Supporting Information

Fixation of carbon dioxide into dimethyl carbonate over titanium-based zeolitic thiophene-benzimidazolate framework

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Synthesis of 2-(thophen-2-yl)-1-((thiophen-2-yl)methyl)-1*H*-benzo[*d*]imidazole

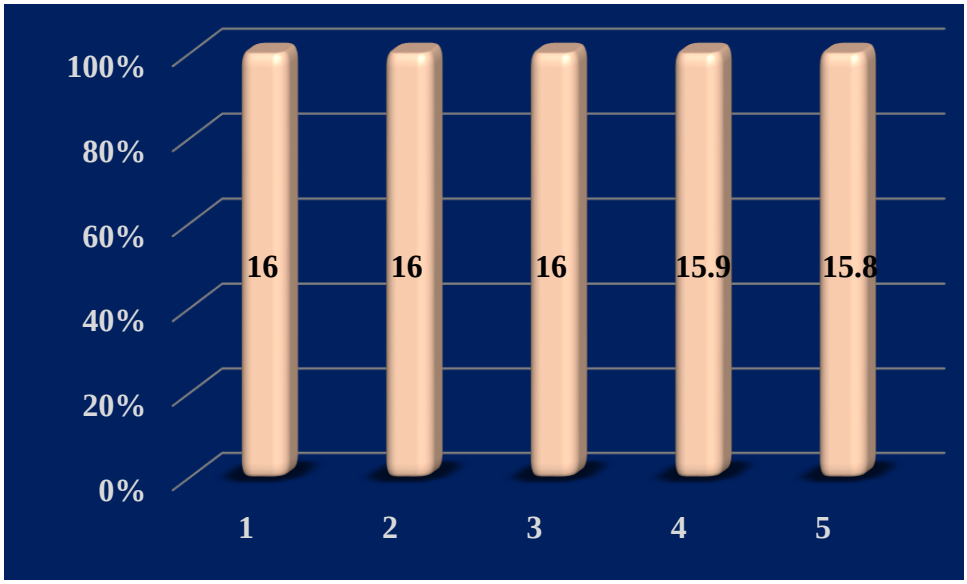
To a mixture of *o*-phenylenediamine (1 mmol; 108 mg) and thiophen-2-carboxyladehhyde (1 mmol; 112 mg) in 5 mL of ethanol, 20 mol % of ammonium chloride was added and the solution was stirred at 80 °C. The progress of reaction was monitored by TLC. After completion of the reaction (6.0 hours), the product was extracted using ethyl acetate, dried over sodium sulfate and concentered under reduced pressure. The product was purified using column chromatography (ethyl acetate: hexane, 1:1) and characterized using GC-MS.

Synthesis of Ti- ZTBF catalyst

Titanium (IV) isobutoxide (2.0 mmol; 680.5 mg), 2-(thophen-2-yl)-1-((thiophen-2-yl)methyl)-1H-benzo*[d]*imidazole (1 mmol; 296 mg) and dimethylformamide (50 ml) were charged in a pressure reactor. The mixture was heated in 140 °C in an oven for 24 hours. After 24 hours, the reaction was allowed to come down to room temperature. An off-white solid appears in the reaction mixture which was isolated using centrifugation.

3. Recycling of Ti-ZTBF catalyst:

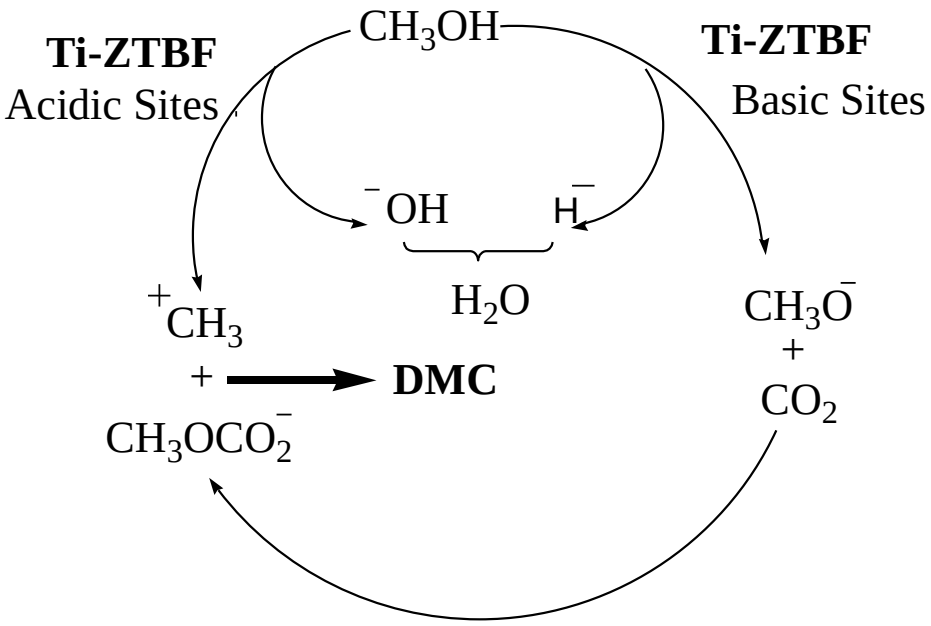
After the completion of each reaction, the Ti-ZTBF catalyst was recovered using a centrifuge, washed with water, dried under vacuum and used for a fresh set of reactants. It was observed that the catalyst remains active even after fifth cycle and could be reused several times without losing activity.



S1. Recycling of Ti-ZTBF catalyst

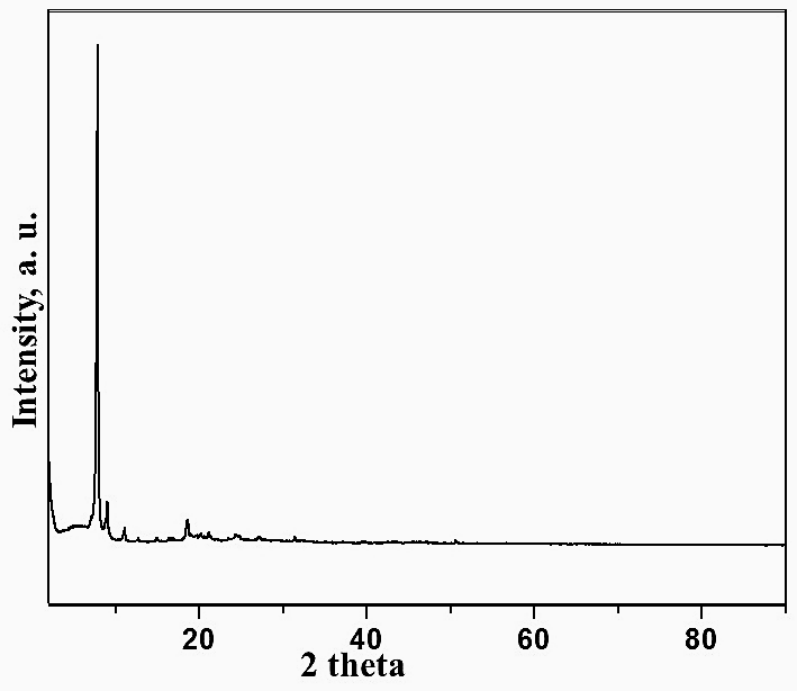
Tentative mechanism for dimethyl carbonate formation from methanol and CO_2

A tentative mechanism is proposed for the synthesis of DMC formation from methanol and CO_2 (S2). Ti-ZTBF catalyst has both, acidic and basic sites which are important factors for the acceleration of the reaction as shown below.



S2. Tentative mechanism for DMC formation from methanol and CO_2

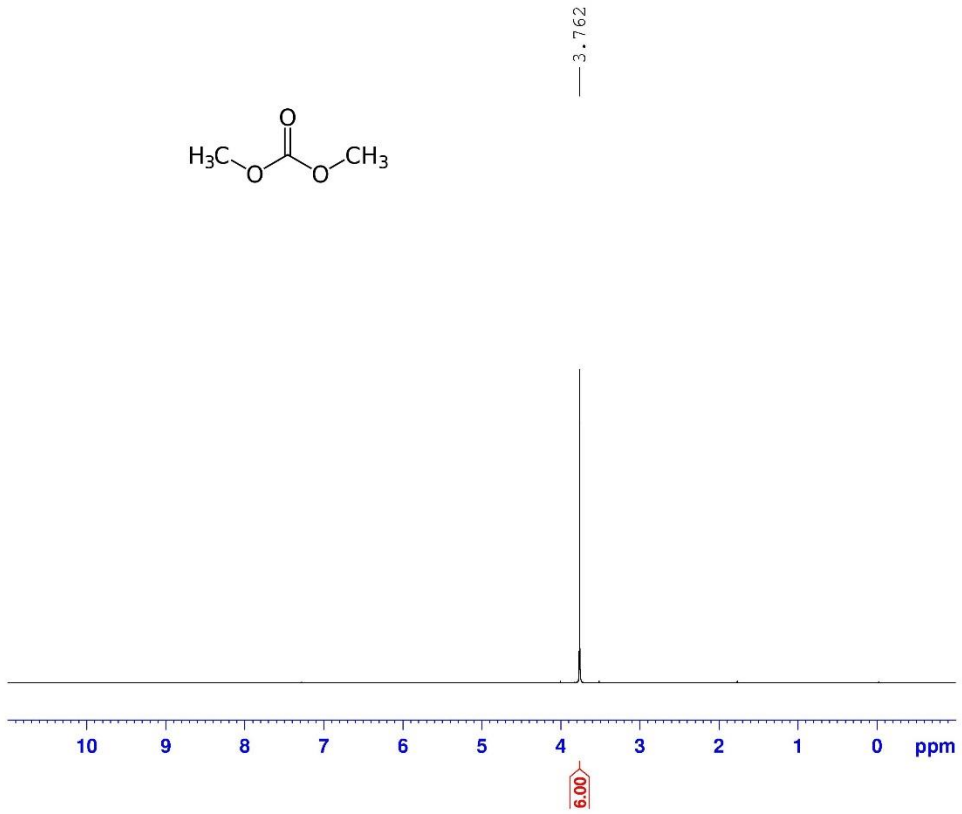
3. XRD spectra of recycled Ti-ZTBF catalyst



S3. XRD spectra of recycled Ti-ZTBF catalyst

^{1}H and ^{13}C NMR of the product

SS-32

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DE                 6.50 usec
TE                303.0 K
D1             1.00000000 sec
TD0                    1

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PL1                3.20 dB
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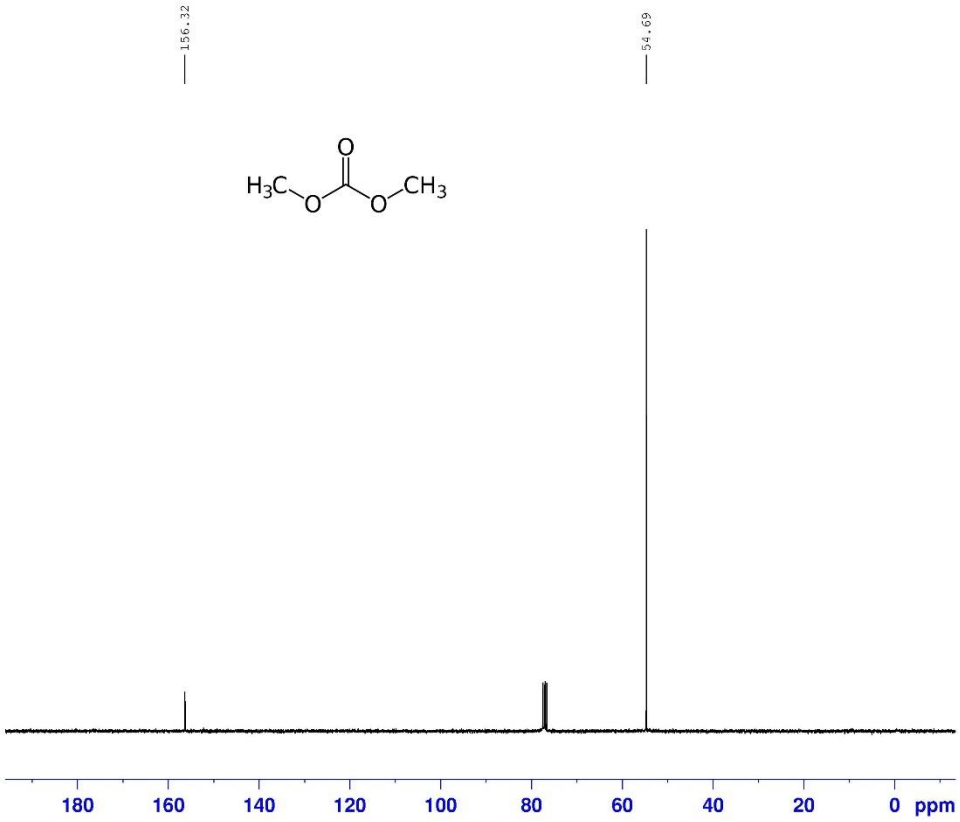
SS-32



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FIDRES	0.548877 Hz
AQ	0.9110282 sec
RG	8192
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TE	303.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
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PL1	1.80 dB
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SFO1	75.4752953 MHz
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PL12	18.98 dB
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PL12W	0.31768745 W
SFO2	300.1312005 MHz
SI	32768
SF	75.4677490 MHz
WDW	EM
SSB	0
LB	1.00 Hz
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