Effect of acidity of Ferrierite synthesized with different amount of seeding material for DME carbonylation to methyl acetate

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Carbonylation dimethyl ether (DME) has been studied to produce methyl acetate (MA), which is useful chemical intermediates for the production of renewable ethanol fuel through hydrogenation or for acetic acid (AA) by hydration [1,2]. Solid acid zeolites have been largely investigated for selective DME carbonylation to MA for the production of AA to develop an alternative method of methanol carbonylation in a commercial liquid-phase reaction [3]. Mordenite (MOR) and Ferrierite (FER) with 8 membered ring channels between different sizes of zeolite have been recently reported for DME carbonylation reaction [4].

From our previous study [5], Lab-made FER zeolite showed a remarkable activity in DME carbonylation reaction to MA. For a comparative study, FER was synthesized by using seeding material of the previously lab-made FER to reduce a synthetic period and to increase the crystallinity and acidity as well. A lab-made FER (Si/Al ratio of 10.4) was denoted as a pristine FER with 0 % seed, and the FER was synthesized with different amount of seeding material of FER(10.4) from 0 to 19 wt%, and the synthesized FER(x) with seed was denoted with its content(x). FER prepared with seed showed a decreased total amount of acid sites compared with pristine FER measured by NH_3-TPD and Py-IR, while the ratio of Bronsted/Lewis acid sites was maximized on FER(7), which showed a higher DME conversion of 40.5%.

As summarized in **Table 1**, FER(7) showed a higher DME conversion and relatively faster deactivation due to the increased amount of coke deposition possibly. A smaller grain size of FER with an optimal amount of seeding material as shown in **Figure 1** seems to be responsible for a higher content of Bronsted acid sites, where Bronsted acid sites can be most active sites for DME carbonylation [4,5].

Consequently, FER zeolite having a larger Bronsted acid site with a higher crystallinity can be synthesized with a proper amount of seeding material, which is responsible for a higher DME conversion and MA selectivity.

Table. 1 Reaction results and acidity analysis of FER(x) catalysts, where x represent the amount of seeding material

Seed (wt%), FER(x)	DME Conv. (%)	MA Select. (%)	NH_3-TPD (mmol NH_3/g)		Pyridine-IR (mmol/g)		
			Weak	Strong	B/L ratio	Bronsted	Lewis
0	16.3	97.0	0.87	0.59	40.5	1.42	0.04
7	40.5	98.6	0.80	0.83	92.4	1.61	0.02
14	38.8	99.1	0.69	0.61	48.4	1.27	0.03
19	34.8	99.2	0.61	0.57	47.2	1.16	0.02

Reaction conditions: T = 220 °C, P = 1.0 MPa, space velocity = 2000 L/(kg_{cat}·h) and CO/DME molar ratio of 9.

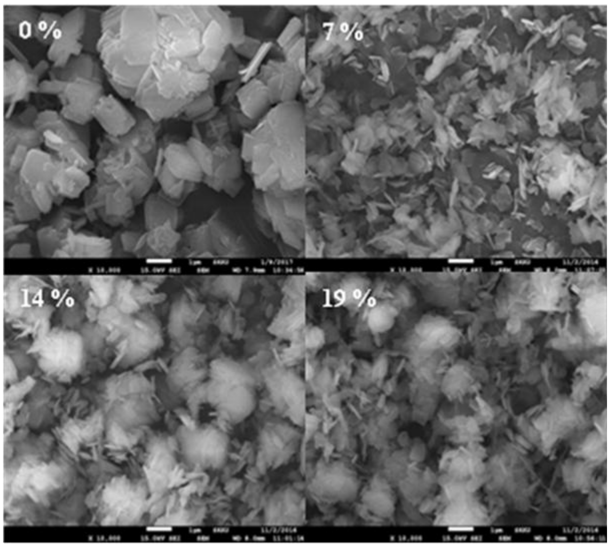

Fig. 1 SEM images of FER-Seed catalysts

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