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Efficient synthesis of cyclic carbonate from carbon dioxide catalyzed by polyoxometalate: the remarkable effects of metal substitution

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Abstract

Tetraalkylammonium salts of transition-metal-substituted polyoxometalates, such as $[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Co]$ and $[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Mn]$, efficiently catalyze cyclic carbonate synthesis from carbon dioxide and epoxide. The catalytic activity is significantly influenced by the type of transition metal and the countercation ($Co^{2+} \approx Mn^{2+} > Ni^{2+} > Fe^{3+} \gg Cu^{2+}$; $(n\text{-}C_7H_{15})_4N^+ > (n\text{-}C_4H_9)_4N^+ \gg K^+$). Co- or Mn-substituted catalysts required neither additional organic solvents nor additives. Thus, polyoxometalates are promising as nonhalogen anionic components of catalysts for cyclic carbonate synthesis.

Keywords: Propylene carbonate; Carbon dioxide; Propylene oxide; Polyoxometalate

1. Introduction

The efficient transformation of carbon dioxide into useful chemical compounds is very attractive because it is a potentially inexpensive and abundant C_1 building block, and it is environmentally benign (nontoxic, noncorrosive, and nonflammable) [1]. Cycloaddition of CO_2 to epoxides to produce cyclic carbonates (e.g., ethylene carbonate and propylene carbonate) is one of a few industrial synthetic processes that utilize CO_2 as a raw material. Cyclic carbonates are widely used as electrolyte components in lithium batteries, polar solvents, and chemical intermediates [2,3]. Recently, a phosgene-free process for the manufacture of polycarbonates via ethylene carbonate has been commercialized [4]. Therefore, there is an increasing demand for cyclic carbonates. For cycloaddition reactions, quaternary ammonium salts (e.g., Et_4NBr) or alkali halides (e.g., KI) are typically used as homogeneous catalysts [5,6]. A large number of homogeneous catalytic systems have also been reported to be effective in the production of cyclic carbonates [7]. Recent examples include LiBr [8], $ZnBr_2(pyridine)_2$ [9], salen complexes such as Cr-salen-Cl/base [10–13], ionic liquids such as imidazolium salts [14–16], molten tetrabutylammonium halides [17], and polyfluoroalkyl phosphonium iodides [18]. However, in most of these cases, the anionic parts of the catalysts are limited to halides. In addition, additives and/or co-catalysts as well as organic solvents are often needed. Although several heterogeneous catalysts based on metal oxides have been proposed [19–22], the activity and selectivity of these catalysts are unsatisfactory, and the presence of halogens [23–25] and/or the addition of a polar organic solvent, such as DMF (N,N-dimethylformamide), are necessary to achieve high yields. Here we report that the tetraalkylammonium salt of transition-metal-substituted silicotungstate, a type of polyoxometalate, is an efficient catalyst for propylene carbonate synthesis from CO_2 and propylene oxide (Scheme 1) [26]. Very recently, propylene carbonate synthesis with the use of zinc-substituted polyoxometalate has been reported; however, the selectivity of this reaction is unsatisfactory in the absence of dimethyl-

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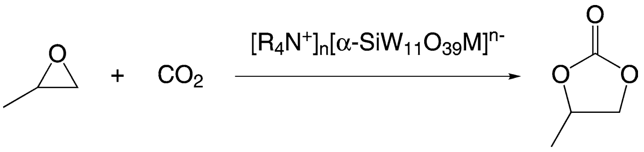


Scheme 1.

aminopyridine [27]. On the other hand, our catalyst does not require additional organic solvents or additives.

2. Experimental

2.1. Synthesis of polyoxometalates

The potassium salts of α-$SiW_{12}O_{40}{}^{4-}$ and α-$SiW_{11}MO_{39}{}^{n-}$ ($M = Mn^{2+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) were synthesized by methods reported in the literature [28]. The IR and UV/vis spectra of these compounds were characteristic of α-Keggin structure (see Fig. 1). The contents of the metal substitute were confirmed by inductively coupled plasma spectrometry. For example, the Si/W/Mn ratio for α-$SiW_{11}MnO_{39}{}^{6-}$ was 1.00:10.9:0.97, the Si/W/Co ratio for α-$SiW_{11}CoO_{39}{}^{6-}$ was 1.00:10.7:0.97, and the Si/W/Cu ratio for α-$SiW_{11}CuO_{39}{}^{6-}$ was 1.00:10.7:0.99. The tetra-n-heptylammonium salts of α-$SiW_{12}O_{40}{}^{4-}$ and α-$SiW_{11}MO_{39}{}^{n-}$ were prepared by cation exchange of an aqueous solution of the corresponding potassium salts with a toluene solution of tetra-n-heptylammonium bromide by the method of Refs. [29,30]. We prepared the tetra-n-butylammonium salt of α-$SiW_{11}MnO_{39}{}^{6-}$ by adding an excess amount of tetra-n-butylammonium bromide to $K_6[\alpha\text{-}SiW_{11}O_{39}Mn]$ in aqueous solution with the method of Ref. [31].

2.2. Reaction procedure

The cycloaddition of CO_2 to propylene oxide was carried out in a stainless-steel autoclave (20 cm^3 inner volume). A typical reaction was carried out as follows. In an autoclave, CO_2 was added to a mixture of propylene oxide (2 cm^3), DMF (2 cm^3), a catalyst (0.1 mol%), and biphenyl (200 mg, internal standard for GC analysis) at room temperature. The autoclave was then heated to 150 °C, and the pressure was adjusted to 3.5 MPa. After the reaction had proceeded for 2 h at a pressure of 3.5 MPa, the autoclave was cooled and the reaction products were analyzed by GC and further characterized by GC-MS.

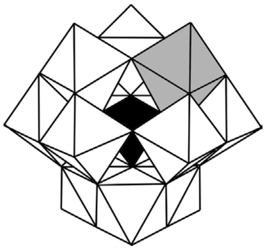


Fig. 1. Polyhedral representation of α-$SiW_{11}MO_{39}{}^{n-}$ ($M = Mn^{2+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}). The internal black tetrahedron represents the SiO_4 core. The white octahedra represent WO_6 fragment with a tungsten atom in the center of the octahedra and oxygen atoms at each corner. The shaded octahedron contains the substituted transition metal, M.

Table 1
Propylene carbonate synthesis from carbon dioxide and propylene oxide catalyzed by transition-metal-substituted silicotungstates[a]

Entry	Catalyst	Yield (%)	Selectivity (%)
1	$[(n\text{-}C_7H_{15})_4N]_4[\alpha\text{-}SiW_{12}O_{40}]$	2	73
2	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Co]$	83	99
3	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Mn]$	73	99
4	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Ni]$	37	98
5	$[(n\text{-}C_7H_{15})_4N]_5[\alpha\text{-}SiW_{11}O_{39}Fe]$	28	93
6	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Cu]$	4	90
7	$[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}SiW_{11}O_{39}Mn]$	17	99
8	$K_6[\alpha\text{-}SiW_{11}O_{39}Mn]$	1	99

[a] Reaction conditions: catalyst (0.1 mol%), propylene oxide (2 cm^3), DMF (2 cm^3), total pressure (3.5 MPa), 150 °C, 2 h.

3. Results and discussion

We first investigated the catalytic performance of various silicotungstates, especially with regard to the effects of metal substitution. Table 1 summarizes the yield and selectivity of propylene carbonate formation at 150 °C and 3.5 MPa, with DMF as a solvent. The products other than propylene carbonate were isomers of propylene oxide, such as propionaldehyde and acetone. Although $[(n\text{-}C_7H_{15})_4N]_4[\alpha\text{-}SiW_{12}O_{40}]$ was inactive in this reaction, mono-substitution of tungsten(VI) with cobalt(II) or manganese(II) greatly increased the catalytic activity. For example, when a small amount of $[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Co]$ (0.1 mol%) was used as a catalyst over a short reaction time (2 h), propylene carbonate was produced in good yield (83%) with excellent selectivity (99%). Interestingly, the catalytic activity is highly dependent on the type of newly introduced metal; nickel(II) and iron(III) substitution had a moderate effect, whereas copper(II) substitution was ineffective.

The choice of countercation was also important. The tetra-n-butylammonium salt of manganese(II)-substituted silicotungstate was not as effective as the tetra-n-heptylammonium salt, and the potassium salt was an ineffective catalyst. The tetra-n-heptylammonium and tetra-n-butylammonium salts were soluble in the reaction mixture, whereas the potassium salt was not completely dissolved. Thus, it is possible that the low catalytic activity of the potassium salt is due to the poor solubility of this catalyst.

Next, we examined the effects of the reaction media with the use of the tetra-n-heptylammonium salts of cobalt(II)- and manganese(II)-substituted silicotungstates (Table 2). In industrial cyclic carbonate synthesis, the product is utilized as a solvent [5,6]. Therefore, we performed the reaction with ethylene carbonate as a solvent (Table 2, entries 1 and 2).

Table 2
Propylene carbonate synthesis from carbon dioxide and propylene oxide[a]

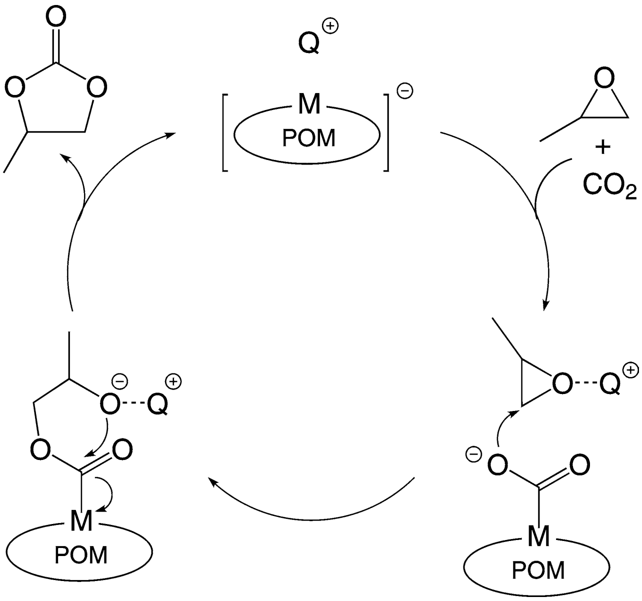
Entry	Catalyst	Solvent	Yield (%)	Selectivity (%)
1	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Co]$	EC[b]	97	99
2	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Mn]$	EC	85	99
3	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Mn]$	$scCO_2$[c]	96	97
4	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Co]$	None	97	97
5	$[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Mn]$	None	96	97
6	$(n\text{-}C_7H_{15})_4NBr$	None	12	97
7	Et_4NBr	None	3	85
8	KI	None	2	83
9	Et_4NBr	DMF[d]	23	99
10	KI	DMF	34	99

[a] Reaction conditions: catalyst (0.1 mol%), propylene oxide (2 cm^3), total pressure (3.5 MPa), 150 °C, 2 h.

[b] Ethylene carbonate (2.1 g).

[c] Supercritical CO_2 (total pressure of 10 MPa).

[d] N,N-Dimethylformamide (2 cm^3).



Scheme 2.

The reaction proceeded more efficiently in the presence of ethylene carbonate than in the presence of DMF (Table 1, entries 2 and 3). We also attempted to perform the reaction under supercritical CO_2 conditions (10 MPa), where CO_2 could act not only as a reagent but also as a solvent (Table 2, entry 3). In supercritical CO_2, the yield was higher than when the reaction was carried out in ethylene carbonate. More importantly, the reaction was efficiently catalyzed without any additional solvents, and more than 95% yield and selectivity could be obtained even at 3.5 MPa (Table 2, entries 4 and 5). We visually inspected the phase behavior of the reaction through sapphire windows attached to the autoclave. Both $[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Co]$ and $[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Mn]$ were initially soluble in the propylene oxide charged into the reactor at room temperature. When the reactor was pressurized with CO_2 and the temperature was increased to 150 °C (total pressure of 3.5 MPa), most of the propylene oxide vaporized while the catalyst was deposited from the gas phase. However, once a small amount of propylene carbonate (liquid phase) was formed, the carbonate solubilized the catalyst and the reaction was accelerated. This phenomenon was easily recognized by the color of the propylene carbonate.

The tetra-n-heptylammonium salts of cobalt(II)- and manganese(II)-substituted silicotungstates were more active than tetra-n-heptylammonium bromide, indicating the importance of the polyoxoanion in promoting the reaction. The activities of the silicotungstate catalysts were much higher than the activities of conventional halide-based catalysts such as tetraethylammonium bromide or potassium iodide [5,6], even when the activity was compared in the presence of DMF. Although the reaction mechanism in the presence of the polyoxometalate catalyst is currently unclear, the activation of CO_2 and/or propylene oxide by the replacement transition metal presumably plays an important role, because $[(n\text{-}C_7H_{15})_4N]_4[\alpha\text{-}SiW_{12}O_{40}]$ was not an effective catalyst (vide supra). Kozik et al. have investigated the interaction of various transition-metal-substituted silicotungstates with CO_2 in nonpolar solvents and have demonstrated that manganese(II)-, cobalt(II)-, and nickel(II)-substituted silicotungstates coordinate CO_2, whereas copper(II)-substituted silicotungstate does not [30]. Thus, it is possible that the high catalytic activities of the manganese(II)- and cobalt(II)-substituted silicotungstates and the low activity of the copper(II)-substituted silicotungstate are related to the difference in the ability of these catalysts to coordinate CO_2. Scheme 2 shows a postulated reaction mechanism, in which CO_2 coordinated to the substituted transition metal attacks propylene oxide activated by Q^+ (tetra-n-heptylammonium or even the replacement transition metal of another silicotungstate) to open the ring, leading to the formation of propylene carbonate.

In summary, we have developed a new homogeneous catalytic system for cyclic carbonate synthesis from carbon dioxide and epoxide. The tetra-n-heptylammonium salt of cobalt- or manganese-substituted silicotungstate demonstrated excellent catalytic activity and selectivity for propylene carbonate synthesis, even in the absence of additional solvents. These findings are important in the following two respects: (1) polyoxoanions are effective as nonhalogen anionic components of catalysts for cyclic carbonate synthesis, and (2) the catalytic activities of polyoxometalates are significantly influenced by metal substitution.

References

[1] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-

Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Chem. Rev. 101 (2001) 953.

[2] A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.

[3] J.H. Clements, Ind. Eng. Chem. Res. 42 (2003) 663.

[4] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, Green Chem. 5 (2003) 497.

[5] C.H. McMullen, J.R. Nelson, B.C. Ream, J.A. Sims Jr., US Patent 4,314,945 (1982), to Union Carbide Corporation.

[6] B.C. Ream, US Patent 4,877,886 (1989), to Union Carbide Chemicals and Plastics Company Inc.

[7] D.J. Darensbourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155.

[8] T. Iwasaki, N. Kihara, T. Endo, Bull. Chem. Soc. Jpn. 73 (2000) 713.

[9] H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang, Angew. Chem. Int. Ed. 39 (2000) 4096.

[10] R.L. Paddock, S.T. Nguyen, J. Am. Chem. Soc. 123 (2001) 11498.

[11] Y.-M. Shen, W.-L. Duan, M. Shi, J. Org. Chem. 68 (2003) 1559.

[12] X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang, R. Zhang, J. Am. Chem. Soc. 126 (2004) 3732.

[13] M. Alvaro, C. Baleizao, D. Das, E. Carbonell, H. García, J. Catal. 228 (2004) 254.

[14] J. Peng, Y. Deng, New J. Chem. 25 (2001) 639.

[15] Y.-J. Kim, M. Cheong, Bull. Korean Chem. Soc. 23 (2002) 1027.

[16] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, Chem. Commun. (2003) 896.

[17] V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561.

[18] L.-N. He, H. Yasuda, T. Sakakura, Green Chem. 5 (2003) 92.

[19] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, Chem. Commun. (1997) 1129.

[20] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526.

[21] M. Tu, R.J. Davis, J. Catal. 199 (2001) 85.

[22] B.M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, Appl. Catal. A 219 (2001) 259.

[23] T. Zhao, Y. Han, Y. Sun, Phys. Chem. Chem. Phys. 1 (1999) 3047.

[24] H. Yasuda, L.-N. He, T. Sakakura, J. Catal. 209 (2002) 547.

[25] M. Aresta, A. Dibenedetto, J. Mol. Catal. A 182–183 (2002) 399.

[26] H. Yasuda, C. Hu, L.-N. He, T. Sakakura, Jpn. Kokai Tokkyo Koho JP 2004-250349A (2004) (applied date February 18, 2003).

[27] M. Sankar, N.H. Tarte, P. Manikandan, Appl. Catal. A 276 (2004) 217.

[28] C.M. Tourné, G.F. Tourné, S.A. Malik, T.J.R. Weakley, J. Inorg. Nucl. Chem. 32 (1970) 3875.

[29] D.E. Katsoulis, M.T. Pope, J. Chem. Soc., Dalton Trans. (1989) 1483.

[30] S.H. Szczepankiewicz, C.M. Ippolito, B.P. Santora, T.J. Van de Ven, G.A. Ippolito, L. Fronckowiak, F. Wiatrowski, T. Power, M. Kozik, Inorg. Chem. 37 (1998) 4344.

[31] N. Mizuno, C. Nozaki, I. Kiyoto, M. Misono, J. Am. Chem. Soc. 120 (1998) 9267.