

Synthesis of High-Molecular Weight Poly(trimethylene terephthalate) Catalyzed by MoO₃ Supported Al₂O₃-TiO₂ Catalysts

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ABSTRACT: Poly(trimethylene terephthalate) (PTT) is an excellent fiber materials. Although it was synthesized as early as 1940s, obtaining high-molecular weight PTT suitable for spinning is not easy due to no evident breakthrough in the catalysts for PTT synthesis. Patents and literatures disclosed a lot of the catalysts of preparing PTT, but which are more or less disadvantageous. Based on acid catalytic mechanism of PTT preparation, a series of solid acid as $x\%$ MoO₃/(50% Al₂O₃ – 50% TiO₂) (briefly written as $xM/(A - T)$, $x = 0, 10, 15, 20$ by weight) were prepared by sol-gel coprecipitation and wetting impregnation methods, and first used for PTT synthesis in this work. When 50% Al₂O₃ – 50% TiO₂ (briefly written as A – T) was supported by MoO₃ using wetting impregnation technique of (NH₄)₆Mo₇O₂₄·4H₂O aqueous solution, a lot

of Brønsted acid and Lewis acid sites were formed on $xM/(A - T)$ catalyst surfaces, which was confirmed by the characteristics of their NH₃-TPD (temperature programmed desorption). All the prepared catalysts were highly active ones toward synthesis of PTT. PTT with high-intrinsic viscosity (IV) was obtained in the presence of trace amount of the catalysts. IV ranging of the PTT synthesized from 0.66 to 0.95 dL g⁻¹ corresponds to weight average molecular weight (\overline{M}_w) from 49,197 to 73,004. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3401–3408, 2010

Key words: synthesis of PTT; MoO₃ supported Al₂O₃-TiO₂ catalysts; polycondensation; polyesters

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is an aromatic polyester synthesized from terephthalic acid (TPA) and 1,3-propanediol (PDO), which has intensely attracted the researchers recently^{1–3} because of its outstanding performances as synthetic fibers.^{4,5} In 1941, Calico Printers Ass Company⁶ successfully synthesized PTT via polycondensation of TPA and PDO, but PTT was not available production at a large scale due to expensive PDO till 1990s. With the rapid development of polyester industry, the inexpensive synthesis technologies of PDO have been

developed by several companies such as Shell, Dupont, and Degussa.

Conventional synthesis of PTT is carried out at high temperature and in high-vacuum reactive system as well as in the presence of valid catalyst. Highly active catalysts can decline remarkably the manufacture conditions of PTT with high-molecular weight. Generally, there are three kinds of different catalyst systems for synthesis of PTT to be disclosed in some patents, that is, (1) titanium-containing catalysts, which mainly include titanium dioxide, tetrabutyl titanate, tetraisopropyl titanate, ethylene glycol titanate, and so forth; (2) stannum serial, such as butyl stannic acid, butyltin tris(2-ethylhexanoate), stannous octoate, and so forth; (3) antimony serial, such as antimony oxide, antimony acetate, and so forth. In all these catalysts, the titanium-containing catalysts have demonstrated high activity for the synthesis of PTT. For example, Chen et al.⁷ disclosed the synthesis process of PTT from TPA and PDO in the presence of MoO₃/TiO₂-SiO₂, the resulting PTT exhibited superior properties such as high-intrinsic viscosity (IV) of 0.96 dl g⁻¹, end-carboxyl group of 13 mol t⁻¹, b^* yellow value of 0 and dipropylene glycol content of 1.08% (mol) relative to TPA; Kuo et al.² described preparation of PTT from 1,

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3-propanediol and TPA using ethylene glycol titanate as catalyst. The resulting polyester had the performances of $IV = 0.89$, end-carboxyl group = $26.77 \text{ meg kg}^{-1}$ and $b^* = 9.46$. In summary, titanium-containing catalysts are highly effective⁸ for synthesis of PTT.

Sol-gel coprecipitation technique for the preparation of catalyst is a preferred one, because it provides nearly homogeneous mixing effect among the compositions composing of the catalyst, furthermore, some bonds are possibly formed, and a large number of Brønsted acid and Lewis acid sites⁹ are produced in process of the preparation. Therefore, the catalyst with the excellent performances can be obtained by using sol-gel preparing technology. Moreover, the oxides supported by other assistant component can result in the increase of number of acidic sites on the supported catalyst surface. As a result, the supported catalyst shows highly effective catalytic activity in view of the reactions of acidic catalysis.

In this article, we report the MoO_3 supported Al_2O_3 - TiO_2 catalysts, which were used to synthesize PTT. As-synthesized PTTs have high IVs of 0.66–0.95 dl g^{-1} corresponding to weight average molecular weight (\overline{M}_w) of 49,197–73,004,¹⁰ the method of finding molecular weight is EG one. The catalysts have general formulation of $x\% \text{ MoO}_3 / (50\% \text{ Al}_2\text{O}_3 - 50\% \text{ TiO}_2)$ ($x = 0, 10, 15, \text{ and } 20 \text{ wt } \%$). They can be briefly written as A – T, 10 M/(A – T), 15 M/(A – T), and 20 M/(A – T) in this context.

EXPERIMENTAL

Materials

Titanium isopropylate was obtained from Shanghai Shunqiang Biology, China, aluminum isopropylate from Dalian Ruier Fine Ceramic, hexaammonium heptamolybdate tetrahydrate from Guangzhou Chemical Reagent Factory, Guangzhou, China. TPA was purchased from Shanghai Hushi Chemical Reagent Analysis Instrument, China, PDO was kindly presented by Henan Tianguan Enterprise Corporation Group, Henan Province, China. All reagents and reactants are of analytic grade.

Preparation of $x\% \text{ MoO}_3 / (50\% \text{ TiO}_2 - 50\% \text{ Al}_2\text{O}_3)$ catalysts

To a 150 mL of flask were charged 100 mL of isopropanol, 6.13 g (0.03 mol) of aluminum isopropylate, and 5.7 mL (0.019 mol) of titanium isopropylate. The content of the flask was magnetically stirred under flow of nitrogen. Thereafter, the reaction mixture was heated up to refluxing of isopropanol, and stirred for 2 h. Subsequently, the mixture was cooled naturally to ambient temperature; a white suspend-

ing liquid was obtained. The liquid was dropwise added to deionic water in a 300 mL of beaker under magnetic stirring. The reactants were stirred unceasingly for another 1 h, and then white sol was formed. After 12 h aging, the sol was treated with centrifugal operation at a rate of 7000 rpm, and washed with appropriate amount of deionic water. The treatment was repeated for three times. Finally, the white gel was obtained. The as-obtained gel of Al_2O_3 - TiO_2 hydrate was dried in an oven at 110°C for 12 h, which changed into white solid that was allowed to grind using ceramic mortar till the powder particles size is about 80 mesh. The white powder was divided into four parts, and three of the four parts were impregnated by appropriate amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ aqueous solution, respectively. Subsequently, the 50% $\text{TiO}_2 - 50\% \text{ Al}_2\text{O}_3$ impregnated by $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ aqueous solution were transferred into a drying oven at 110°C till the water was evaporated completely. The molybdate salt impregnating catalysts along with 50% $\text{TiO}_2 - 50\% \text{ Al}_2\text{O}_3$ were calcined in a muffle oven at 500°C for 6 h to afford green-yellowish powders except for 50% $\text{TiO}_2 - 50\% \text{ Al}_2\text{O}_3$ as white powder.

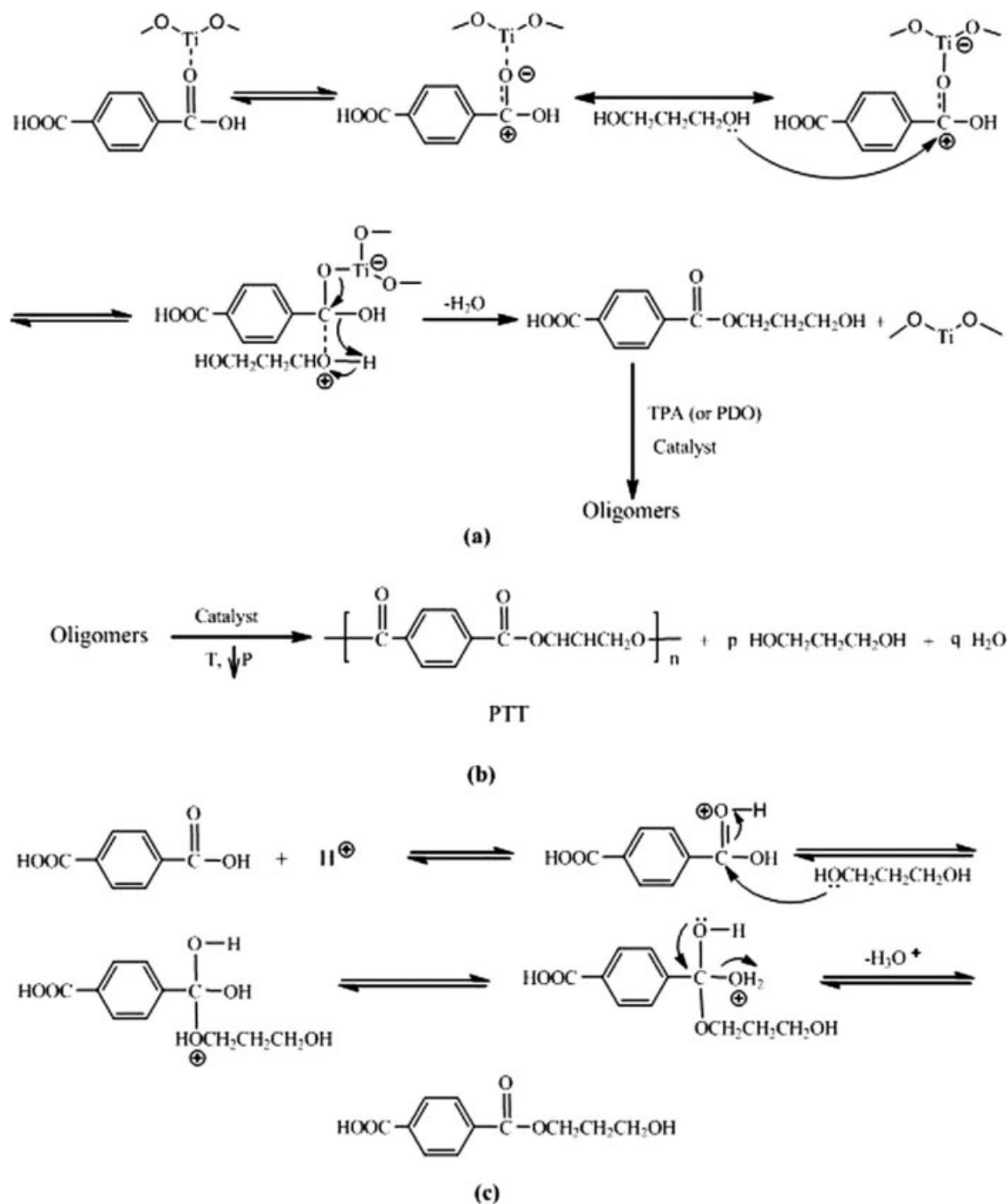
Characterization and instrumentation

X-ray diffraction patterns (XRD) of the catalysts were recorded on a D/max-III A diffractometer (Rigaku corporation, Japan) with a copper target as radiation source ($\lambda = 1.54056 \text{ \AA}$). The diffractometer was operated at 35 kV and 25 mA. Scanning profiles were recorded at $12^\circ (2\theta)$ per minute.

FTIR spectra for the catalysts were recorded on a Nicolet (Avatar 360) FTIR spectrophotometer using KBr pellet technique. About 15 mg of the sample was pressed (under a pressure of 2 tons cm^{-2}) into a self-supported wafer of 13-mm diameter.

Raman spectra were recorded at room temperature using microconfocal Raman spectroscopy combined Raman-IR microanalytical spectrometer equipped with a motorized x - y stage and autofocus. The spectra were generated by Ar laser excitation source; the samples were excited at 514.5 nm. The laser power was 9 mW on the sample surfaces. The spectral resolution of this apparatus is estimated to be $<0.5 \text{ cm}^{-1}$ for a slit width of 150 μm and a confocal hole of 300 μm .

X-ray photoelectron spectra (XPS) were acquired on a VG Microtech Multilab ESCA 3000 spectrometer using a nonmonochromatized $\text{MgK}\alpha$ X-ray source ($h\nu = 1253.6 \text{ eV}$) on the powder samples of catalysts. Selected spectra were recorded with $\text{AlK}\alpha$ X-ray ($h\nu = 1486.6 \text{ eV}$) to eliminate the overlap between different Auger and core levels. Base pressure in the analysis chamber was maintained in the range of $3\text{--}6 \times 10^{-10}$ torr. Energy resolution



Scheme 1 (a) Catalytic mechanism of TiO₂ moiety as Lewis acid in the catalysts for the esterification of TPA and PDO; (b) chain growth via transesterification with evolving PDO and/or esterification with evolving water among the oligomers; and (c) catalytic mechanism of Brønsted acid for the esterification of TPA and PDO.

of the spectrometer was set at 0.8 eV with MgK α (AlK α) radiation at a passing energy of 20 eV. The error in the binding energy (BE) value reported is ± 0.1 eV.

Measurement of acidity was performed by temperature programmed desorption of NH₃ (NH₃-TPD) using Chemosorb 2705 unit (Micromeritics Instrument, Amer) equipped with thermal conductivity detector. Typically, about 0.2 g of catalyst was

pretreated in flowing helium at 300°C for 2 h, cooled to 100°C and allowed to expose 10% NH₃ in helium with a flow rate of 70 mL min⁻¹ for 2 h, and subsequently the adsorbed NH₃ was purged with helium gas at the same temperature for 1 h to remove the physisorption NH₃. The chemisorption NH₃ was measured in flowing helium gas with the flow rate of 40 mL min⁻¹ from ambient temperature to about 900°C at the heating rate of 10°C min⁻¹.

TABLE I
Experimental Results for the Synthesis of PTT Using Different Catalysts Under Varying Conditions

Catalyst	50% Al ₂ O ₃ – 50% TiO ₂ (<i>w/w</i>)			10% MoO ₃ /50% Al ₂ O ₃ – 50%TiO ₂			
	Esterification	Prepolymerization	Polymerization	Esterification		Prepolymerization	Polymerization
				Stage I	Stage II		
Catalyst content (ppm)	75	–	–	100	50	–	–
<i>T</i> (°C)	226	236	256	226	226	220	256
Time (min)	390	48	260	210	60	30	160
Pressure (Pa)	0.1 MPa	250	20	0.1 MPa	0.1 MPa	75	18
IV(dL/g), (\overline{M}_w)		0.74, 49197				0.66, 40951	

Catalyst	15% MoO ₃ /(50% Al ₂ O ₃ – 50% TiO ₂)				20% MoO ₃ /(50% Al ₂ O ₃ – 50%TiO ₂)			
	Esterification		Prepolymerization	Polymerization	Esterification		Prepolymerization	Polymerization
	Stage I	Stage II			Stage I	Stage II		
Catalyst content (ppm)	70	40	–	–	40	22	–	–
<i>T</i> (°C)	226	226	236	256	226	226	236	256
Time (min)	255	60	40	180	300	74	40	240
Pressure (Pa)	0.1 MPa	0.1 MPa	50	22	0.1 MPa	0.1 MPa	50	25
IV (dL/g), (\overline{M}_w)			0.87, 63490				0.95, 73004	

The catalyst content means the titanium mass in the catalysts relative to terephthalic acid's by weight. Molar ratio of TPA to PDO equals to 1 : 1.8.

Synthesis of PTT

Typical synthetic procedure of PTT is given as following: To a 150 mL two-necked flask were charged with 8.31 g of TPA, 6.85 g of PDO (molar ratio of TPA to PDO = 1 : 1.8) and 5.4 mg of the catalyst. After the flask was purged thoroughly with N₂, the mixture was mechanically stirred, meanwhile, the temperature was increased to 226°C, and the esterification between TPA and PDO was performed for about 300 min. the conversion of the esterification was measured by the evolving water collected in a Dean-Stark. Following prepolymerization among the oligomers (see Scheme 1) was carried out in the same flask. The reaction temperature was increased to 236°C, and the pressure of the reactive system was decreased to about 50 Pa, prepolymerization was conducted for ~ 40 min. Subsequently, the pressure of the reaction system was further reduced to about 25 Pa, and the content of the flask was mechanically stirred for additional 240 min at 256°C. Finally, the resulting polyester was cooled to room temperature and taken out carefully from the flask. The experimental details and results as well as reaction conditions are listed in Table I.

Measurement of intrinsic viscosity of PTT

The IV of PTT was determined by a model 1835 Ubbelohde viscometer with a 0.5 dL g⁻¹ of the polyester in 1 : 1 (*w/w*) of phenol/1,1,2,2-tetrachloroethane at 25°C.

RESULTS AND DISCUSSION

Structure of the catalysts

XRD patterns of the catalysts calcined at 773 K for 5 h are shown in Figure 1. The intense sharp peaks of XRD patterns of A – T at 2θ = 25.2, 38.2, 47.6, 54.7, and 63.2° with relative intensities of 100, 51, 47, 44, and 27% represent the crystalline phase of anatase,^{11,12} some minor peaks at 2θ = 19.3, 32.1, 39.2, 45.5, 56.8, 60.8, and 76.1° are XRD patterns of γ-Al₂O₃, in addition, A – T shows that no 100% crystallinity can be observed from Figure 1(a). From XRD patterns of *xM*/(A – T) catalysts, no crystalline phase characteristic is shown, that is, both crystalline phases of anatase and γ-Al₂O₃ in A – T changed into amorphous phases after A – T was supported by MoO₃. This suggests damaging of crystalline phases of anatase and γ-Al₂O₃, which usually results in more acid sites and stronger acidity^{13,14} for the MoO₃ supported catalysts. A possible reason for the case is that lots of local imbalance charges are formed under assistant of impregnation compositions as MoO₃ and molybdate anions (these species can be confirmed by their Raman spectra, see following text). There is no crystalline phase of MoO₃ observed in the MoO₃ supported catalysts, which shows high dispersion of the MoO₃ on the surface of catalyst at amorphous phase.

Raman spectroscopies of A – T and *xM*/(A – T) are shown in Figure 2. In Figure 2(a), four peaks at 641, 518, 402, and 149 cm⁻¹ correspond to the emissions of various Ti-O stretching vibrating modes.^{15,16} In Figure

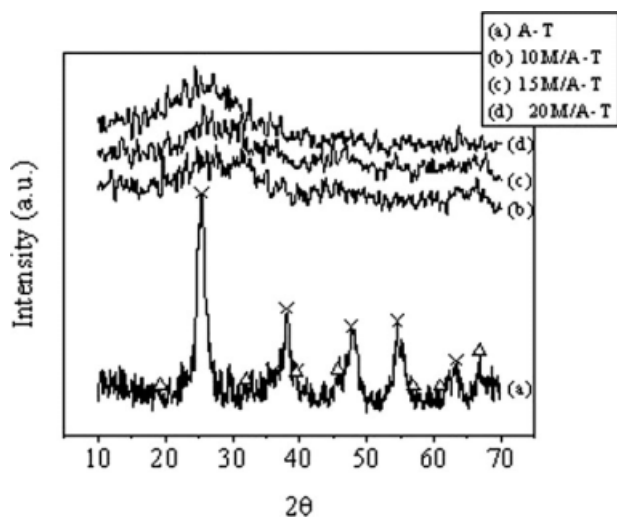


Figure 1 XRD patterns of the catalysts. In (a), “x” corresponds to those of anatase, and Δ to those of γ - Al_2O_3 .

2(b), 220 and 949 cm^{-1} bands are attributed to the bending vibration and symmetric stretching mode of $=\text{MoO}_2$ of the tetrahedral molybdate, respectively. While 846 cm^{-1} band is assigned to the asymmetric stretching mode of $\text{Mo}-\text{O}-\text{Mo}$ of octahedral molybdate.¹⁷ In Figure 2(c), the peaks of 862 and 954 cm^{-1} are the asymmetric stretching modes of $\text{Mo}-\text{O}-\text{Mo}$ of octahedral molybdate species and the symmetric stretching mode of $=\text{MoO}_2$ of tetrahedral molybdate, respectively. In Figure 2(b-d), the photoluminescence from MoO_3 is observed, intensity of the photoluminescence increases with the increasing MoO_3 content till no Raman emission peaks of various Ti-O stretching vibrating modes can be observed in Figure 2(d) due to mask of the strong photoluminescence emission. All these indicate there were MoO_3 and molybdate anion species on the surfaces of the MoO_3 supported catalysts. The pres-

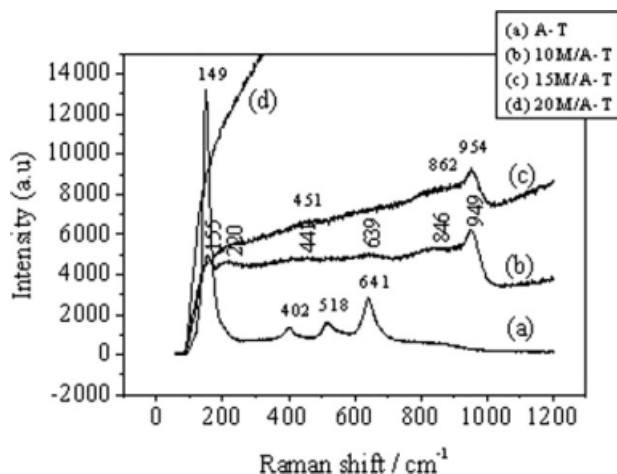


Figure 2 Raman spectra of A - T and $x\text{M}/(\text{A} - \text{T})$.

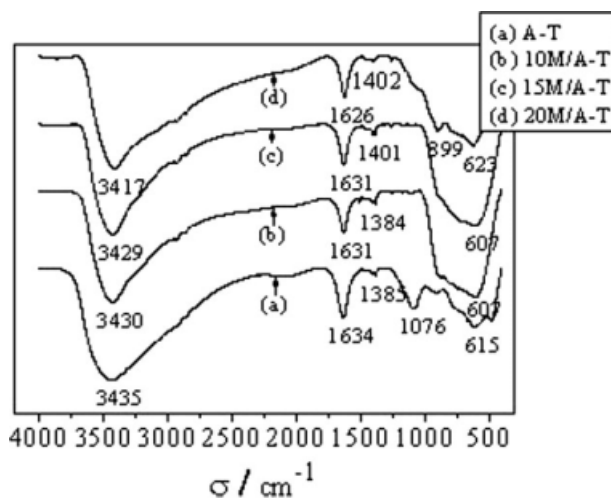


Figure 3 Characteristics of IR spectra for the catalysts. Some weaker bands at 1384–1402 cm^{-1} from bending vibrations of the O—H chemically bond to the metals of the catalysts, so the catalysts show behavior of Brønsted acid.

ence of these Mo-containing species increases greatly number of acid sites and acid strength for $x\text{M}/(\text{A} - \text{T})$ catalysts (see the profiles of NH_3 -TPD of the catalysts).

Figure 3 shows the FTIR spectra of the catalysts. The absorption peaks at 607, 623, 615, 899, and 1076 cm^{-1} are assigned to the stretching vibrations of $\text{Mo}=\text{O}$, $\text{Ti}-\text{O}-\text{Ti}$ and $\text{Al}-\text{O}-\text{Al}$ bonds.^{18–20} Again in Figure 3, two well-resolved peaks at about 3430 and 1630 cm^{-1} are assigned to stretching vibration and bending vibration modes of $-\text{O}-\text{H}$ group from the H_2O adsorbed on the catalyst surfaces. Some weaker bands at 1384–1402 cm^{-1} are tentatively assigned to bending vibrations of the $-\text{O}-\text{H}$ chemically bond to the metals of the catalysts by bridge bonds, that is, $\text{Al}^{\ominus}-\text{H}^{\oplus}-\text{O}-\text{Ti}$.^{21,22} So, the catalysts are Brønsted acid.

To confirm formation of $\text{Al}-\text{O}-\text{Ti}$ in 50% $\text{Al}_2\text{O}_3 - 50\%$ TiO_2 support catalyst, XPS for 50% $\text{Al}_2\text{O}_3 - 50\%$ TiO_2 (A - T), Al_2O_3 and TiO_2 (Al_2O_3 and TiO_2 were prepared under the same condition as that of A - T prepared) were conducted. Their XPS profiles are shown in Figure 4. $\text{Al}2\text{p}$ BE value of Al_2O_3 is 74.17 eV,^{23,24} $\text{Ti}2\text{p}_{3/2}$ and $\text{Ti}2\text{p}_{1/2}$ BE values of TiO_2 are 458.58 and 460.40 eV,²⁵ respectively. However, $\text{Al}2\text{p}$ BE value of A - T is 73.67 eV, which is 0.5 eV difference with 74.17 eV (experimental error is only ± 0.1 eV). This suggests that chemical environment of Al atom in A - T is difference with that of Al atom in Al_2O_3 , and indicates the formation of $\text{Al}-\text{O}-\text{Ti}$ in A - T. However, the $\text{Ti}2\text{p}_{1/2}$ and $\text{Ti}2\text{p}_{3/2}$ BE values of A - T are the same as that of TiO_2 . Presumably, the chemical environment difference of Ti atom in A - T and TiO_2 is not big enough to result in a difference of $\text{Ti}2\text{p}_{1/2}$ or $\text{Ti}2\text{p}_{3/2}$ BE values in A - T and TiO_2 .

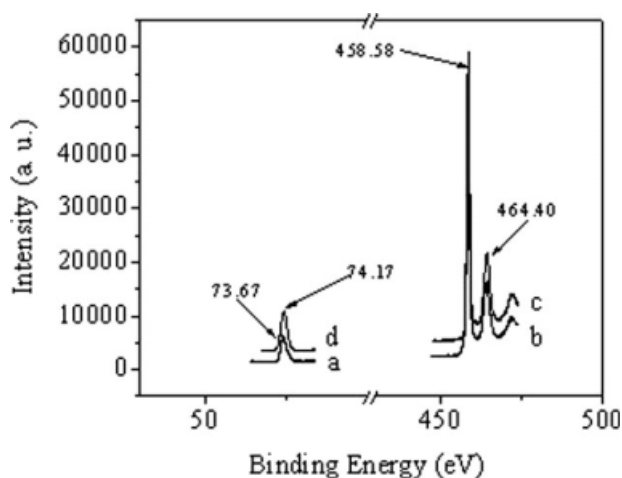


Figure 4 (a) Al2p XPS spectra of A – T, (b) Ti2p XPS spectra of A – T, (c) Ti2p XPS spectra of TiO₂, and (d) Al2p XPS spectra of Al₂O₃.

Structure of Al₂O₃-TiO₂, origin of Lewis acid and acidity of the catalysts

Based on the formation of Al–O–Ti in A – T and the theory of Tanabe⁹ on the origin of Brønsted acid and Lewis acid for compound-metal oxide, structure of 50% Al₂O₃ – 50% TiO₂ (wt %) is given in Figure 5. Al₂O₃ and TiO₂ units in A – T maintain their respective octahedral structures of pure Al₂O₃ and TiO₂. Alumina octahedral and titanyl octahedral in A – T are combined by the Al–O–Ti bond. It can be seen from Figure 5 that both Ti and Al locate at the center of the octahedral unit, respectively; Ti and Al atom have six ligands toward oxygen, while oxygen has four ligands toward Al or Ti in the supported catalyst. Based on the structure, the electric charge number of Ti in the Al₂O₃ – TiO₂ unit is +1. In this sense, the oxide possesses the characteristic of Lewis acid too because of Ti positive electronic property.

The acidic nature of A – T and $xM/(A - T)$ catalysts was determined using well-known NH₃-TPD technique. As shown in Figure 6, the NH₃-TPD patterns indicate the acidic sites are distributed uniformly in the form of strong acid in the four catalysts because all NH₃ desorption occurred at high temperatures. For instance, initial NH₃-desorption temperature for $xM/(A - T)$ catalyst was over 300°C, whereas the NH₃-desorption temperature for A – T catalyst was at nearly 400°C. The NH₃-desorption temperature for $xM/(A - T)$ catalysts is approximately divided into two stages, one of which is in the range of 300–500°C relating to desorption of the NH₃ being absorbed by Lewis acid sites, another of which in the range of 500–900°C relating to desorption of the NH₃ being absorbed by Brønsted acid sites.²⁶ Therefore, the MoO₃ supported catalysts are Lewis acid and Brønsted acid. It can be seen

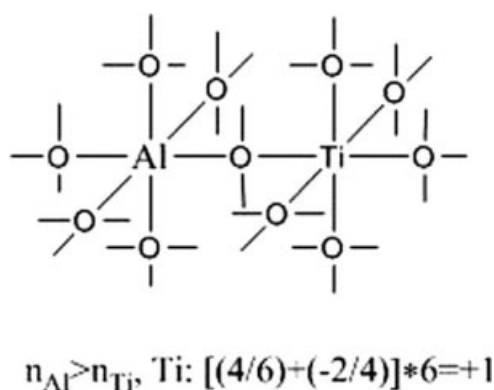


Figure 5 Structure of 50%Al₂O₃ – 50%TiO₂ (wt %), $n_{Al} : n_{Ti} \approx 3 : 2$ (mole ratio), based on the theory of Tanabe on the origin of Lewis acid, this oxide shows behavior of Lewis acid.

that the number of acidic sites in the MoO₃ supported catalysts ($xM/(A - T)$) is much more than A – T catalysts because NH₃-TPD patterns of $xM/(A - T)$ show much larger peak area for each one than that of A – T. In addition, the number of acid sites for the MoO₃ supported catalysts is different too. The number of acid sites for $xM/(A - T)$ catalysts from more to less is as 10 M/(A – T) > 20 M/(A – T) > 15 M/(A – T). The more acid sites and the stronger acidity for the catalysts are more advantageous to promote synthesis of PTT, as demonstrated by the experimental results.

Performance of the catalysts

It can be seen from Table I that the MoO₃ supported catalysts exhibited higher catalytic activities in terms of higher IV of the PTTs obtained in the presences of

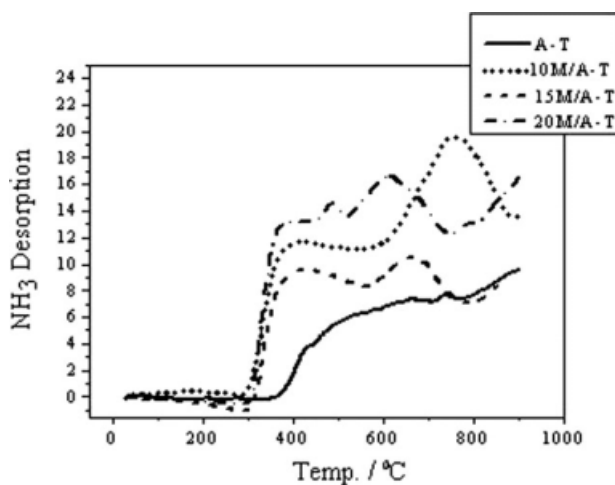


Figure 6 NH₃-TPD patterns of 50% Al₂O₃ – 50% TiO₂ (A – T) and $x\%$ MoO₃/(50% Al₂O₃ – 50% TiO₂) [$xM/(A - T)$, $x = 10, 15,$ and 20 wt %]. From this plot, the latter have more acid sites than the former. So, $xM/(A - T)$ enhance greatly catalytic esterification of terephthalic acid (TPA) and 1,3-propanediol (PDO) and subsequent polycondensation of the oligomers.

the MoO₃ supported catalysts than 50% Al₂O₃ – 50% TiO₂ catalyst, which is attributed to the MoO₃ supported catalysts having stronger acidity and more acidic sites than 50% Al₂O₃ – 50% TiO₂ catalyst. However, catalytic activity of 10% MoO₃/50% Al₂O₃ – 50% TiO₂ seemed to be lower than that of other MoO₃ supported catalysts according to the PTT obtained with lower IV in the presence of 10% MoO₃/(50% Al₂O₃ – 50% TiO₂). The main reason for this phenomenon is probably due to comparatively shorter time of the esterification using 10 M/ (A – T) to promote the esterification of TPA and PDO (see Table I), the conversion of the esterification was not high enough to meet the need that obtain PTT of high IV because chain growth of PTT only takes place among the oligomers but not between TPA and PDO in the polycondensation stage [see Scheme 1(b)]. Generally, to obtain PTT of high IV, over 92% conversion of the esterification is required in industries.²⁷

To test the activity of only MoO₃ for PTT synthesis, the typical procedure of esterification aforementioned was repeated but the catalyst was alone changed into MoO₃ under the same condition. The conversion of the esterification was about 60% based on generating water volume for 10 h. The polymerization could not be conducted because so low conversion of esterification. So, only MoO₃ has nearly no activity for synthesis of PTT. The reason is probably that MoO₃ is not Lewis acid and/or Brønsted acid.

Catalytic mechanism for Al₂O₃-TiO₂ promoting the synthesis of PTT

A proposed catalytic mechanism²⁸ for synthesis of PTT using Al₂O₃-TiO₂ as Lewis acid is depicted in Scheme 1(a). In process of the esterification, first, Ti atom of –O–Ti–O– moiety in Al₂O₃-TiO₂ acts as Lewis acid to coordinate with carbonyl group of TPA. A carbonyl group is activated as the formation of polar-charge C=O, then the polar-charge C=O is attacked nucleophilically by the –OH of PDO. Subsequently, the hydroxyl and proton binding as H₂O, H₂O, and –O–Ti–O– moiety are released, 4-((3-hydroxypropoxy)carbonyl)benzoic acid is generated. The esterification carries out continuously in the presence of the catalysts; a lot of oligomers are evolved. When conversion of the esterification reaches as high as 92%, afterward, polycondensation is conducted. Chain growth of PTT takes place in the stage of polycondensation among the oligomers. In the stage of polycondensation, the transesterification predominately occurs by evolving PDO but less esterification takes place by evolving water [see Scheme 1(b)]. The catalytic mechanism of Lewis acid for transesterification in the stage of polycondensa-

tion is similar to that of Lewis acid for esterification, that is, Lewis acid activates ester group but not carboxyl group in the process of transesterification. The mechanism that promotes Brønsted acid esterification of TPA and PDO is also described in Scheme 1(c).

CONCLUSIONS

The MoO₃ supported catalysts [x% MoO₃/(50% Al₂O₃ – 50% TiO₂) (x = 0, 10, 15, and 20, by weight)] were carefully synthesized by sol-gel coprecipitation, followed by wetting impregnation method. According to the various characterizations of the as-prepared catalysts, they showed the characteristics of Brønsted acid and Lewis acid. The catalysts showed high-catalytic activities for the synthesis of PTT. The activities were based on their strong acidity and a large number of acid sites in the catalysts. After 50% Al₂O₃ – 50% TiO₂ was supported by MoO₃, the number of acid sites and acid strength for the MoO₃ supported catalysts enhanced greatly. High-molecular weight PTT can be effectively synthesized using trace amount of the as-prepared catalysts. The synthesized PTT has IV as high as 0.95 dL g⁻¹ corresponding to weight average molecular weight (\bar{M}_w) of 73,004.

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