polymer communications

Supported solid acids as polymerization catalysts*

Yuhsuke Kawakami*, Wataru Sato, Yoshiaki Miki and Yuya Yamashita
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464, *Japan*

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Introduction

Titanium deposited alumina and silica showed greatly enhanced reactivity in the polymerizations of styrene and α-methylstyrene compared with the corresponding binary solid acids prepared by the calcination of the mixed hydroxides obtained from the mixed metal chlorides. The reactivity enhancement is apparently caused by efficient Al–O–Ti or Si–O–Ti bond formation through the chemical reaction of titanium chloride with the hydroxyl groups on the alumina or silica surface. The reactivity of titanium deposited alumina is almost comparable with that of acid clay. However, aluminium deposited titania showed much lower reactivity than the above titanium deposited alumina. This is because of the much lower concentration of hydroxyl groups on the titania surface.

In the 1960's, considerable interest was devoted to solid acids as polymerization catalysts stimulated by the rapid growth in the heterogeneous olefin polymerizations which were initiated in the 1950's. Gaylord and Mark reviewed the progress in 1950's[2]. Although the reduced form of the transition metals are mainly used in the Ziegler systems, oxide forms are also used as catalysts; chromium oxide on silica or alumina, and nickel oxide on alumina or carbon, and molybdenum oxide on alumina, in Phillips on Standard Oil processes. The combination of two or more metal oxides usually shows higher acid strength than the individual metal oxide[3]. These solid acids are also used as the polymerization catalysts for vinyl ethers. Mosley[4] and Lal *et al.*[5,6] reported the stereospecific polymerizations of alkyl vinyl ethers giving crystalline polymers. The combination of ferric sulphate and sulphuric acid used by Lal[6] is thought to be a superacid[7-9].

The so called 'highly active Ziegler, Phillips or Standard catalysts' were developed extensively in the last decade, and new interests have arisen on the highly active supported catalyst systems.

We reported the dimerization of α-methylstyrene by binary metal oxides[10]. Although binary Al_2O_3–TiO_2 (molar ratio of Al to Ti is 9:1), which showed the highest reactivity among the binary solid acids examined, catalysed the dimerization of α-methylstyrene, it was slightly active in the polymerization of styrene.

Meanwhile, it is known that the hydroxyl groups on silica or alumina surface can react with various reagents[11-17]. Kol'tsov *et al.* reported the reactions of various kinds of metal chloride vapours with silica[18-21]. Recently, Soga *et al.* reported the titanium chloride deposited silica for the polymerization catalyst of propylene[22].

There are some reports on the polymerization of styrene by using mineral clay as the catalyst[23-27]; in these studies attention was mainly directed toward the initiation reaction. Recently, considerable interest has been shown in the oligomerization of styrenes. Higashimura *et al.*[28-30] and Hamaya *et al.*[31-32] reported the oligomerization of substituted styrenes. However, there is no report on the selectivity of the isomer distribution in oligomer fractions by solid acids.

We also have been interested in getting highly active catalysts for the cationic polymerization using deposited catalyst systems. In this communication, we would like to describe the effect of the preparation method of the deposited metal oxides on the reactivity in the polymerization of styrene and α-methylstyrene, and selectivity of the isomer distribution in the oligomerization of α-methylstyrene.

Experimental

Several kinds of deposited binary metal oxides, namely titanium deposited alumina or silica, and aluminium deposited titania or silica were prepared. Alumina, titania, and silica were calcined at 500°C or 300°C for 4 h under nitrogen atmosphere.

Firstly, titanium chloride was reacted with alumina prepared from aluminium isopropoxide or triethylaluminium by hydrolysis and calcination (in case of triethylaluminium, equimolar amounts of water were used in the hydrolysis), or silica prepared from sodium silicate by neutralization, washing, and calcination, under a constant nitrogen stream (25 ml min^{-1}) at 180°C until no more titanium chloride reacted (about 4 h of reaction, the reservior of titanium chloride was maintained at 30°C). The titanium chloride deposited system was evacuated at 180°C for 4 h in order to remove the remaining titanium chloride and hydrogen chloride (TiCl type catalysts). The TiCl type catalysts thus prepared were hydrolysed with water vapour under a constant nitrogen stream (25 ml min^{-1}) at 180°C for 3 h, and the resulting systems were evacuated at 180°C for 4 h to remove the remaining water and hydrogen chloride (TiOH type catalysts, TiOH–Et type from triethylaluminum).

Secondly, aluminium chloride vapour was reacted with titania under a constant nitrogen stream under a reduced pressure of 3 mm Hg at 250°C for 6 h. The aluminum

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* Reference 1

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Table 1 Polymerization of α-Methylstyrene by various catalysts[a]

No.	Catalyst	Time (h)	Wt % of Dimers and Oligomers PT–1	PT–2	IND	Olg	Yield (%)
1	Al_2O_3(300, –)[b]	18	–	–	–	–	trace
2	Al_2O_3(500, –)	20	–	–	–	–	0.3
3	Al_2O_3(500, Et)[c]	90	–	–	–	–	trace
4	Al_2O_3(300, TiCl)	18	2	0	73	25	100
5	Al_2O_3(500, TiCl)	18	2	0	73	23	98
6	Al_2O_3(300, TiOH)	18	48	20	6	22	96
7	Al_2O_3(500, TiOH)	18	43	16	2	31	92
8	Al_2O_3(500, TiOH, HCl)[d]	20	–	–	–	–	trace
9	Al_2O_3(500, TiOH–Et)[c]	20	–	–	–	–	trace
10	SiO_2 (300, –)	18	–	–	–	–	0
11	SiO_2 (300, TiCl)	18	20	8	21	19	68
12	SiO_2 (500, TiCl)	18	26	10	37	25	98
13	SiO_2 (300, TiOH)	18	4	0	0	1	5
14	SiO_2 (500, TiOH)	18	29	2	0	10	41
15	SiO_2 (500, AlOH–Et)[e]	20	2	0	0	0	2
16	TiO_2 (500, –)	90	–	–	–	–	0
17	TiO_2 (500, AlCl)	20	8	0	13	32	53
18	Al_2O_3–(TiO_2 (9:1)[f]	90	40	23	2	25	90
19	Al_2O_3(500, TiOAlCl)[g]	20	4	1	36	42	83
20	Al_2O_3(500, TiOAlOH)	20	6	1	0	0	7
21	Al_2O_3(500, TiOAlOH–Et)[h]	20	–	–	–	–	0
22	Al_2O_3(500, TiOAlOAlOH–Et)[i]	20	2	0	0	0	2
23	SiO_2 (500, AlOTiOH–Et)[j]	20	7	0	0	2	9
24	$AlCl_3$[k]	20	0.2	0	8	15	23.2
25	$TiCl_4$[k]	0.3	29	20	21	30	100
26	Acid clay[l]	1	4	2	65	23	94

[a] 30°C bulk condition with 5 wt % catalyst
[b] The temperature of the calcination of the support and the type of the catalyst are given in parentheses
[c] Triethylaluminium was used in the preparation of alumina
[d] The catalyst system 7 was washed with 1N HCl on a glass filter several times, dried and evacuated at 180°C for 4 h
[e] Triethylaluminium was reacted with SiO_2 in boiling hexane, and the resulting system was hydrolyzed and evacuated at 180°C for 4 h
[f] Prepared by the calcination of binary metal hydroxide by the hydrolysis of the mixture of metal chlorides at 500°C
[g] Aluminium chloride was reacted with the catalyst system 7
[h] Triethylaluminium was reacted with catalyst system 7, hydrolyzed by water vapour and evacuated at 180°C for 4 h
[i] Triethylaluminium was reacted with the catalyst system 21, hydrolyzed and evacuated at 180°C
[j] Titanium chloride was reacted with the catalyst system 15, hydrolyzed and evacuated at 180°C
[k] 0.6 mol % to monomer was used
[l] Taken from ref 2

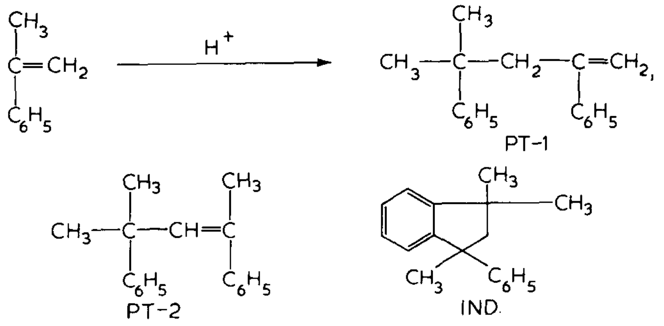
chloride deposited system was evacuated at 250°C for 4 h to remove the remaining aluminum chloride and hydrogen chloride (AlCl type catalysts). The AlCl type catalysts thus prepared were hydrolysed with water vapour under a constant nitrogen stream (25 ml min^{-1}) at 180°C, and the resulting systems were evacuated at that temperature for 4 h in order to remove the remaining water and hydrogen chloride (AlOH type catalysts).

Thirdly, triethylaluminium was reacted with silica and titania in boiling hexane under a nitrogen atmosphere, the aluminium deposited systems were hydrolysed with water and evacuated at 180°C for 4 h (AlOH–Et type catalysts). In some cases, triethylaluminum was reacted with Metal–OH type catalysts and hydrolysed alternatively to obtain layered deposited solid acids.

The concentrations of titanium of TiOH and TiOH–Et type catalysts and those of aluminum of AlOH type and AlOH–Et type were roughly estimated by chelate titration to be 0.3–1.5 mmol/g catalyst and 0.1–0.5 mmol/g catalyst, respectively. The accurate analysis of the amount of deposited metal is now under way.

Results and Discussion

α-Methylstyrene was shown to give three isomeric dimers by binary metal oxides[10].



[and oligomers (Olg)] [and oligomers (Olg)]

The results of the polymerization of α-methylstyrene are shown in *Table 1*. Deposition of titanium on alumina or silica enhance the reactivity of the catalyst systems. The TiCl types tend to produce the indan dimer (Nos. 4, 5, 11, 12). The TiCl type alumina predominantly gave IND and oligomers (Nos. 4, 5). The TiOH types gave unsaturated dimers. TiOH type alumina gave both PT-1 and PT-2 (Nos. 6, 7), contrary to this, TiOH type silica predominantly gave PT-1 (Nos. 13, 14). As PT-2 was shown to be an isomerized product from PT-1 by relatively strong acid sites[10], it can be presumed that TiOH type Al_2O_3 is a stronger acid than the TiOH type SiO_2, and isomerized PT-1 to PT-2. Aluminium deposited systems showed

Table 2 Polymerization of α-Methylstyrene by supported catalysts on alumina[a]

No.	Catalyst	Time (h)	Conversion (%)
1	Al_2O_3(500, TiOH)[b]	0.5	48
2	Al_2O_3(500, TiOH)[b]	1.0	88
3	Al_2O_3–TiO_2(9 : 1)[c]	5.0	33
4	Al_2O_3–TiO_2(9 : 1)[c]	20	60
5	Al_2O_3–TiO_2(9 : 1)[c]	45	83

[a] 30°C, with 5 wt % of catalyst to monomer in bulk
[b] Contains 0.3 mmol of Ti per g of catalyst
[c] Contains 1.8 mmol of Ti per g of catalyst

Table 3 Polymerization of Styrene by various initiators[a]

No.	Catalyst	Time (h)	Conversion (%)
1	Al_2O_3	90	1
2	SiO_2	90	0
3	Al_2O_3–TiO_2(9 :1)	97	6
4	Al_2O_3(300, TiCl)	0.5	94
5	Al_2O_3(500, TiCl)	0.5	98
6	SiO_2(300, TiCl)	0.5	33
7	SiO_2(500, TiCl)	0.5	38
8	Al_2O_3(300, TiOH)	15	64
9	Al_2O_3(500, TiOH)	15	88
10	SiO_2(300, TiOH)	45	3
11	SiO_2(500, TiOH)	45	10
12	Acid Clay	0.5	80

[a] 30°C in bulk condition with 5 wt % catalyst

much lower catalytic activity. The AlCl type TiO_2 gave IND as the major product (No. 17). The AlOH type titania showed low activity giving only a trace of the product. The layered catalysts showed weak activity, except for No. 19 catalyst system which gave IND as the major product and gave PT-1 as the major component (Nos. 20, 21, 22, 23). This is consistent with the above speculation that stronger acid sites are responsible for the isomerization of PT-1 to PT-2. The treatment of these catalysts with dilute hydrochloric acid resulted in the loss of the catalytic activity (No. 8) (even with the catalyst system No. 7). These facts clearly indicate that the effective formation of Al–O–Ti or Si–O–Ti bonds on the surface of alumina or silica is essential in order to obtain highly catalytic active sites. Aluminum chloride and titanium chloride showed different activity and selectivity by deposition. Deposition of $TiCl_4$ on Al_2O_3 increased IND considerably compared with $TiCl_4$ itself (Nos. 4, 5, 25). Deposition on SiO_2 did not have as much effect on the selectivity (Nos. 11, 12, 25). Deposition of $AlCl_3$ on TiO_2 moderately increased the formation of PT-1 compared with $AlCl_3$ itself (Nos. 17, 24). The effect of the method of the preparation of the support on the catalytic activity is interesting. Deposited systems on Al_2O_3 from triethylaluminium showed much lower catalytic activity compared with those on Al_2O_3 from aluminium isopropoxide (No. 9). This is probably because the concentration of hydroxyl groups on the surface of the former alumina is much lower than the latter alumina. It is reported that the triethylaluminium–water system is even active in the polymerization of styrene when prepared with the monomer, however, no activity was seen when the prepared and aged catalyst was added to the monomer[33]. The hydroxyl groups may have been lost by calcination at 180°C.

The reactivity of the TiOH type Al_2O_3 was compared with that of the binary Al_2O_3–TiO_2. The results are shown in *Table 2*.

The ratio of initial activity calculated from the conversion of α-methylstyrene is approximately $(48/0.5 \times 0.3)/(33/5.0 \times 1.8) = 87$. Thus, the titanium deposited alumina (TiOH type Al_2O_3) showed about 100 times higher reactivity than the corresponding binary Al_2O_3–TiO_2 (9:1). As it was shown that the reactivity of TiOH type Al_2O_3 was very much enhanced, the polymerization of styrene was carried out using the system as an initiator. The results are given in *Table 3*.

Although the reactivity of the TiOH type Al_2O_3 and SiO_2 was lower than that of acid clay in the polymerization of styrene, both catalyst systems were sufficiently activated in order to polymerize styrene. Such activation was apparently caused by the effective chemical bond formation of Al–O–Ti or Si–O–Ti. Moreover, the TiOH type Al_2O_3 selectively gave unsaturated dimers among dimers in the polymerization of α-methylstyrene. This indicates that the active site of TiOH type Al_2O_3 is different from that of acid clay.

As shown above, simple synthetic deposited binary solid acid systems have been developed, showing considerably higher reactivity and different selectivity from acid clay in the polymerizations of styrene and α-methylstyrene. The detailed analyses of the catalysts are now in progress.

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Eutectic crystallization of poly(L-lactic acid) and pentaerythrityl tetrabromide

R. Vasanthakumari
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, *India*

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Introduction

Diluents (either low molecular weight compounds or other polymers) are known to modify the morphology, the rates of nucleation and growth of polymers[1-4]. Recently binary systems in which both the components crystallize simultaneously to give a eutectic solid have been studied with great interest. Carbonnel *et al.*[5] have studied binary systems containing polyester and a variety of low molecular weight crystalline diluents and recently crystallization and melting behaviour of polyoxymethylene and glutaric acid has been reported[6]. Smith and Pennings[7,8] have studied the morphology resulting from the eutectic crystallization of polyethylene and a number of diluents and the porous microstructure that remains after the removal of the low molecular weight diluent from the solidified eutectics.

It has been shown[9] that poly(L-lactic acid) of molecular weight $M_v = 1.5 \times 10^5$ forms a eutectic with the dendritic growing diluent, penetaerythrityl tetrabromide, the eutectic composition being 46% by weight of the polymer at the eutectic temperature of 422K and the removal of the diluent from the solidified eutectic produces porous material. Here the studies have been extended to determine the influence of molecular weight of the polymer on the eutectic forming system consisting of poly(L-lactic acid), PLLA and pentaerythrityl tetrabromide. Extensive work has been carried out on crystallization kinetics of homopolymers and copolymers whereas no work has been reported on the crystallization kinetics of eutectic mixtures. Thus the present work is concerned with (i) the systematic study of the influence of molecular weight on the eutectic system PLLA-pentaerythrityl tetrabromide (ii) the kinetics of isothermal crystallization of a eutectic mixture at different temperatures since this will provide information about the mechanism underlying the eutectic crystallization process.

Experimental

Samples of different molecular weight were obtained by cationic ring-opening polymerization[10] of (L-) dilactide (supplied by Boehringer and Sions, Ingelheim, Germany) using a catalyst, stannous octoate. The samples were stored over phosphorus pentoxide. Viscosity average molecular weight (M_v) was determined in chloroform at 25°C with an Ubbelohde viscometer using the relation[10]: $[\eta] = 5.45 \times 10^{-4}\ M_v^{0.73}$. The solvent employed for the eutectic crystallization of PLLA was pure pentaerythrityl tetrabromide. The polymer solutions (about 5 mg) of different compositions were heated 20°C above their melting points in sealed aluminium pans, kept for 30 min for homogenizing, quenched fast to 100°C and then scanned at the rate of 8°C $\min^{-1}$ using a Perkin Elmer DSC IB in order to obtain the melting thermograms. Similar experiments were carried out for PLLA samples of different molecular weight. Calibration of d.s.c. has been carried out using standard samples with melting point in the measured range of temperature.

PLLA used for eutectic crystallization kinetics study had molecular weight $M_v = 1.8 \times 10^5$. The eutectic samples (46% by weight of PLLA) of about 5 mg were heated 30°C above the melting point, cooled fast to the respective crystallization temperature and rates of isothermal crystallization were folltowed using the Perkin Elmer DSC IB with a high chart speed of 160 mm $\min^{-1}$.

Results and Discussion

As PLLA was prepared by cationic ring-opening polymerization, it contained a relatively small molecular weight distribution[10]. The thermal behaviour of the PLLA-pentaerythrityl tetrabromide mixtures was investigated by means of differential scanning calorimeter and the melting point-composition phase diagram of the above system was drawn for PLLA samples of different molecular weight. The melting points obtained for all the eutectic samples are not true equilibrium melting points but they correspond to that at the crystallization temperature, 100°C. The corresponding values of eutectic composition, C_E and eutectic temperature, T_E were determined from the phase diagrams. *Table 1* gives eutectic com-

Table 1 Values of eutectic composition and eutectic temperature for PLLA of different molecular weight

$[\eta]$	$M_v \times 10^{-5}$	C_E wt % of polymer at eutectic point	T_E (K) Eutectic temperature
1.85	0.68	50.00	421
2.45	1.00	49.34	421
3.3	1.50	46.0	422
3.8	1.80	46.1	422
4.9	2.60	45.45	422
6.1	3.5	45.21	423

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