Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information

The Decarboxylation of Dialkyl Carbonates to Dialkyl Ethers over Alkali Metal-exchanged Faujasites

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Table. Synopsis of MS signals for major gaseous and liquid products, including DME, CO_2, propylene, diethyl ether, diproyl ether, dioctyl ether, isomeric octenes, and glycidol

Compound	GC/MS (EI, 70 eV)	Match Qality, % (Ref. database Wiley)
DME	m/z: 46 ($[M]^+$, 42%), 45 (90), 29 (100), 17 (17), 15 ($[CH_3]^+$, 64), 14 (15)	91 (265)
CO_2	m/z: 44 ($[M]^+$, 100%), 28 ($[M\text{-}O]^+$, 59), 16 (10)	95 (178)
Propylene	m/z: 42 ($[M]^+$, 45%), 41 ($[M\text{-}H]^+$, 100), 40 ($[M\text{-}(H)_2]^+$, 23), 39 ($[M\text{-}(H)_3]^+$, 55), 38 ($[M\text{-}(H)_4]^+$, 14), 37 ($[M\text{-}(H)_5]^+$, 9), 16 (11), 14 (10)	45 [a] (156)
Diethyl ether	m/z: 74 ($[M]^+$, 65%), 59 ($[M\text{-}CH_3]^+$, 100), 45 ($[M\text{-}CH_2CH_3]^+$, 94), 43 (29), 41 (27)	90 (1853)
Dipropyl ether	m/z: 102 ([M]+, 8%), 73 ($[M\text{-}CH_2CH_3]^+$, 19), 59 ($[M\text{-}CH_2CH_2CH_3]^+$,11), 55 (6), 43 ($[CH_2CH_2CH_3]^+$, 100), 41 (26)	80 (7877)
Dioctyl ether	m/z: 242 ($[M]^+$, 0%), 131.10 (2), 113 (11), 112 (12), 111 (7), 84 (28), 83 (23), 71 (84), 70 (25), 69 (31), 68 (12), 57 (100), 56 (29), 55 (30), 43 (59), 42 (20), 41 (43)	91 (128177)
1-octene	m/z: 112 ($[M]^+$, 11%), 84 ($[M\text{-}(CH_2)_2]^+$, 23), 83 (39), 71 (12), 70 ($[M\text{-}(CH_2)_3]^+$, 88), 69 (50), 57 (16), 56 ($[M\text{-}(CH_2)_4]^+$, 86), 55 (100), 54 (11), 53 (10)	91 (116372)
2-octene	m/z: 112 ($[M]^+$, 40%), 84 ($[M\text{-}(CH_2)_2]^+$, 10), 83 (21), 70 ($[M\text{-}(CH_2)_3]^+$, 53), 69 (29), 57 (18), 56 ($[M\text{-}(CH_2)_4]^+$, 53), 55 (100), 54 (10)	91 (3597)
Glycidol	m/z: 57 (2%), 53 (1), 55 (2), 45 (9), 44 (85), 43 (100), 42 (16), 31 (65)	78 (1716)

[a] The low match quality for propylene was due to a partial overlap of its signal to that of CO_2 during the GC/MS analysis/separation.

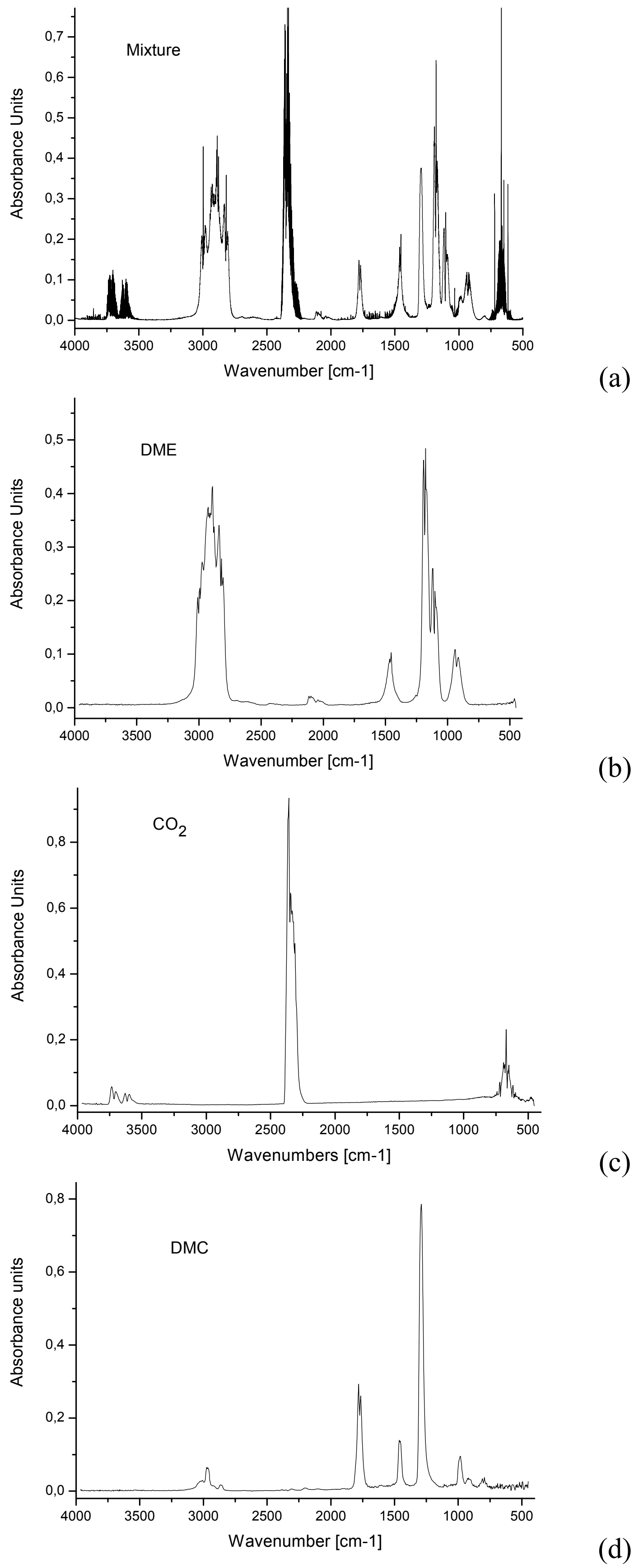

Figure 1. Comparison of IR spectra: (a) reaction mixture from the decarboxylation of DMC over NaY, including DME, CO_2, and DMC; (b) standard sample of DME; (c) standard sample of CO_2; (d) standard sample of DMC.

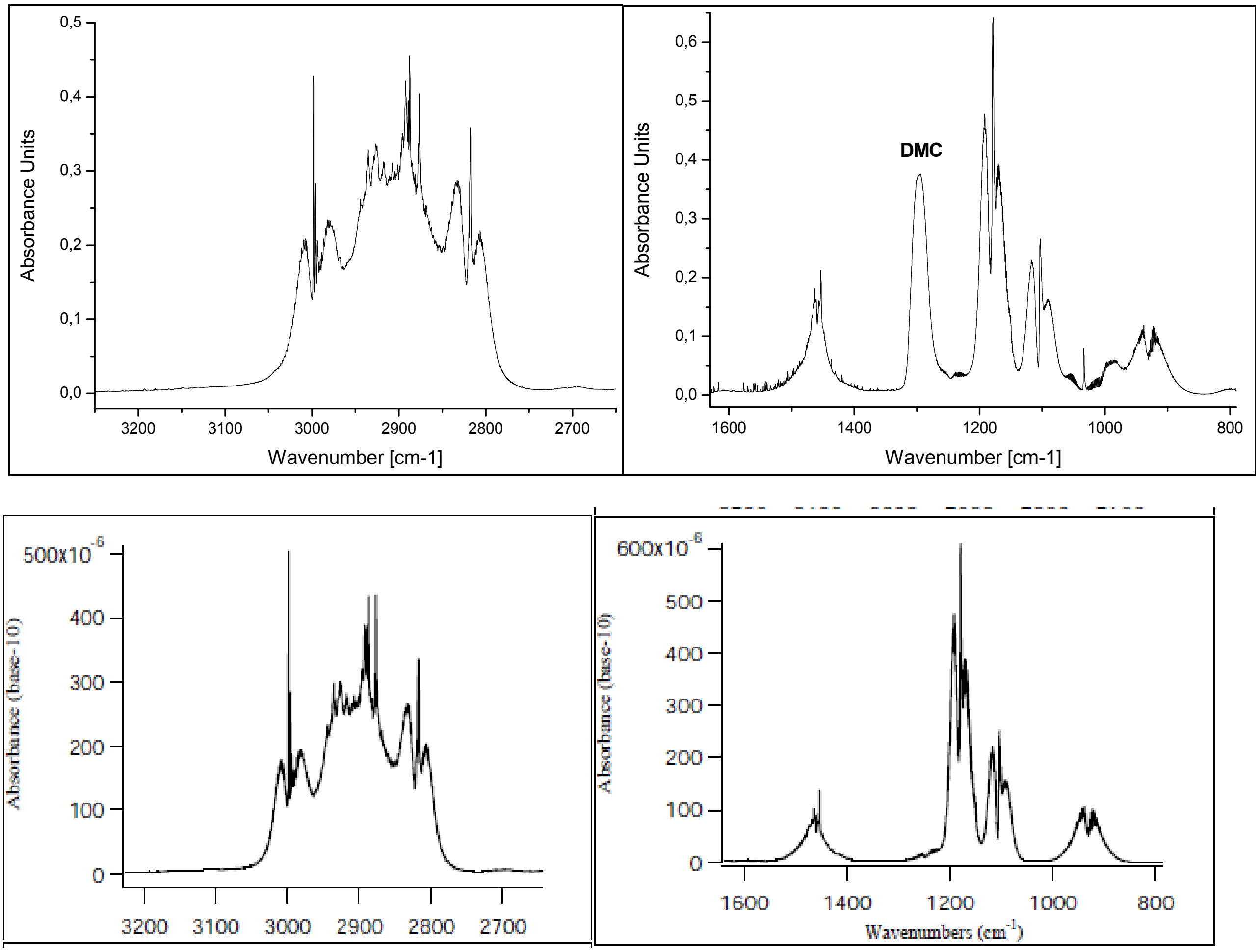

Figure 2. Enlargements of IR spectral regions including the adsorption bands of DME. Top: reaction mixture after the decarboxylation of DMC over NaY; bottom: standard sample of DME.

In the regions of 2800-3000 cm^{-1} and 900-1500 cm^{-1}, the IR spectrum of a standard sample of DME (bottom) showed an excellent overlap with the IR spectrum of a reaction mixture recovered after the decarboxylation of DMC, thereby confirming the presence of DME among the products. In the mixture (top), a signal of DMC appeared at 1300 cm^{-1} (compare Figure 1, d).