

DEVELOPMENT OF A NOVEL SOLID-TYPE MAO ACTIVATOR FOR OLEFIN POLYMERIZATIONS

Eiichi Kaji and Yujin Takemoto, Tosoh Finechem Corporation, Shunan, Yamaguchi, JP

Abstract

Methylaluminoxane (MAO) supported on SiO₂ (SiO₂/MAO) has been widely used as an effective activator for slurry and gas phase processes in homogeneous polymerization systems. Extensive research has been conducted to improve catalyst performances of a metallocene complex combined with SiO₂/MAO. Nevertheless, strong requirements to develop more effective solid activators than SiO₂/MAO still exist.

We have developed an original and unique solidified MAO (Solid MAO) produced by a self-aggregation method which is significantly different from previous experiments. The size of particles obtained can be well controlled by modifying the reaction conditions. Solid MAO having both functions of support and activator of a metallocene complex, shows high performances in olefin polymerization as compared to SiO₂/MAO.

Introduction

Methylaluminoxane ([-Al(Me)-O-]_n, MAO) which is produced by partially hydrolyzed compound of trimethylaluminum, is known as an effective activator of metallocene complex for olefin polymerization. In order to control polymer morphology, MAO has been generally supported on some solid compounds with controlled shape, such as SiO₂, Al₂O₃ and similar supports to form solid-type catalyst.

In case of SiO₂, it is necessary to calcinate it under defined conditions (time, temperature etc.) to control a concentration of hydroxyl group on the solid surface. In addition, MAO supported on SiO₂ generally shows lower activity compared to MAO itself. Higher activity of a catalyst is very important to reduce the amount of residue of inorganic compounds such as SiO₂ in the polymer produced because inorganic residue sometimes causes product defects such as fish eyes in polymer film. Higher activity also has a positive impact on the cost effectiveness of the catalyst system.

From these viewpoints, there have been some proposals to obtain MAO solidified without a support such as SiO₂ in order to enhance the activity. The following are representative examples.

(i) utilization of pre-polymerization [1]

(ii) utilization of MAO micelle in fluorinated organic solvent [2]

(iii) utilization of nonionic surfactant [3]

(iv) utilization of poor solvent [4]

First, we have carried out a supplementary experiment according to the literature [4]. Solidification using a poor solvent and MAO, gave aggregated particles with varying sizes as seen in SEM image (figure 1). Then, we tried to find a new method to make solidified MAO having higher particle uniformity than any methods reported so far.

I have originally found that solidified MAO particles can be obtained by heating of specific MAO solution without any additives and supports which showed extremely high activities for olefin polymerization when combined with metallocene complex. We named the resultant product Solid MAO for this novel solidified MAO. In this paper, our advances of Solid MAO development will be reported in detail.

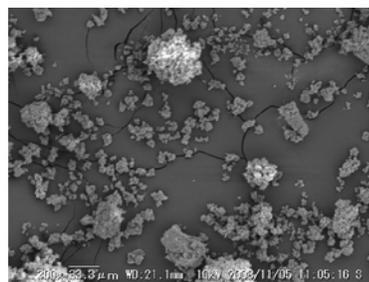


Figure 1. SEM image of solid-type MAO with varying particle sizes as produced according to the literature [4].

Experiments

All experiments have been conducted under dry nitrogen gas. The typical synthetic procedure is described hereunder.

1) Synthesis of MAO toluene solution for Solid MAO production [5]

Trimethylaluminum and dehydrated toluene were added into a flask with a condenser, a thermometer and a stirring device. The solution was cooled to around 15°C. Benzoic acid was added slowly to the solution so that the temperature range was controlled from 15 to 23°C. After this addition, the solution was heated at 60 to 80°C to form MAO structure.

2) Synthesis of Solid MAO [5]

MAO toluene solution obtained above was added into the similar reactor vessel and heated for 8hrs at 100°C under moderate stirring. Then, Solid MAO particles could be prepared by self-aggregation of MAO.

3) Preparation of metallocene complex supported Solid MAO catalyst

Metallocene toluene slurry was added to Solid MAO toluene slurry under moderate stirring for 24hrs at ambient temperature. Zr content and Al content in the catalyst prepared were quantitatively analyzed by an induced coupled plasma measurements of the hydrolyzed sample.

4) Ethylene polymerization

Dehydrated hexane was added into an autoclave reactor with a thermometer and a stirring device. Then, triethylaluminum as a scavenger was added. After ethylene replacement, the catalyst was added. The polymerization was started at 70 °C to pressurize to 0.7MPa by ethylene gas and conducted for 1hr at the temperature.

Results and Discussions

1) Preparation of Solid MAO

MAO itself is almost insoluble in aromatic solvents like toluene. This means that MAO shows solubility in some solvents by coordination of trimethylaluminum. Taking this into consideration, a hypothesis was built that MAO solution having less residual trimethylaluminum, would be suitable for Solid MAO production. So, we have tried to prepare Solid MAOs by using MAO solutions with different Al/O molar ratio. The SEM images of Solid MAOs prepared by using various MAO solutions are shown below.

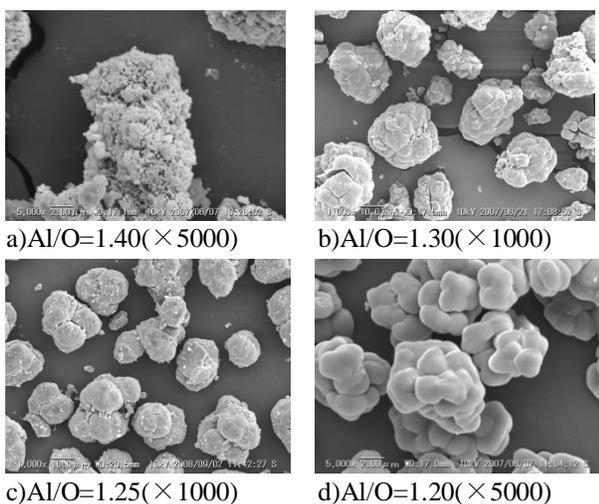


Figure 2. SEM images of Solid MAOs prepared by using various MAO solutions with different Al/O molar ratios.

As shown in the SEM images, the Solid MAO particle structures changed drastically. As Al/O molar ratio was decreased, the uniformity of Solid MAO particle could be improved. According to the results, we believe that MAO solution with decreased trimethyl-aluminum content is suitable for Solid MAO production because residual trimethylaluminum might be an inhibition factor for solidification of MAO.

2) Results of ethylene polymerizations using metallocene supported Solid MAO catalysts

The Solid MAO (6.1µm, Al content 41wt% in solid) base catalysts with various metallocene complexes were prepared and those catalytic activities were evaluated for ethylene polymerization. The results are shown in table 1.

Table 1. Results of ethylene polymerizations using Solid MAO base catalysts.

Metallocene complex	Activity, kg/g-cat · hr	BD* ¹ , g/cc
<i>rac</i> -Et(Ind) ₂ ZrCl ₂	9,000	0.39
Ind ₂ ZrCl ₂	9,000	0.37
(1,3-Me ₂ Cp)ZrCl ₂	6,300	0.41
(<i>n</i> BuCp) ₂ ZrCl ₂	12,000	0.39
Ref.* ²	1,100	0.34
<i>rac</i> -Et(Ind) ₂ ZrCl ₂		

*1 : Bulk density of polymer, *2 : SiO₂/MAO used (Al content 13.9wt% in solid)

It was concluded from this table that Solid MAO base catalysts showed higher activities and BDs than that of SiO₂/MAO. The aluminum content in Solid MAO was almost 3 times higher than SiO₂/MAO. But taking that difference into consideration, Solid MAO still showed higher activity.

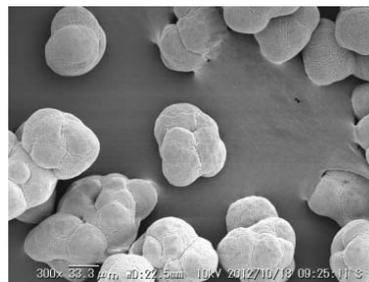


Figure 3. SEM image of polymer obtained by using *rac*-Et(Ind)₂ZrCl₂ supported Solid MAO catalyst shown in table 1 (x300).

SEM image of polymer particles is shown in figure 3. As understood in this image, the polymers seem to have replicas of Solid MAO particles. Additionally, it was recognized that the polymer particles produced have high homogeneity. Neither fine particles nor coarse particles are observed.

Solid MAO particle size can be well controlled by changing some solidification conditions like agitation speed. As usually observed, Solid MAO catalytic activities also decreased as the particle size increases. The results are shown in figure 4 (conventional, blue line). We have found a novel solidification procedure which gave Solid MAO that maintained high activity even with increased particle size (improved, red line). The detailed procedure can be reported after the publication of the patent. It is noteworthy that metallocene catalyst supported on Solid MAO by the improved procedure gives ethylene polymer with high BD. This means that structure and active sites of Solid MAO can be changed by the solidification procedures.

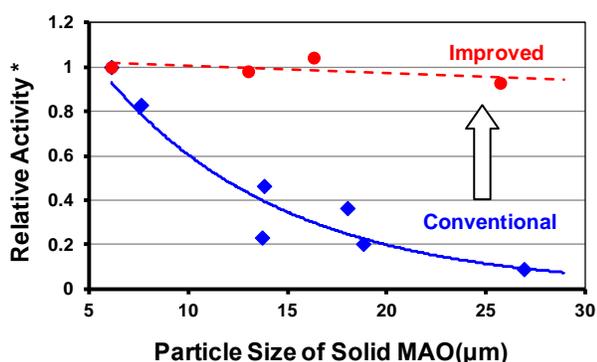


Figure 4. Relationship between particle size of Solid MAO and relative activity showing maintenance of high activity with increased particle size with the improved procedure.

*Activity of Solid MAO for that of 6.1µm in a diameter.

3) Some analyses of Solid MAOs

3-1) BET analyses

BET analyses of Solid MAOs were conducted using N₂ gas to understand the structure of Solid MAO. The results of relative surface area and micropore volume are shown in table 2.

Table 2. Results of BET analysis of Solid MAO.

Average particle diameter, d(50), µm	Relative surface area, m ² /g	Pore volume, cm ³ /g
5.7	475	0.26
7.6	484	0.28
14.2	472	0.25
20.0	382	0.21
30.0	424	0.23

From this table, the relative surface areas of Solid MAOs were around 350 to 500m²/g and its pore volume were around 0.2 to 0.3cm³/g. These results showed that Solid MAOs tested have large specific surface area comparable to SiO₂ normally used as an inorganic support and smaller pore volume than SiO₂.

3-2) Solid State NMR measurements

We have conducted solid state NMR analyses of Solid MAO and SiO₂/MAO to find any differences. The results are shown in figure 5 and 6.

In both solid-type MAOs, there was one peak derived from methyl groups of MAO having the same chemical shift (around -5ppm). It was considered that these methyl groups were deemed to be in similar environments by NMR measurement. The strength of peaks could reflect aluminum contents in the solids. But there was no difference among the samples due to the same circumstances of methyl groups in the solids.

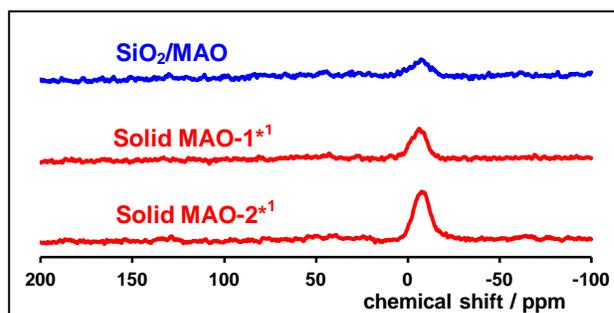


Figure 5. ¹³C CP/MAS NMR spectra of Solid MAO and SiO₂/MAO showing the -5 ppm shifts from MAO methyl groups.

*1 : Al content in Solid MAO-2 was higher than Solid MAO-1.

²⁷Al MAS NMR spectra of Solid MAOs and SiO₂/MAO were also measured. The result shows in figure 6. There were two peaks (around 35ppm and -15ppm) in SiO₂/MAO, whereas a single peak (around -4ppm) in Solid MAO. We currently consider that four coordinated and six coordinated Al sites exist in SiO₂/MAO. In contrast, six coordinated Al sites mainly exist in Solid MAO. We are continuing examination of the structure of active sites on Solid MAO in greater detail.

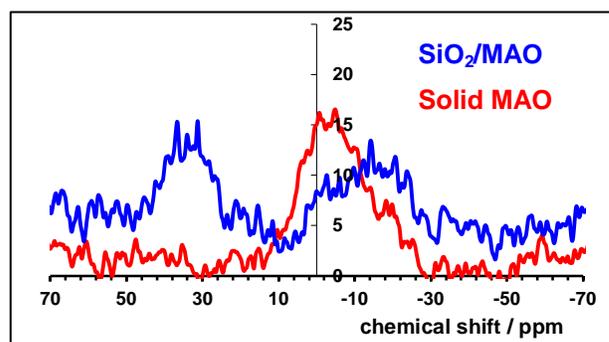


Figure 6. ²⁷Al MAS NMR spectra of Solid MAO and SiO₂/MAO indicating coordinated Al sites.

3-3) TEM analysis

We have measured TEM images of Solid MAO to obtain some information on primary particles. The results are shown in figure 7 and 8.

From figure 7, it seems that Solid MAO is composed of aggregate of small primary particles and the sizes of the primary particles are estimated about 15 to 30nm. In addition, we have found new results on Solid MAO structure from further detailed TEM observation. That is, some lattice patterns were found in the primary particles of Solid MAO in TEM image as you can see in the red circles of figure 8. Most parts of Solid MAO were non-crystallized solid which did not have any lattice pattern (figure 9). At first, I supposed that these lattice patterns might be derived from crystallized MAO itself. As far as I know, there is no report on crystallized MAO. So, we have examined to give light on the structure having lattice patterns shown here.

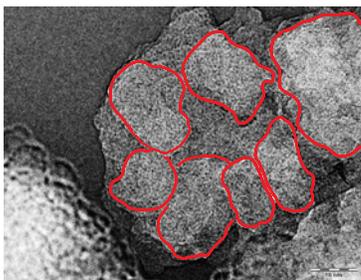


Figure 7. TEM image of Solid MAO-1($\times 300,000$).

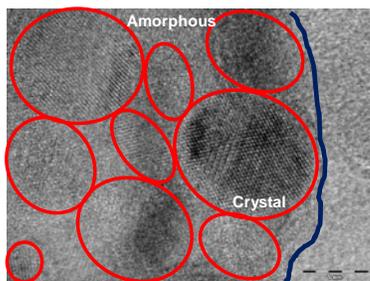


Figure 8. TEM image of Solid MAO-1($\times 500,000$).

*Deep blue line shows a border of Solid MAO particle and a supporting film for TEM measurement.

To confirm what the existence of lattice patterns in Solid MAO means, the electron diffraction (ED) pattern was simulated from the lattice pattern and compared to that of some known compounds. As a result, it was concluded that the ED pattern of alumina with corundum structure was identified to simulated ED pattern of crystal phase in Solid MAO. This means that alumina structure exists in Solid MAO. The existence of alumina structure in Solid MAO is thought to enhance the strength of this solid-type activator.

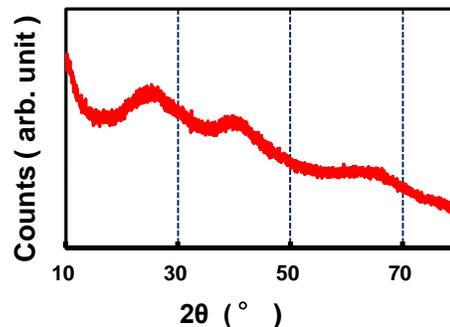


Figure 9. XRD measurement of Solid MAO.

Conclusions

Metallocene catalysts supported on Solid MAO showed higher activity than SiO_2/MAO base catalyst in ethylene polymerization and also gave good morphology of polymer produced. In addition, we have found a novel solidification procedure to obtain larger size Solid MAO showing high activity and gives polyethylene with high BD.

There are still some unknowns to elucidate on Solid MAO structure and its active sites. But it is assumed that Solid MAO base catalyst might have a different active site from one of SiO_2/MAO base catalyst from the data of ^{27}Al MAS NMR spectroscopy. In addition, the existence of alumina structure in Solid MAO was found by TEM analyses and may contribute to the formation and performances of Solid MAO.

We continue exploring Solid MAO to elucidate the structure and to enhance the catalytic performance.

Acknowledgements

We would like to thank Michael East and Steve White for helpful discussions to prepare the manuscript.

References

1. S.P. Diefenbach, U.S. Patent 6,730,758 (2004).
2. L. Resconi, P. Castro and L. Huhtanen, E. Patent 2,383,299 (2011).
3. B. Lu, J. Wang, X. Hong and Z. Jing, J. Patent 9216908 (1997).
4. M. Kioka and N. Kashiwa, J. Patent H07-042301(1995).
5. E. Kaji, E. Yoshioka, U.S. Patent 8,404,880 (2013).