

## Remarkable Improvement of Catalytic Performance in Dimethyl Ether to Olefin Reaction over CeO<sub>2</sub>-modified Calcium-containing MFI Type Zeolite

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(Received January 30, 2008; CL-080109; E-mail: ysugi@gifu-u.ac.jp)

Dimethyl ether to olefin (DTO) reaction was examined over CeO<sub>2</sub>-modified Ca-MFI as a catalyst. The CeO<sub>2</sub>-modified Ca-MFI (Ce/Ca-MFI) showed excellent catalytic performance to give propene as a main product. Activity was 28 times higher than conventional MFI type zeolite and seven times higher than Ca-MFI.

The transformation of methanol to gasoline (MTG) or olefins (MTO) has been a pivotal chemical process in the petrochemical industry since Mobil firstly reported the methanol to hydrocarbon process over MFI type zeolite as catalyst.<sup>1</sup> Light olefins such as ethene, propene, and butene are utilized as raw materials that can be applied for a broad range of chemical production. Many researchers, not only academic but also industrial, have also made attempts towards a methanol to light olefin process to enable more practical technology. Chang et al. have reported that modified MFI type zeolite offers high selectivity of light olefins and high conversion and claimed that zeolite catalysts with small pores would be promising candidates to obtain C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> olefins as main products.<sup>2</sup>

Although MFI type zeolite is a high potential catalyst in the MTO process, a drawback has been deactivation by severe coke deposition. Okado et al. reported that calcium (Ca<sup>2+</sup>)-containing MFI type zeolite showed the good catalytic activity and lifetime in the MTO process as due to an effective decrease of acidity by calcium ion.<sup>3</sup> Recently, another approach based on dimethyl ether (DME) has also been proposed.<sup>4,5</sup> DME to olefin (DTO) process has been demonstrated by conventional zeolites such as MFI and calcium-containing MFI catalysts. They generally give propene as a principal product in 40 to 50% yield although formation of ethene and butenes also occurs. Their advantages are long lifetimes due to the less coke-accumulation compared with MTO processes. Improvement of catalyst life of Ca-MFI has demonstrated by modification with alkaline earth metal carbonate.<sup>6</sup> Thus, development of DTO reactions, in particular, development of catalysts showing excellent performance is as emerging topic in petroleum industrial chemistry.

Recently, we reported an effective improvement of shape-selectivity in the ethylation of ethylbenzene over MFI type zeolite and found that rare earth metal oxide-modified MFI shows good para-selectivity due to suitable pore adjustment and deactivation of external acid sites.<sup>7</sup> These results encouraged us to apply rare earth metal oxide-modified MFI type zeolite to DTO reactions. Here, we report a remarkable improvement of catalytic performance in the DTO reaction over CeO<sub>2</sub>-modified Ca-MFI type zeolite.

The Ca-MFI (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 200, CaO/SiO<sub>2</sub> = 0.025) was prepared by conventional hydrothermal synthesis,<sup>9</sup> followed by ion exchange to form H-type using a 0.6 M aqueous HCl solution and then calcination at 500 °C for 6 h. The resulting

solid of Ca-MFI was impregnated by a EtOH solution containing a prescribed amount of Ce(NO<sub>3</sub>)<sub>3</sub> at room temperature. After evaporation of EtOH, the resulting solid was recalcined at 550 °C for 10 h to give CeO<sub>2</sub>-modified Ca-MFI. DTO reaction was carried out in a fixed-bed flow reactor at 530 °C under atmospheric pressure of N<sub>2</sub> (Details are given in Supporting Information<sup>9</sup>). The flow rates of DME and N<sub>2</sub> were equal to 21.2 cm<sup>3</sup> min<sup>-1</sup>. The space velocity (WHSV; weight of installed DME per hour and per weight of catalyst) was 9.52 h<sup>-1</sup> (amount of Ca-MFI was 0.275 g). Reaction products were analyzed by on-line gas chromatography using a HP-5890 apparatus to determine the conversion of DME and yields of olefins.

CeO<sub>2</sub>-modified Ca-MFI in this report is expressed as Ce(*x*)/Ca-MFI, where *x* is the amount of CeO<sub>2</sub> (wt %). In order to compare catalytic activity in the DTO reaction, we defined and used the index, (total grams of consumed DME)/(amount of used zeolite based on Ca-MFI) (g of DME/g of Ca-MFI), as catalytic activity.

Figure 1 shows the results of a DTO reaction over CeO<sub>2</sub>-modified Ca-MFI. Typical MFI showed low activity (160); however, Ca-MFI showed higher activity (610). This indicates that Ca-MFI shows good catalytic performance in DTO reaction, owing to the decrease of acidity by calcium cation.<sup>3</sup> It was surprising that Ce(35)/Ca-MFI exhibited excellent catalytic performance. The consumed amount of DME per Ca-MFI reached about 4500, which was over seven times more active than conventional Ca-MFI zeolite. However, CeO<sub>2</sub>-modified MFI catalyst gave results similar to Ca-MFI; further, bulk CeO<sub>2</sub> did not exhibit catalysis. These results suggest that both the existence of Ca<sup>2+</sup> in MFI zeolite and the modification by CeO<sub>2</sub> seems to be quite essential in order to achieve excellent catalytic performance in DTO reaction.

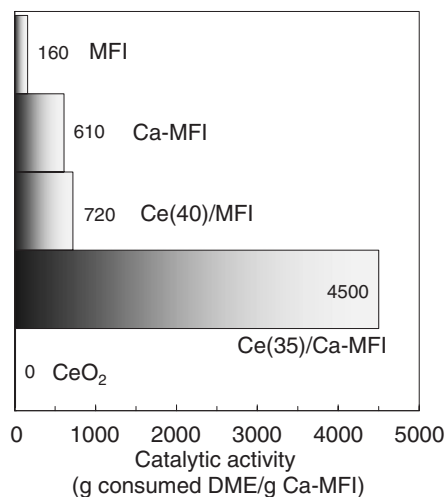
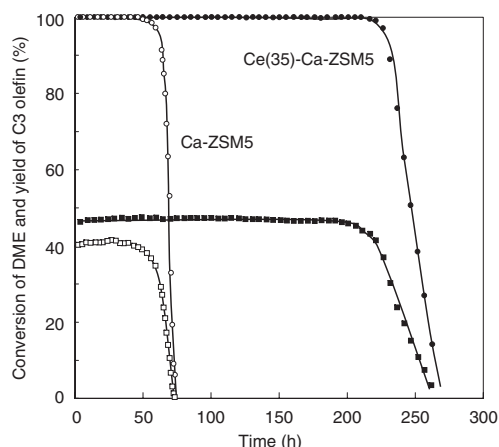


Figure 1. DTO reaction over Ce/Ca-MFI zeolite.



**Figure 2.** TOS in DTO reaction over Ca-MFI and Ce(35)/Ca-MFI zeolite. Conversion of DME: ● for Ce(35)/Ca-MFI and ○ for Ca-MFI, propene (C3 olefin) yield: ■ for Ce(35)/Ca-MFI and □ for Ca-MFI.

Basic metal oxides often catalyze reformation of methanol to give CO<sub>2</sub>, CO, and H<sub>2</sub> gases;<sup>8</sup> however, we could not detect such gases in DTO reaction over Ce(35)/Ca-MFI catalyst. This result indicates that the DTO reaction over CeO<sub>2</sub>-modified Ca-MFI proceeds without any side reactions.

We then examined the effects of loading amount of CeO<sub>2</sub> in the DTO reaction over Ce(*x*)/Ca-MFI (*x* = 0 to 50) (see Figure S3 in Supporting Information).<sup>9</sup> Increased loading of CeO<sub>2</sub> in Ca-MFI showed gradual improvement in activity: 880 (*x* = 10), 1430 (*x* = 20), and 1580 (*x* = 30), the maximum activity can be observed at 35 wt% loading of CeO<sub>2</sub>. However, under high loading of CeO<sub>2</sub>, the Ce(40)/MFI and Ce(50)/Ca-MFI activity declined to 2950 and 1430, respectively. These results show that the catalytic activity depends on the loading amount and that an appropriate amount of CeO<sub>2</sub> triggered excellent catalytic activity.

Figure 2 shows the results of time-on-stream (TOS) over Ca-MFI and Ce(35)/Ca-MFI, respectively. The distribution of products (ethene, propene, and butenes) over Ce(35)/Ca-MFI is similar to that of Ca-MFI (only yield of C3 olefin in Figure 2). The complete conversion of DME over Ca-MFI took about 40 h, and then the activity was gradually decreased and completely lost at 90 h. The yield of propene also declined with decreasing conversion of DME. In contrast, the Ce(35)/Ca-MFI proved to keep catalytic activity over 200 h (>99% conversion of DME) to give propene in 45% yield as a main product. It is obvious that Ce(35)/Ca-MFI shows excellent catalytic performance in DTO reaction.

We note that the DTO reaction over CeO<sub>2</sub>-modified Ca-MFI has a similar reaction path as over Ca-MFI, because the distribution of produced olefins such as ethene, propene, and butenes is not significantly different from that of Ca-MFI, and CeO<sub>2</sub> onto the zeolite did not affect the catalysis.

In order to clarify why CeO<sub>2</sub>-modified Ca-MFI shows high performance in DTO reactions, N<sub>2</sub> adsorption and NH<sub>3</sub>-TPD analyses were undertaken (Table 1). Modification by CeO<sub>2</sub> reduces the surface area; especially, Ce(40)/MFI showed remarkably decreased surface area compared to that of Ce(35)/

**Table 1.** Properties of CeO<sub>2</sub>-modified MFI catalysts

Zeolite	Surface area /m <sup>2</sup> g <sup>-1</sup>	Pore volume /mm <sup>3</sup> g <sup>-1</sup>	Acid amount /mmol g <sup>-1</sup>	<i>h</i> -Peak /°C
Ca-MFI	350	87	0.117	307
Ce(40)/MFI	175	75	0.052	283
Ce(35)/Ca-MFI	228	114	0.024	307

Ca-MFI. Enhancement of pore volume in CeO<sub>2</sub>-modified Ca-MFI was observed, because the CeO<sub>2</sub> effectively covers only the external surface of zeolite, resulting in deactivation of the external acid site without choking.<sup>6</sup> The significant decrease in acid amount was observed in Ce(35)/Ca-MFI; however, the acid strength corresponding to *h*-peak temperature remained the same as Ca-MFI. In contrast, considerable decrease in *h*-peak temperature was observed in Ce(40)/MFI. These results mean that Ce(35)/Ca-MFI has a strong acid site similar to Ca-MFI, although a smaller amount of acid sites: appropriate adjustment of the acidity of Ca-MFI could be done by modification with CeO<sub>2</sub>. However, further research is necessary to clarify what is responsible for such high catalytic performance by CeO<sub>2</sub> modification.

In conclusion, CeO<sub>2</sub>-modified Ca-MFI showed excellent catalytic performance in the DTO reaction to afford propene in 45% yield with extremely long catalytic life compared with those of conventional Ca-MFI and typical MFI catalyst. Appropriate deactivation of acid sites both at the external surface of zeolite by CeO<sub>2</sub> and in the pore by Ca cation seem to synergistically enhance the catalytic performance in DTO reaction.

Further investigations are now ongoing, and we will report elsewhere in a near future.

## References and Notes

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