or greater that 0.154 mmol/g. There results indicate that polymeric chromate formed in the samples with high-loading of Cr. At same time, a very weak absorption band centered at around 600 nm, which has been assigned to d–d transitions of Cr(III) [20] was observed when Cr-loading is equal to 0.019 mmol/g, and its intensity increased with the further rising of Cr-loading. These results suggest that some amounts of Cr(III) existed on the samples in which the Cr-loading amount is equal to or greater than 0.019 mmol/g. Moreover, with the increasing of Cr-loading amount, absorption edge from 450 to 550 nm and 600 to 800 nm shifted to longer wavelength demonstrating that the domain size of CrHZSM-5 catalysts become longer with the increasing of Cr-loadings.

We conclude that Cr(VI) always predominates in calcined CrHZSM-5 catalysts. Comparing with high Cr(III) concentration loaded, low concentration of Cr(III) is almost oxidized to Cr(VI) after calcinations, which is impossible to obtain Cr(VI) by calcinations of common

Table 2
NH_3–TPD results of CrHZSM-5 catalysts with different Cr(III) loadings

Catalyst	BET (m^2/g)	Peak1		Peak 2		Acid amount (mmol/g)	Acid density (μ mol/m^2)
		Temperature (°C)	Weak acid amount	Temperature (°C)	Strong acid amount		
0#	318.0	277.8	0.113	519.7	0.362	0.475	1.494
1#	331.1	276.8	0.163	517.6	0.382	0.545	1.646
2#	327.6	282.6	0.172	506.1	0.419	0.591	1.804
3#	306.4	283.1	0.169	509.3	0.428	0.597	1.948
4#	291.0	284.8	0.196	512.0	0.443	0.639	2.196
5#	316.8	278.6	0.225	516.1	0.462	0.687	2.169
6#	297.4	302.4	0.216	531.8	0.429	0.645	2.169
7#	295.2	296.6	0.201	509.6	0.414	0.615	2.083

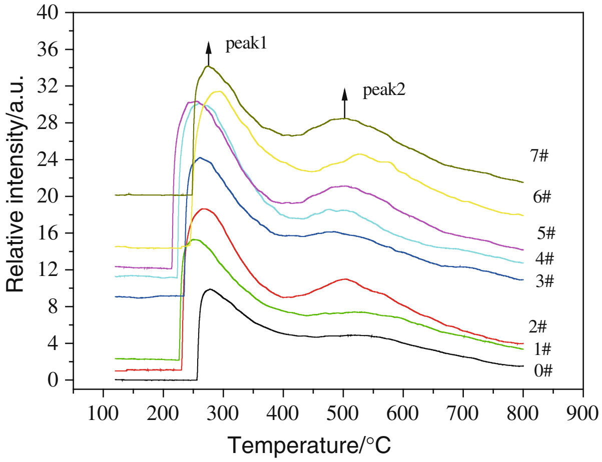

Figure 5. NH$_3$–TPD profile of CrHZSM-5 catalysts.

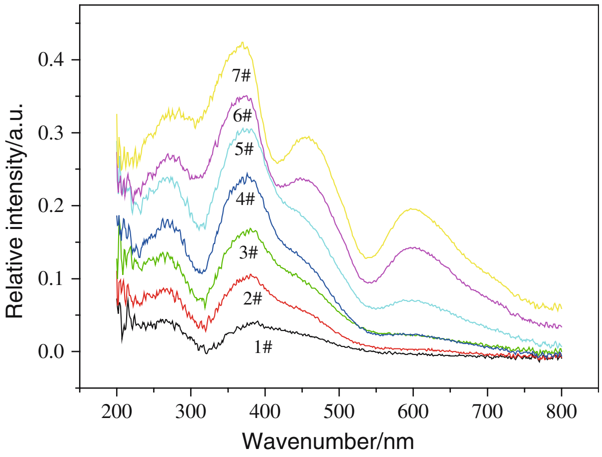

Figure 6. UV–Vis spectra of CrHZSM-5 catalysts.

chromium(III) salts [23]. It is postulated that Cr is uniform, isolated and well dispersed in calcined CrHZSM-5 catalysts. In 1# ∼ 4# and, especially, 1# ∼ 2# samples, the majority species of Cr in catalysts were uniform, isolated and well dispersed, and almost oxidized to Cr(VI) after calcinations.

One conceivable function of a trace amount of Cr is the changing of the acidity of the HZSM-5 catalysts because the suitable strength and amounts of acidity of the catalysts are favorable for getting high selectivity to the light olefins in the catalytic cracking of isobutene. Another reason is that the presence of a small amount of Cr may be favorable for the dehydrogenation of isobutane to isobutene which are easily to be further cracked to light olefins. Therefore, the conversion of isobutane over CrHZSM-5 was enhanced compared with that of unpromoted one, HZSM-5. When the loading amount of Cr was more than 0.038 mmol/g, the reactivity of catalytic cracking of CrHZSM-5 catalysts decreased, which might be due to the existence of a marjory of Cr(III), and Cr(III) with large domain size, which can cover the outer surface of the zeolite catalysts, or combined with acid sites. The further studies are needed to deduce the exact functions of trace amount of Cr for isobutane catalytic cracking.

4. Conclusions

Compared with unmodified HZSM-5 catalysts, the CrHZSM-5 catalyst with trace amount(0.004–0.038 mmol/g) of Cr played an important role in promoting the catalytic performance for cracking of isobutane. Not only did it enhance the reactivity of isobutane catalytic cracking, for instane, 1#CrHZSM-5 catalyst could lower down the cracking temperature of isobutane by 200 °C compared with pyrolysis, but also increased the selectivities to olefins and ethylene. At 625 °C, the very high yield of olefins($C_2 + C_3$) and the high yields of ethylene were 56.1% and 30.8%, respectively.

One reason is that a trace amount of Cr alters the acidity of the HZSM-5 catalysts. The suitable strength and amounts of acidity of the catalysts are favorable for obtaining high selectivity to the light olefins in the catalytic cracking of isobutene. Another reason is that the presence of a little amount of Cr maybe favorable for the dehydrogenation of isobutane to isobutene which are easier than isobutane to be cracked to light olefins.

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References

[1] G.L. Zhao, J.W. Teng, W.Q. Jin, W.M. Yang, Z.K. Xie and Q.L. Chen, Chin. J. Catal. 25 (2004) 3.
[2] G.L. Zhao, J.W. Teng, W.Q. Jin, W.M. Yang, Z.K. Xie and Q.L. Chen, Chin. J. Catal. 24 (2003) 119.
[3] B. Alfons, G. Buekens and G.F. Froment, Ind. Eng. Chem. Process. Des. Develop. 10 (1971) 309.
[4] K.M. Sundaram and G.F. Froment, Ind. Eng. Chem. Fundam. 17 (1978) 174.
[5] J.Y. Lu, Z. Zhao, C.M. Xu and P. Zhang, Petro. Sci. 1 (2005) 52.
[6] D. Ji, B. Wang, G. Qian, Q. Gao, G. Lu, L. Yan and J.S. Suo, Catal. Comm. 6 (2005) 297.
[7] T. Rorvik, H.B. Mostad, A. Karlsson and O.H. Ellestad, Appl. Catal. A Gen. 156 (1997) 267.
[8] A. Feller, I. Zuazo, A. Guzman, J.O. Barth and J.A. Lercher, J. Catal. 216 (2003) 313.
[9] R.D. Cortright and J.A. Dumesic, J Catal. 157 (1995) 576.
[10] H. Shimada, T. Akazawa, N. Ikenaga and T. Suzuki, Appl. Catal. A General 168 (1998) 243.

[11] S.M. Al-Zanhrani, N.O. Elbashir, A.E. Abasaeed and M. Abdulwashed, Ind. Eng. Chem. Res. 40 (2001) 781.

[12] N.Y. Chen and W.E. Garwood, Catal. Rev. Sci. Eng. 28 (1986) 185.

[13] M. Gabriele and A.L. Johannes, J. Catal. 139 (1993) 24.

[14] N.R. Meshram, S.G. Hegde and S.B. Kulkarni, Zeolites 6 (1986) 434.

[15] N. Ararwal, A. Marco, S. Castillo, R.D. Cortright, R.J. Madon and J.A. Dumesic, Ind. Eng. Chem. Res. 41 (2002) 4016.

[16] Y.P. Sun and T.C. Brown, J Catal. 194 (2000) 301.

[17] L. Davydov, E. P. Reddy, P. France and P. G. Smirniotis, J. Catal. 203 (2001) 157.

[18] N. Ulagappan and C.N.R. Rao, Chem. Commun. 9 (1996) 1047.

[19] Z.D. Zhu, Z.X. Chang and L. Kevan, J. Phys. Chem. B 103 (1999) 2680.

[20] B.M. Weckhuysen, I.E. Wachs and R. Schoonheydt, Chem. Rev. 96 (1996) 3327.

[21] M.A. Vuurman and I.E. Wachs, J. Phy.Chem. 96 (1992) 5008.

[22] P. McCarthy, J. Lauffenburger, P. Skonezny and D. Rohrer, Inorg. Chem. 20 (1981) 1566.

[23] M. Maciejewski, K. Köhler, H. Schneider and A. Baiker, J. Solid State Chem. 119 (1995) 13.