Synthesis of dimethyl carbonate from ethylene carbonate and methanol using TS-1 as solid base catalyst

T. Tatsumi,* Y. Watanabe and K. A. Koyano

Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Tokyo 113, Japan

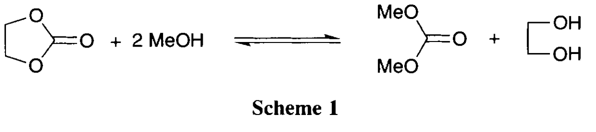
The titanium silicate molecular sieve, TS-1, exchanged with an aqueous solution of K_2CO_3 is an excellent heterogeneous catalyst for the synthesis of dimethyl carbonate by an ester exchange reaction between ethylene carbonate and methanol.

Dimethyl carbonate (DMC) is a useful methylation and carbonylation agent and a precursor of polycarbonate resins. Due to the negligible toxicity of DMC, it is promising as a substitute for phosgene.[1] It also has a potential use as a petrol octane enhancer.[2] DMC has long been synthesized by reaction of methanol with phosgene.[3] A tremendous amount of research has been pursued to establish environmentally compatible non-phosgene routes for the production of DMC, with a number of such processes having been developed. For example, DMC production from methanol, carbon monoxide and oxygen has been industrialized by using a Cu-based catalyst.[4] Recently, a new process has been developed which uses the reaction of methyl nitrite and carbon monoxide catalysed by Pd catalyst.[5]

It is known that DMC can be synthesized concomitantly with ethylene glycol by the ester exchange reaction between ethylene carbonate (EC) and methanol (Scheme 1). For this reaction, various base catalysts and Group IV homogeneous catalysts are reported to be effective.[6] Here we report that TS-1 treated with K_2CO_3 is an excellent solid catalyst for this reaction. It is well-known that TS-1 is active in a variety of oxidation reactions.[7] Recently it has been reported that TS-1 is capable of promoting acid-catalysed reactions such as the Beckmann rearrangement, hydration of epoxides and aldol reactions.[8] Reported herein is a new aspect of TS-1 as a base catalyst.

TS-1 was synthesized according to a literature method using tetrapropylammonium hydroxide (TCI) as the template.[9] This untreated TS-1 is named UT-TS-1 (Si/Ti = 92). H-TS-1 was obtained by treating UT-TS-1 (calcined at 823 K) in aqueous NH_4Cl (1.0 M) solution at 343 K for 2 h followed by calcination at 823 K for 3 h. K-TS-1 was prepared by the treatment of calcined UT-TS-1 in aqueous K_2CO_3 (0.5 M) solution at room temperature for 2 h followed by calcination at 823 K for 3 h. K-silicalite-1 was prepared by treating JRC-Z5-1000H (SiO_2/Al_2O_3 = 1250) in a similar manner to K-TS-1. K-ZSM-5 was prepared by ion-exchange of Na-ZSM-5 (TSZ-850NAA; Tosoh) with 1.0 M aqueous KCl. Ester exchange reactions were carried out under refluxing conditions. Products were analysed by GC–FID.

The results of the ester exchange reaction between EC and methanol are shown in Table 1. UT-TS-1 showed appreciable activity whereas H-TS-1 was virtually inactive. It is known that the 960 cm^{-1} band appears when titanium is incorporated into the zeolite framework and the ratio of the intensities of the 960 to 550 cm^{-1} band (the latter being characteristic of the MFI structure), I_{960}/I_{550}, is proportional to the Ti content of the zeolite.[9] The IR band at 960 cm^{-1} was originally assigned to the stretching vibration of $Si–O^{\delta-}\cdots Ti^{\delta+}$.[10] Camblor *et al.* reported that this band is better assigned to the stretching vibration of the $Si–O^-$ groups where H^+ acts as a counter cation.[11] Khouw and Davis observed that treatment of TS-1 with aqueous NaOH resulted in a decrease in the intensity of the IR band at 960 cm^{-1} and the appearance of a shoulder band at 985 cm^{-1}.[12] They suggested the interconversion illustrated in Scheme 2. It is considered that the I_{960}/I_{550} ratio can be taken as a measure for the number of silanol groups (Si–O–H in Scheme 2) in the neighbourhood of titanium. The I_{960}/I_{550} ratio of H-TS-1 is larger than that of UT-TS-1 as shown in Table 1. The increase in the I_{960}/I_{550} ratio caused by NH_4Cl treatment followed by calcination, indicated that Si–O–M (M = alkali metal) in UT-TS-1 was converted to Si–O–H by this treatment.[12]



Scheme 1

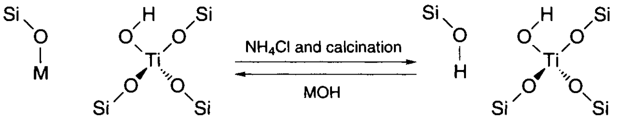
The amount of potassium (K_2O in catalyst) in UT-TS-1 was determined by EDX to be 1.1 wt%. Potassium must have been included as an impurity in the template tetrapropylammonium hydroxide used for the synthesis of TS-1. Although titanium alkoxides are reported to be homogenous catalysts for this ester exchange reaction,[13] H-TS-1 showed negligible activity, suggesting that the activity for this reaction is not due to the titanium in TS-1 but to the potassium-exchanged silanol, Si–O–K, which lies mostly adjacent to titanium in the MFI framework.

In order to confirm the activity of the Si–O–K group, K-TS-1 was prepared by treating UT-TS-1 with K_2CO_3. The K_2CO_3 treatment resulted in a decrease in the I_{960}/I_{550} ratio, indicating that the backward reaction of Scheme 2 did occur. No destruction of the MFI structure was observed by XRD. The amount of potassium in K-TS-1 was determined by EDX to be 1.9 wt%. As shown in Table 1, K-TS-1 showed much higher activity than UT-TS-1; 68% EC conversion and 57% DMC yield were attained after 3 h. The difference between EC conversion and DMC yield was due to the formation of 2-hydroxyethyl methyl carbonate as the intermediate; no other product was observed. The EC conversion and DMC yield at equilibrium at 338 K are estimated to be 80.9 and 64.0%, respectively. After the ester exchange reaction, K-TS-1 was

Table 1 Synthesis of DMC catalysed by various TS-1 compounds[a]

Catalyst	K content (wt%)[b]	K/Ti	I_{960}/I_{550}	EC conversion (%)	DMC yield (%)
H-TS-1	0	0	0.28	0.11	0
UT-TS-1	1.1	0.46	0.20	43	26
K-TS-1	1.9	0.69	0.14	68	57

[a] *Reaction conditions*: 89 mg catalyst, 31 mmol EC, 124 mmol MeOH, under refluxing conditions, 3 h. [b] As K_2O.



Scheme 2

separated by filtration, washed with methanol and calcined at 823 K. Table 2 demonstrates that the recovered K-TS-1 showed no significant difference in activity from fresh K-TS-1, indicating K-TS-1 acted as a heterogeneous catalyst. However, about one third of the potassium leached out of K-TS-1; the potassium released during the reaction apparently did not participate in the reaction and would not have been present at the active basic sites. In contrast, no difference in I_{960}/I_{550} was observed between the recovered K-TS-1 and fresh K-TS-1, in agreement with the negligible change in activity. It is noteworthy that UT-TS-1 and the recovered K-TS-1 were similar in potassium content but markedly different in the activity for DMC formation. Thus we consider the I_{960}/I_{550} ratio to be a better measure of activity than potassium content, which could include the totally inactive potassium (Table 3).

We have prepared K-TS-1 (H) from H-TS-1 by treating it with K_2CO_3 (0.5 M) solution at room temperature. The activity of K-TS-1 (H) proved to be much lower (EC conversion 31%, DMC yield 8.0%, 1.5 h) than that of K-TS-1. In agreement with this, the value of I_{960}/I_{550} of K-TS-1 (H) was 0.20, much higher than K-TS-1, suggesting that the conversion of Si–O–H to Si–O–K was relatively low, *i.e.* the interconversions depicted in Scheme 2 are reversible for only some of the sites at room temperature. We treated H-TS-1 with K_2CO_3 solution at higher temperatures to advance the conversion; however, the MFI structure was destroyed during this treatment. Thus the presence of potassium in the hydrothermal synthesis seems to be necessary for the high activity.

Table 2 Synthesis of DMC catalysed by K-TS-1 and related materials[a]

Catalyst	Reaction time/h	K content (wt%)[b]	EC conversion (%)	DMC yield (%)
K-TS-1	1.5	1.9	49	28
Recovered K-TS-1	1.5	1.2	47	29
UT-TS-1	1.5	1.1	34	8.6
TS-1-KCl	1.5	0.45	25	2.7
K-TS-1	3	1.9	68	57
Silicalite-1	3	0	tr.	0
K-silicalite-1	3	trace	19	0.32
K-ZSM-5	3	4.2	37	16

[a] *Reaction conditions*: 89 mg catalyst, 31 mmol EC, 124 mmol MeOH, under refluxing conditions. [b] As K_2O.

Table 3 Relationship between relative intensity I_{960}/I_{550} and activity

Catalyst	I_{960}/I_{550}	DMC yield (%)[a]
K-TS-1	0.14	28
Recovered TS-1	0.14	29
UT-TS-1	0.20	8.6
K-TS-1 (H)	0.20	8.0
TS-1-KCl	0.22	2.7
H-TS-1	0.28	0

[a] *Reaction conditions*: 89 mg catalyst, 31 mmol EC, 124 mmol MeOH, under refluxing conditions, 1.5 h.

These findings suggest that there is a difference in the activity between the potassium accidently present in UT-TS-1 and the potassium introduced in the K-TS-1. Apparently there are two or more potassium sites on TS-1 catalysts. Once K on the most active site is changed to H, it may be difficult to replace H with K under moderate conditions. Studies on the infrared spectra of the O–H region are ongoing to clarify the difference in the potassium sites.

As shown in Table 2, TS-1-KCl prepared by treating UT-TS-1 with aqueous 1.0 M KCl at 353 K for 2 h exhibited decreased activity for DMC formation. This would be accounted for by the weak acidity of the Si–O–H group; basic conditions were necessary for the conversion of Si–O–H to Si–O–K,[14] and a portion of the K present as Si–O–K was released into the solution during the treatment.

The yield of DMC over K-silicalite-1 was much lower than over K-TS-1 as shown in Table 2; the K_2CO_3 treatment of silicalite-1 was not effective. This is not unexpected since silicalite-1 would scarcely have any exchangeable Si–O–H groups, as are present in TS-1. Actually, the amount of potassium in K-silicalite-1 was too small to be determined by EDX. K-ZSM-5 (SiO_2/Al_2O_3 = 50) yielded only 16% DMC after 3 h and was less active than UT-TS-1. UT-TS-1 and K-TS-1 have higher activities than K-ZSM-5 even though they contain less potassium than K-ZSM-5. These results indicate that potassium present in the silanol group (Si–O–K) in the vicinity of titanium in TS-1 has a much higher activity than potassium present as a charge-compensating cation in zeolite.

Footnote

† E-mail: tatsumi@komiyama.t.u-tokyo.ac.jp

References

1 A.-A. G. Shaikh and S. Sivaram, *Ind. Eng. Chem. Res.*, 1992, **31**, 1167.
2 A. L. Bhattacharya, *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.*, 1995, **40**, 119.
3 E. Abrams, *Encyclopedia of Chemical Technology 3rd edn.*, ed. Kirk-Othmer, Wiley, New York, 1979, p. 758.
4 U. Romano, C. Tesei, M. Massi Mauri and P. Rebora, *Ind. Eng. Chem. Prod. Res. Dev.*, 1980, **19**, 396.
5 K. Nishihira, T. Matsuzaki and S. Tanaka, *Shokubai*, 1995, **37**, 68.
6 J. F. Knifton and R. G. Duranleau, *J. Mol. Catal.*, 1991, **67**, 389.
7 T. Tatsumi, N. Nakamura, S. Negishi and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1990, 476; G. Bellussi and M. S. Rigutto, *Stud. Surf. Sci. Catal.*, 1994, **85**, 177.
8 A. Thangaraj, S. Sivasankerm and P. Ratnasamy, *J. Catal.*, 1992, **137**, 252; M. Sasidharan, S. V. N. Raju, K. V. Srinivasan, V. Paul and R. Kumar, *Chem. Commun.*, 1996, 129.
9 A. Thangarai, R. Kumar, S. P. Mirajkar and P. Ratnasamy, *J. Catal.*, 1991, **130**, 1.
10 M. R. Boccuti, K. M. Rao, A. Zecchina, G. Leofanti and G. Petrini, *Stud. Surf. Sci. Catal.*, 1989, **48**, 133.
11 M. A. Camblor, A. Corma and J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1993, 557.
12 C. B. Khouw and M. E. Davis, *J. Catal.*, 1995, **151** 77.
13 USP 4734518/1987.
14 A. Auroux, A. Gervasini, E. Jorda and A. Tuel, *Stud. Surf. Sci. Catal.*, 1994, **84** 653.

Received, 25th April; Com. 6/02915I