Supplementary Information

Direct Synthesis of Unsymmetrical Ethers from Alcohols Catalyzed by Titanium Cation-exchanged Montmorillonite

Takato Mitsudome,[a] Tsuyoshi Matsuno,[a] Shoichiro Sueoka,[a] Tomoo Mizugaki,[a] Koichiro Jitsukawa,[a] and Kiyotomi Kaneda[*a, b]

[a] *Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka, 560-8531, Japan.*

E-mail: kaneda@cheng.es.osaka-u.ac.jp; Fax: +81 6-6850-6260; Tel: +81 6-6850-6260

[b] *Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka, 560-8531, Japan*

Experimental

General

All organic reagents were purified before use. Na^+-montmorillonite (Kunipia-F) was obtained from Kunimine Industry Co. Ltd. $TiCl_4$ was purchased from Wako Pure Chemical Co. Ltd. Montmorillonite K-10 was Aldrich Inc. H-USY (Si/Al=40), H-Y (Si/Al=2.8), H-moridenite (Si/Al=15), H-ZSM-5 (Si/Al=25) were obtained from N. E. Chemcat Co. Ltd. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Jeol JNM-AL400 spectrometers, respectively. Gas chromatography (GC-FID) was carried out on a Shimadzu GC-2014 equipped with a Silicon SE-30 column (3 m). GC-MS analysis was done using Shimadzu-QP5050 equipped with capillary column (HR-1, 30 m, 0.25 mmID). NH_3-TPD of the samples was carried out in a flow-type fixed bed reactor using BELCAT-A instrument.

Typical reaction procedure

A typical procedure for the etherification of **1a** with **2a** by Ti^{4+}-mont was as follows: Ti^{4+}-mont (0.10 g) was placed in a reaction vessel, followed by addition of **2a** (3 mL) and **1a** (1 mmol). The reaction mixture was vigorously stirred at 30 °C under Ar for 6 h. After the reaction, Ti^{4+}-mont was removed by filtration, and the filtrate was analyzed by GC with naphthalene as an internal standard to determine the conversion and yield. The reactions at higher temperature than the boiling point of the solvent (Table 2, entry 8, 10, 17 and 18) were carried out using pressure glass tube.

Procedure of product isolation

After the reaction, magnesium sulfate was added and then, the mixture was filtered. The resulting filtrate was concentrated and the residue was purified by silica gel column chromatography (hexane : ethyl acetate (10 : 1, v/v)). In the synthesis of tetrahydrofuran (Scheme 1), magnesium sulfate as a drying agent was added to the reaction mixture after the reaction. Then, Ti^{4+}-mont and magnesium sulfate were removed by filtration. The filtrate was evaporated under reduced pressure at 30 ^{o}C, giving tetrahydrofuran. The purity of the isolated tetrahydrofuran was determined to be >99% using GC analysis.

Reuse experiment for the etherification of 1a with 2a

After the etherification of **1a** with **2a** under the above typical reaction conditions, Ti^{4+}-mont was recovered by simple filtration, washed with acetone and water and dried at 110 °C. Additional portions of **1a** (1 mmol) and **2a** (3 mL) were then added, followed by stirring under identical conditions. The yields of **3a** in the three reuse experiments were 97%, 97% and 96%, respectively.

NH_3-TPD study of montmorillonite K-10 and USY

Table 1S NH_3-TPD measurement of USY

Temp. range of NH_3 desorption	25-100 °C	100 - 200 °C	200 - 300 °C	300 - 400 °C	400 - 500 °C
Amouts of partial acid sites (mmol/g)	0.010	0.016	0.024	0.022	0.014
USY (treatment tem.)	USY (100)	USY (200)	USY (300)	USY (400)	USY (500)
Yield of **3a** (%)[a]	0	1	17	22	23
TONs[b]	0	3	73	19	7

[a]Reaction conditions: USY (0.1 g), *p*-methoxybenzyl alcohol (1 mmol), *n*-butanol (3 mL), 30 °C, Ar, 4 h. [b]TONs of USY(X) = (the amounts of **3a** using USY(X) - the amounts of **3a** using USY (X-100))/the amounts of partial acid sites of USY(X).

Table 2S NH_3-TPD measurement of K-10

Temp. range of NH_3 desorption	25 -100 °C	100 - 200 °C	200 - 300 °C	300 - 400 °C	400 - 500 °C
Amouts of partial acid sites (mmol/g)	0.01	0.06	0.04	0.03	0.01
K-10 (treatment tem.)	K-10 (100)	K-10 (200)	K-10 (300)	K-10 (400)	K-10 (500)
Yield of **3a** (%)[a]	trace	1	25	36	38
TON[b]	<1	1	56	32	18

[a]Reaction conditions: K-10 (0.1 g), *p*-methoxybenzyl alcohol (1 mmol), *n*-butanol (3 mL), 30 °C, Ar, 4 h. [b]TON of K-10(X) = (the amounts of **3a** using K-10(X) - the amounts of **3a** using K-10 (X-100))/the amounts of partial acid sites of K-10(X).

Product identification

The products were determined by GC, GC-MS and NMR. Retention times and chemical shifts (^{1}H and ^{13}C NMR) of the products were in agreement with those of authentic samples (commercially available) and/or reported data[1S-8S].

Table 2, Entries 1-4

4-methoxybenzy *n*-butyl ether

CAS registry No. [5333-52-8] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 1S.

Entry 5

4-methoxybenzyl ethyl ether

CAS registry No. [55249-73-5] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 2S.

Entry 6

4-methoxybenzyl *sec*-butyl ether

CAS registry No. [732286-12-3] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 1S.

Entry 7

4-methoxybenzyl *t*-butyl ether

CAS registry No. [56636-80-7] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 2S.

Entry 8

benzyl *n*-butyl ether

CAS registry No. [588-67-0] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 3S, SDBS No. 4873.

Entry 9

vanillyl butyl ether

CAS registry No. [82654-98-6] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 1S.

Entry 10

n-butyl *p*-chlorobenzyl ether

CAS registry No. [101005-10-1] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 4S.

Entry 11

phenylethyl *n*-butyl ether

CAS registry No. [4157-77-1] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 5S.

Entry 12

diphenylmethyl *n*-butyl ether

CAS registry No. [7495-83-2] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 6S.

Entry 13

cinnamyl *n*-butyl ether

CAS registry No. [78877-09-5] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 7S.

Entry 14

tert-butyl 3-phenylpropyl ether

CAS registry No. [199275-18-8] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 2S.

Entry 15

tert-butyl octyl ether

CAS registry No. [51323-70-7] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 8S.

Entry 16

tert-butyl ethyl ether

CAS registry No. [637-92-3] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 3S, SDBS No. 2468.

Entry 17

tetrahydrofuran

CAS registry No. [109-99-9] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 3S, SDBS No. 497.

Entry 18

tetrahydropyran

CAS registry No. [142-68-7] ^{1}H NMR, ^{13}C NMR were consistent with previously reported values. See Ref. 3S, SDBS No. 2399.

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