TOSOH FINECHEM CORPORATION

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

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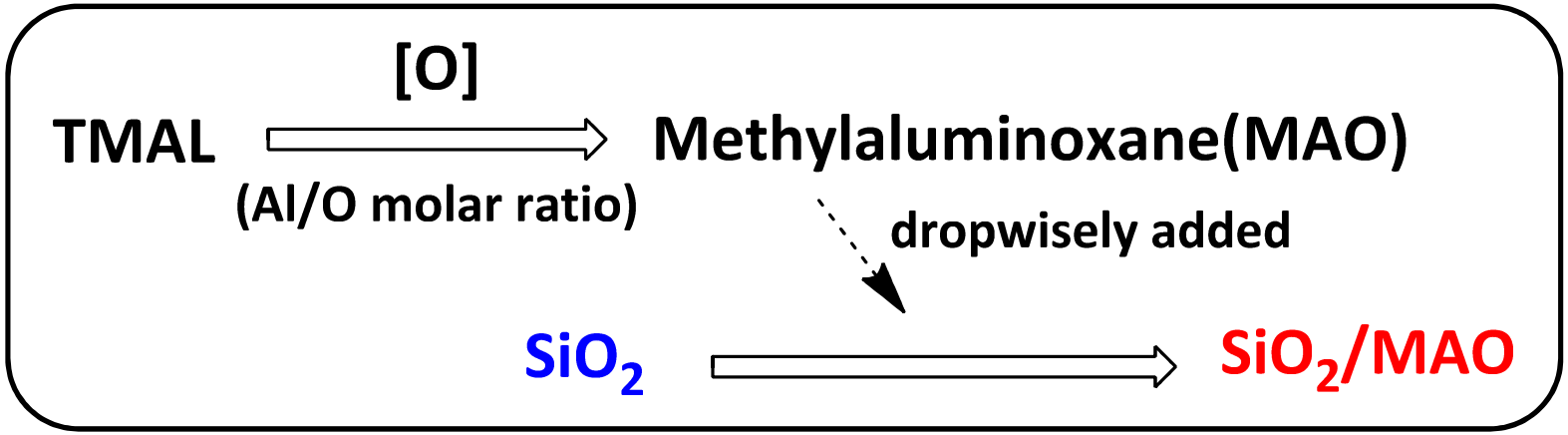
Conventional Solid-type Activator



- SiO_2 has usually been used to control the morphology of solid activator.
- The amount of hydroxyl-group on SiO_2 surface should be controlled.
- MAO supported on SiO_2(SiO_2/MAO) shows lower activity than that in homogeneous polymerization.

Contents of This Presentation

i) Solid-type MAOs without supports

ii) Preparation of Solid MAO

This Work

iii) Performances of Solid MAO in ethylene polymerization

iv) Analytical evaluations of Solid MAO

v) Summary

Proposals for Solid-type MAO without Supports

Utilization of

- Pre-polymerization [1)]
- MAO micelle in fluorinated organic solvent [2)]
- Nonionic surfactant [3)]
- Poor solvent [4)]

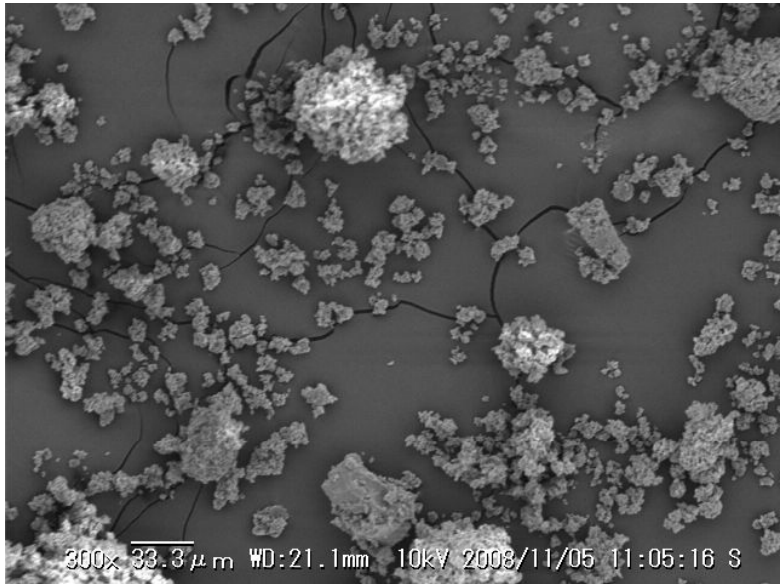
1) S.P. Diefenbach, U.S. Patent 6,730,758 (2004).

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)

Utilization of Poor Solvent by The Patent



SEM Image of solid-type MAO(× 300)

- Solidification yield 63.5%-Al
- d(50) 22.2μm
- Specific surface area 264m^2/g
- Solubility*(@25℃)

  8.3mol%-Al (n-hexane)

  23.6mol%-Al (toluene)

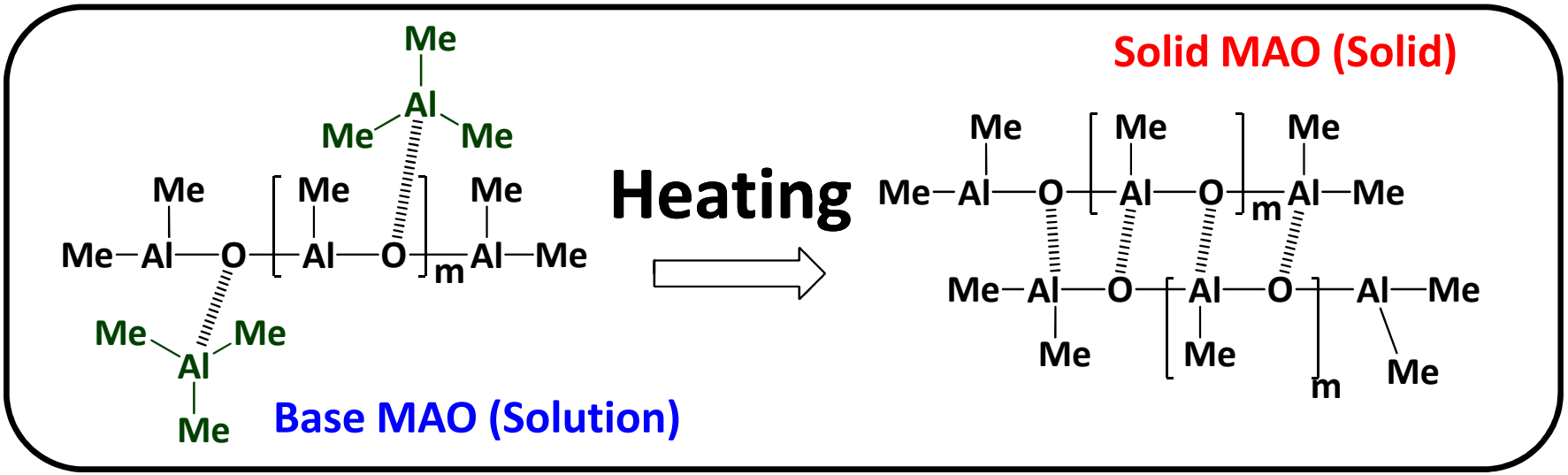
*Solid 2g in 50ml for 2hr

Procedure according to the patent :

Decane added to MAO toluene solution → Toluene evaporation → Filtration

Concept for Solid MAO

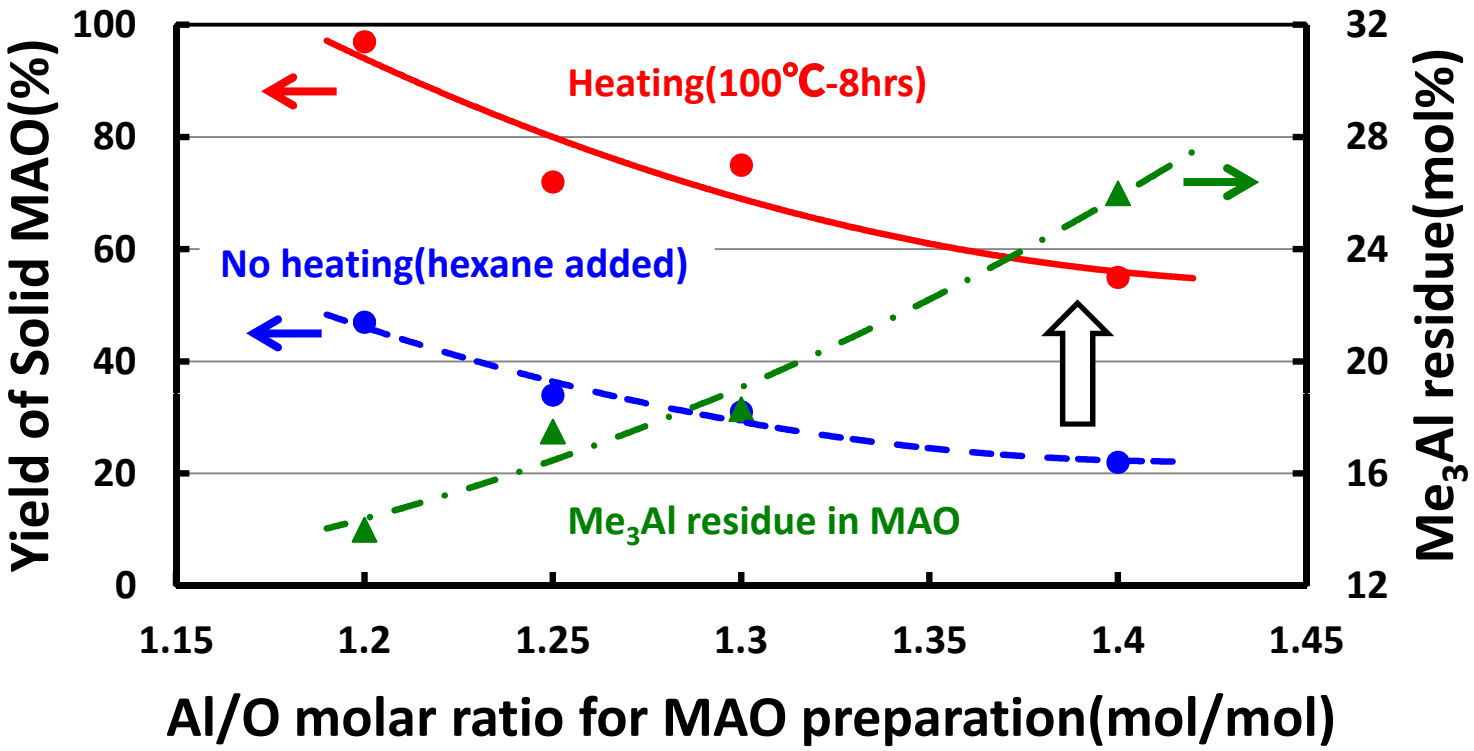
MAO self-aggregation based on Al⇔O affinity



Key :

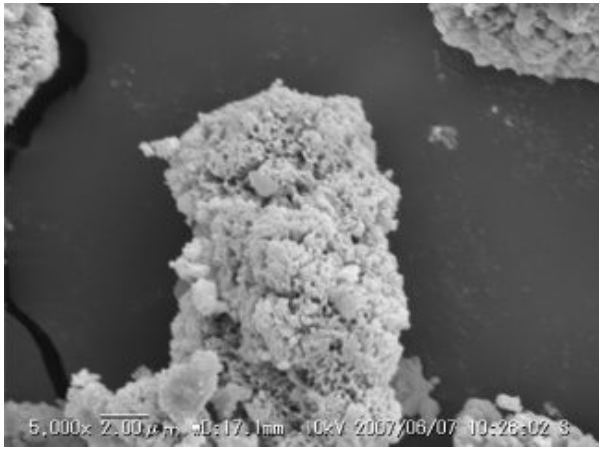
- **A positive utilization of MAO gelation.**
- **Necessary to control Me_3Al content.**

Solid MAO Preparation-1
-Effect of Al/O Molar Ratio-

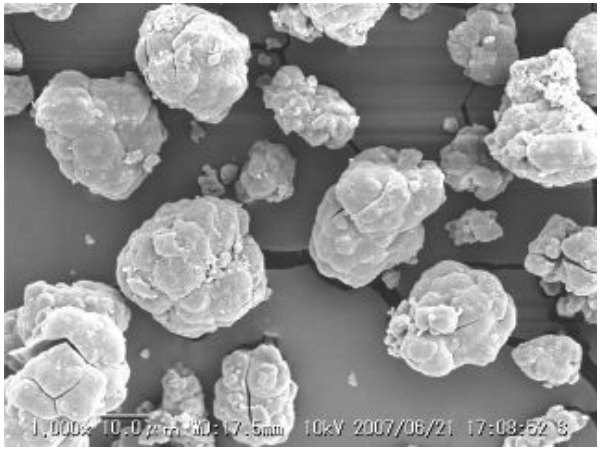


- Me_3Al residue showed a high level of effectiveness in the yield.
- Heating of MAO solution was an effective method to form Solid MAO.

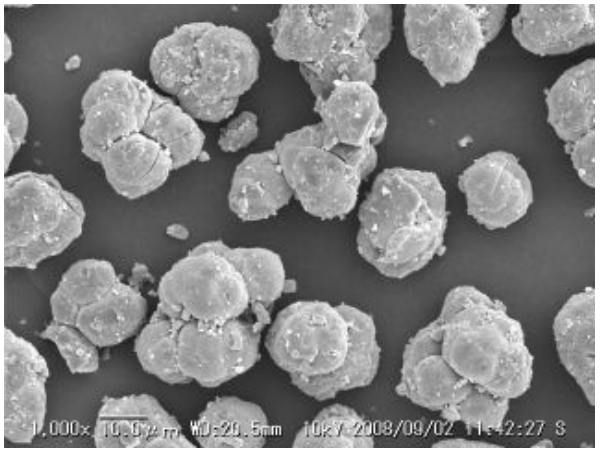
Solid MAO Preparation-2
- Effect of Al/O Molar Ratio -



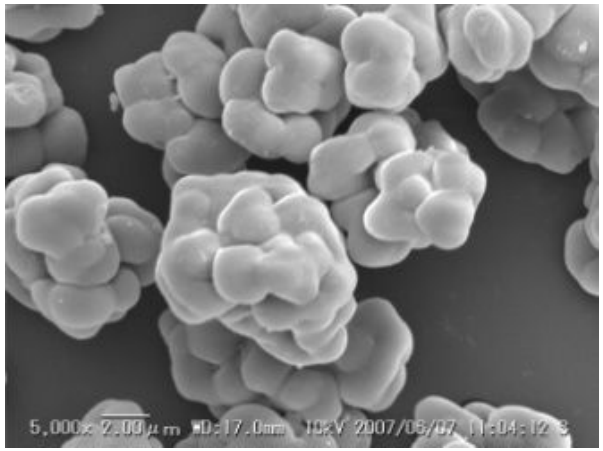
Al/O=1.40
(×5000)



Al/O=1.30
(×1000)



Al/O=1.25
(×1000)

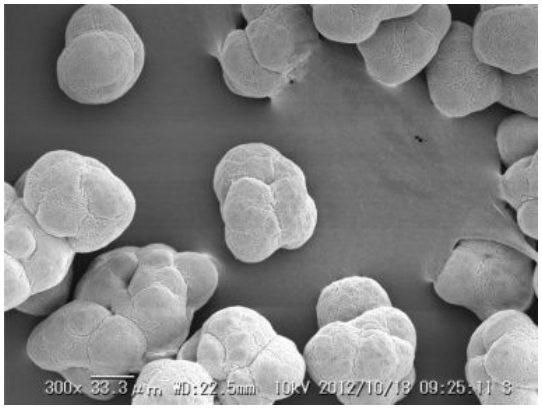


Al/O=1.20
(×5000)

- As Al/O molar ratio increased, Solid MAO homogeneity increased.

Results of Ethylene Polymerizations Using Solid MAO Base Catalysts

Metallocene complex	Activity* (g-PE/g-cat・hr)	Bulk density (g/cc)	Others
rac-Et(Ind)$_2$ZrCl$_2$	9,000	0.39	
Ind$_2$ZrCl$_2$	9,000	0.37	
(1,3-Me$_2$Cp)$_2$ZrCl$_2$	6,300	0.41	
(*n*BuCp)$_2$ZrCl$_2$	12,000	0.39	
Ref. *rac*-Et(Ind)$_2$ZrCl$_2$	1,100	0.34	SiO$_2$/MAO(13.9wt%-Al in solid)



SEM image of polymer
by Solid MAO/*rac*-Et(Ind)$_2$ZrCl$_2$ (× 300)

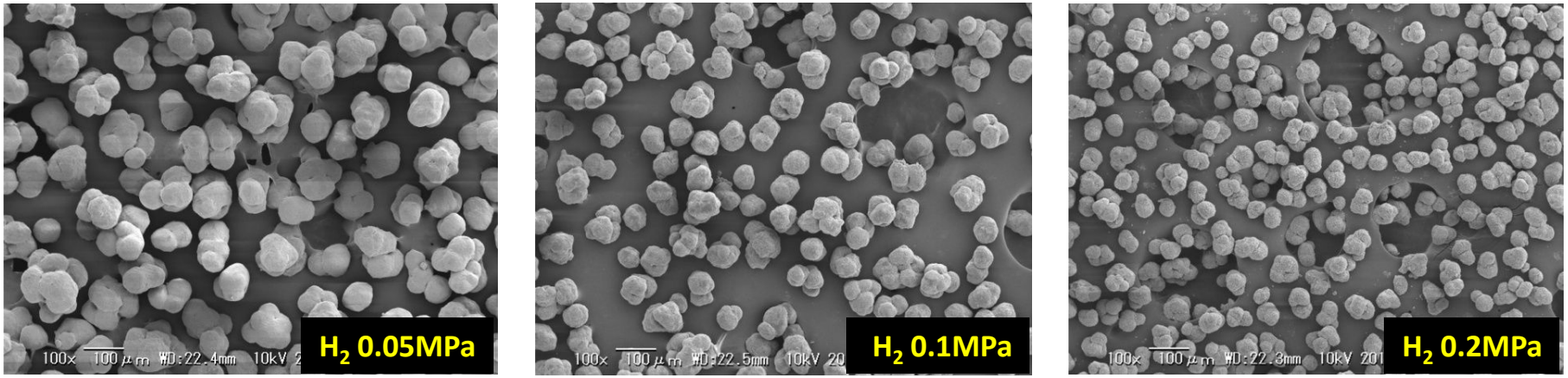
- Polymerization cond. : Hexane 800ml, Cat.20mg(6.1μm-Solid MAO, Al/Zr=200, 41wt%-Al in solid), Et$_3$Al(0.5mmol), C2 0.7MPa, Temp. 70℃, Time 1hr.

- **Solid MAO base catalysts showed high activities and gave high BD polymers.**

Effect of Hydrogen in Ethylene Polymerization Using Solid MAO/*rac*-Et(Ind)$_2$ZrCl$_2$

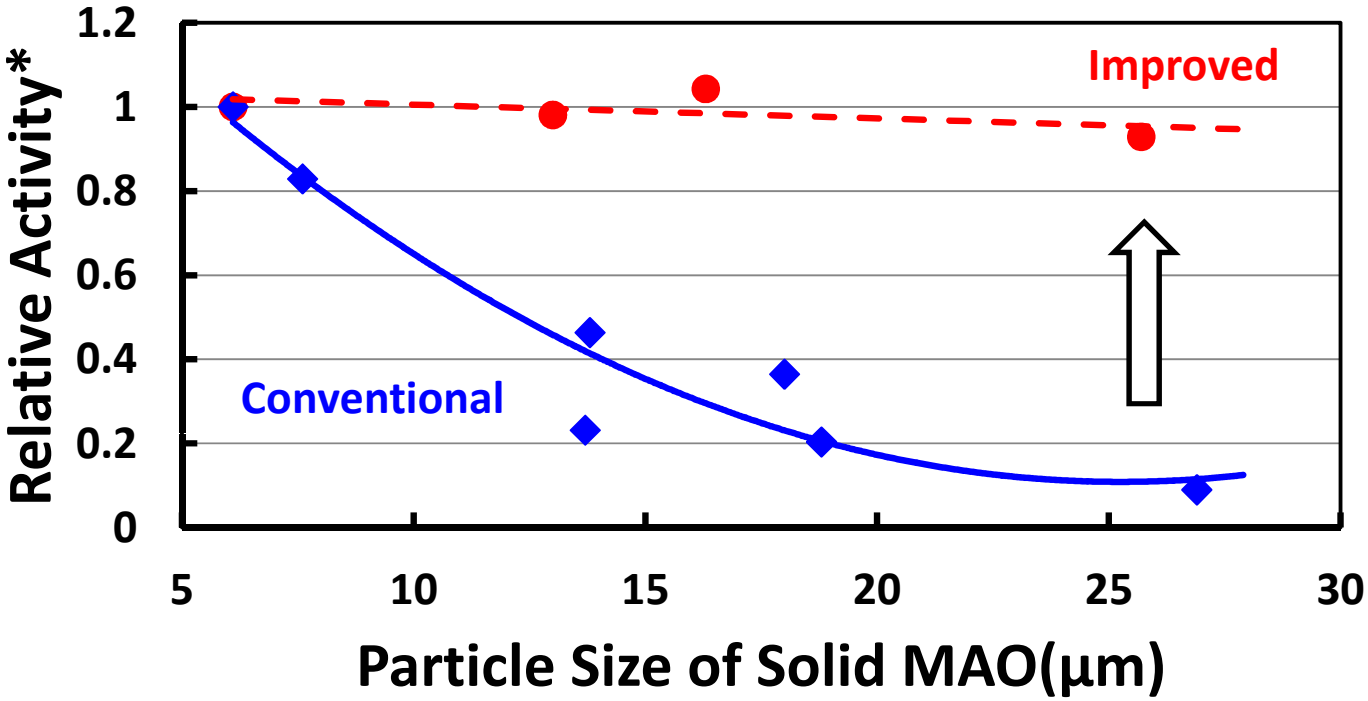
H_2 added (MPa)	Activity* (g-PE/g-cat・hr)	Bulk density (g/cc)	MFR (g/10min@190℃, 2.16kg-wt)
0.05	9,400	--	1.53
0.1	3,700	0.40	330
0.2	1,400	--	over 330

* Polymerization cond. : Hexane 800ml, Cat.20mg(6.9µm-Solid MAO, Al/Zr=200), Et_3Al(0.5mmol), C2 0.8MPa, Temp. 70℃, Time 1hr.



SEM image of polymer by Solid MAO/*rac*-Et(Ind)$_2$ZrCl$_2$ (× 1000)

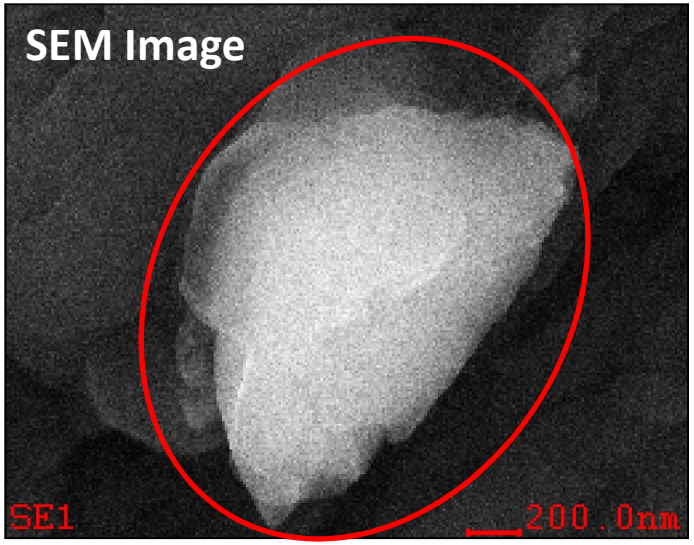
Relationship between Particle Size and Relative Activity

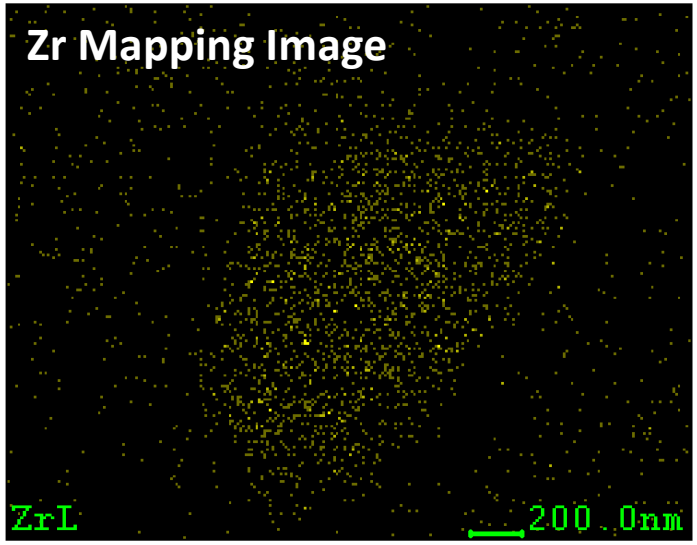


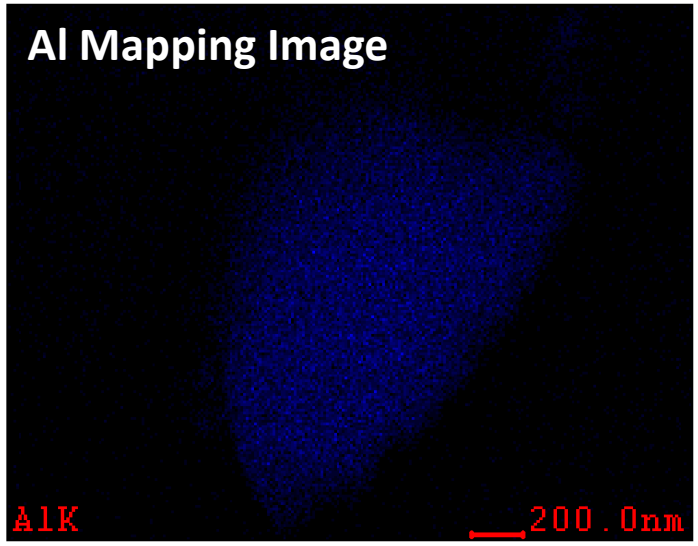
- **The catalytic activities using improved Solid MAO unchanged with increase in the particle size.**

*** Polymerization cond. : Hexane 800ml, Cat.20mg(6.1µm-Solid MAO, Ind_2ZrCl_2, Al/Zr=200), Et_3Al(0.5mmol), C2 0.8MPa, Temp. 80℃, Time 1hr.**

Elemental Mapping Images of Solid MAO/Ind_2ZrCl_2 Catalyst

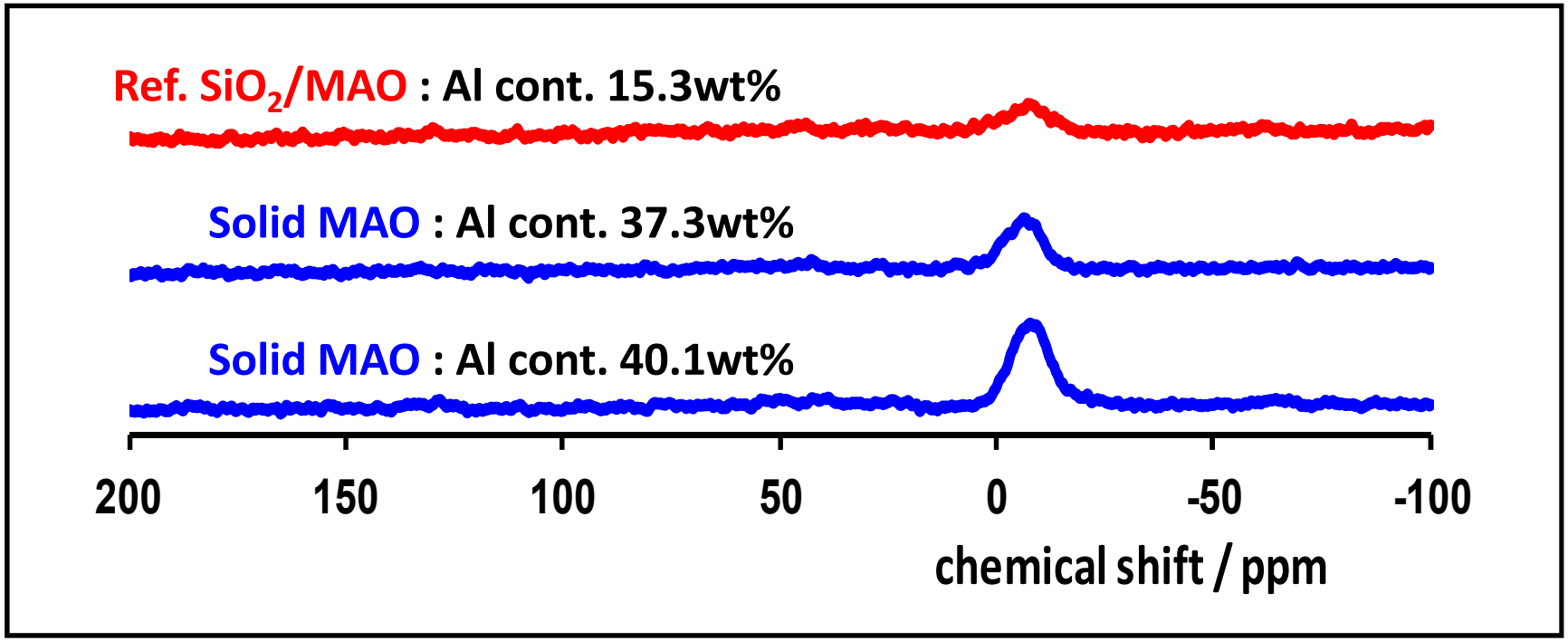






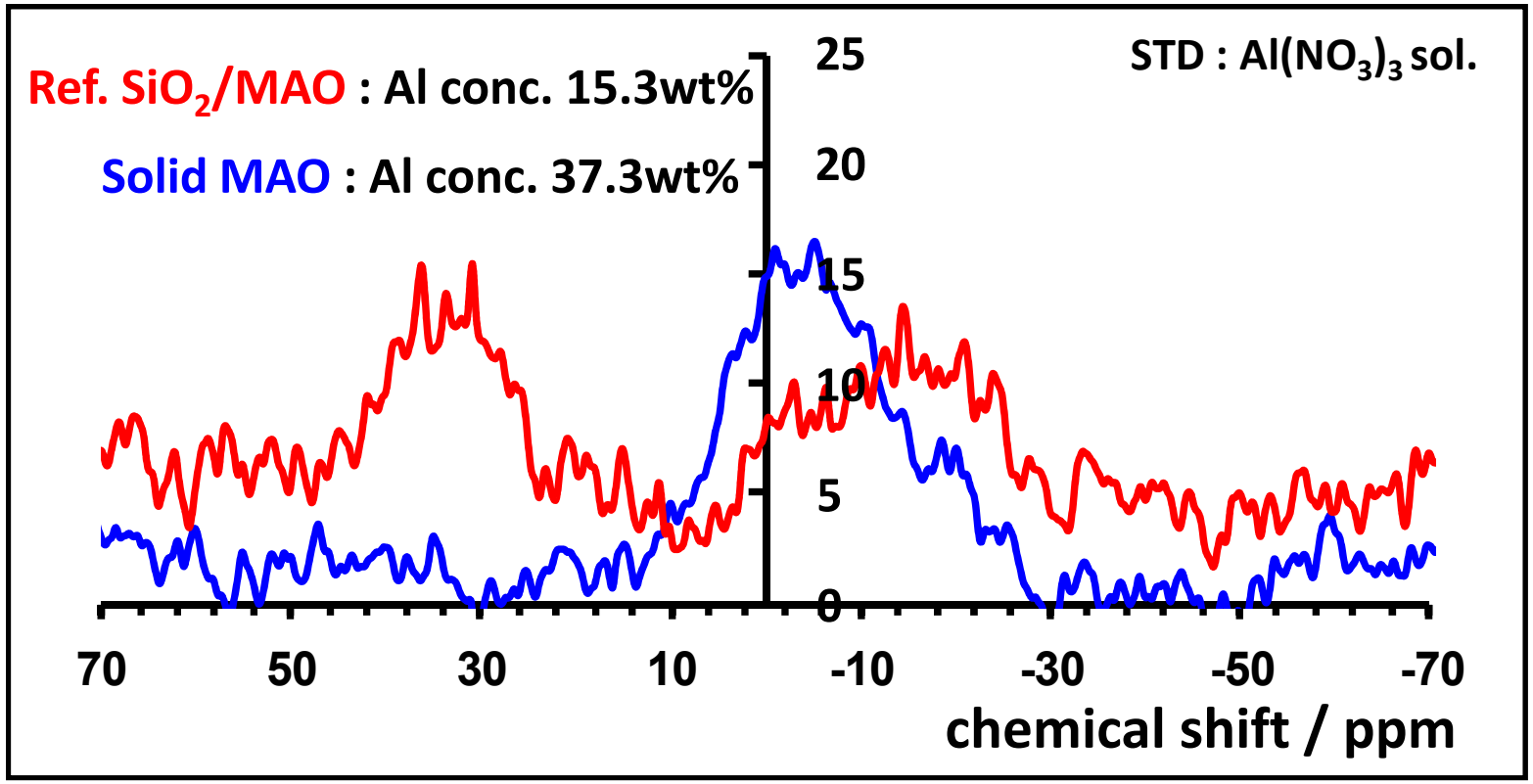
- **Zr have been uniformly dispersed in Solid MAO.**

^{13}C CP/MAS NMR of Solid MAO



- There was no difference in the chemical shift of Me-group.
- The peak strength reflected Al content in the solid.

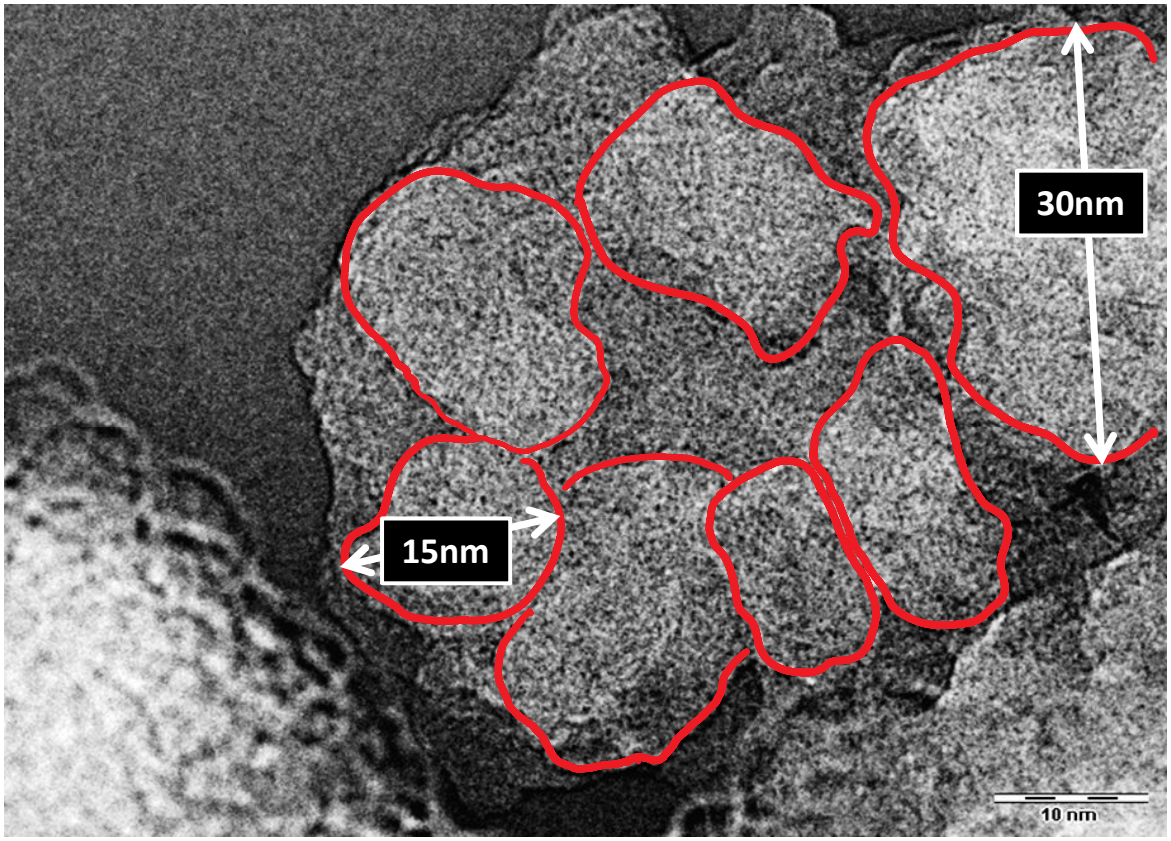
^{27}Al MAS NMR of Solid MAO

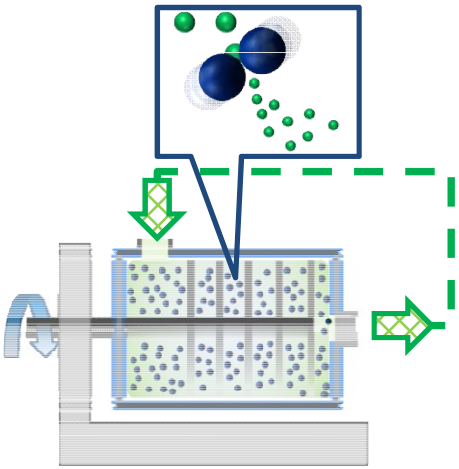


- Two peaks in SiO_2/MAO, whereas a single peak in Solid MAO.
- Assumed that six coordinated site (higher magnetic field side), four coordinated site (lower magnetic field side).

TEM* Image of Solid MAO

* TEM : JEOL JEM-2010(Miyazaki Univ.)



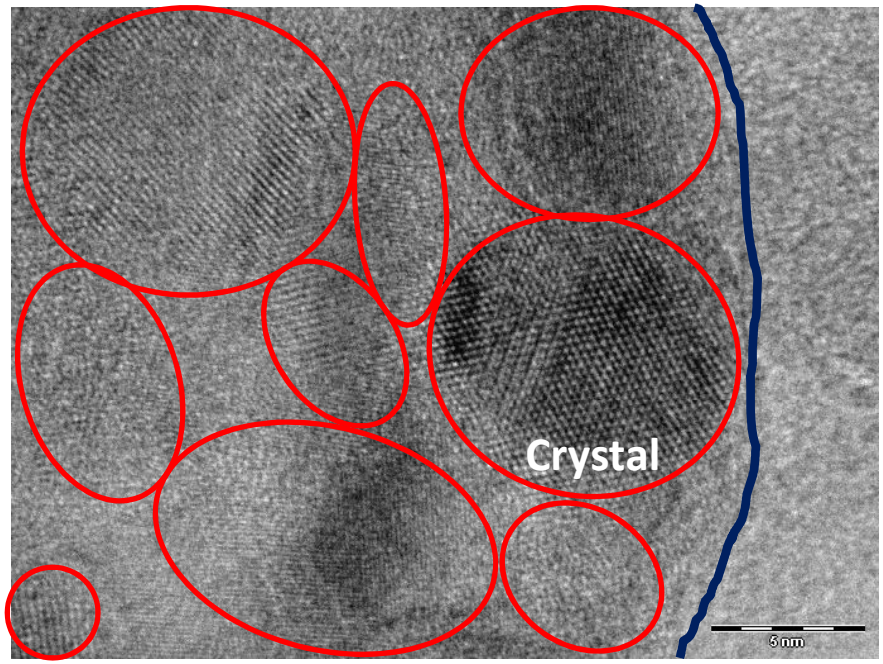


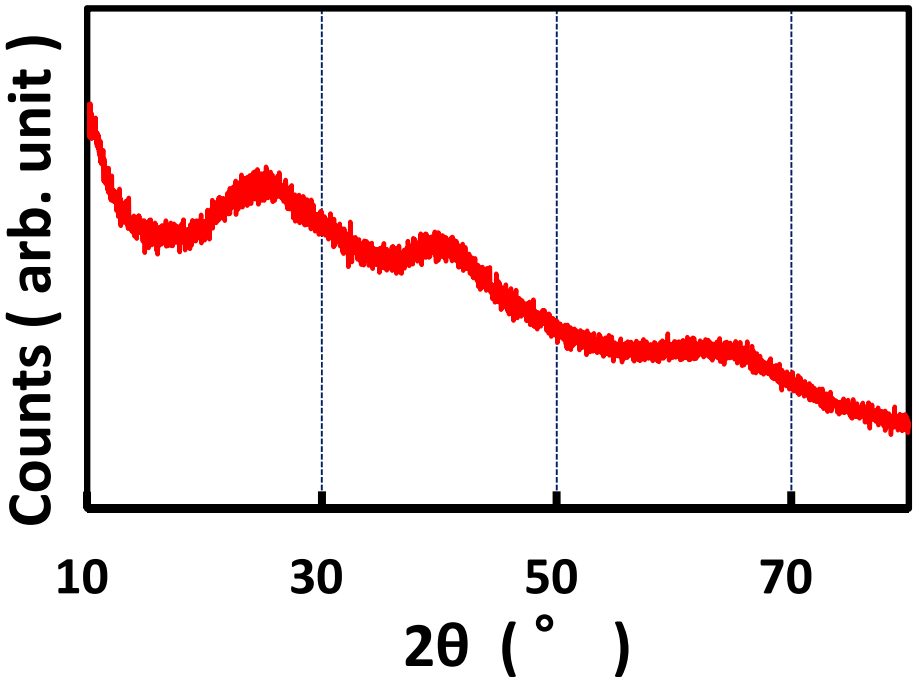
Sample preparation : Fracturing method

- **The size of the primary particles was about 15 to 30nm.**

TEM* Image and XRD pattern of Solid MAO

* TEM : JEOL JEM-2010(Miyazaki Univ.)





- Some lattice patterns were found in TEM image.
- The amount of crystal part was less than 10%.

Analysis of Lattice Image of Solid MAO

How to identify crystal lattice pattern :

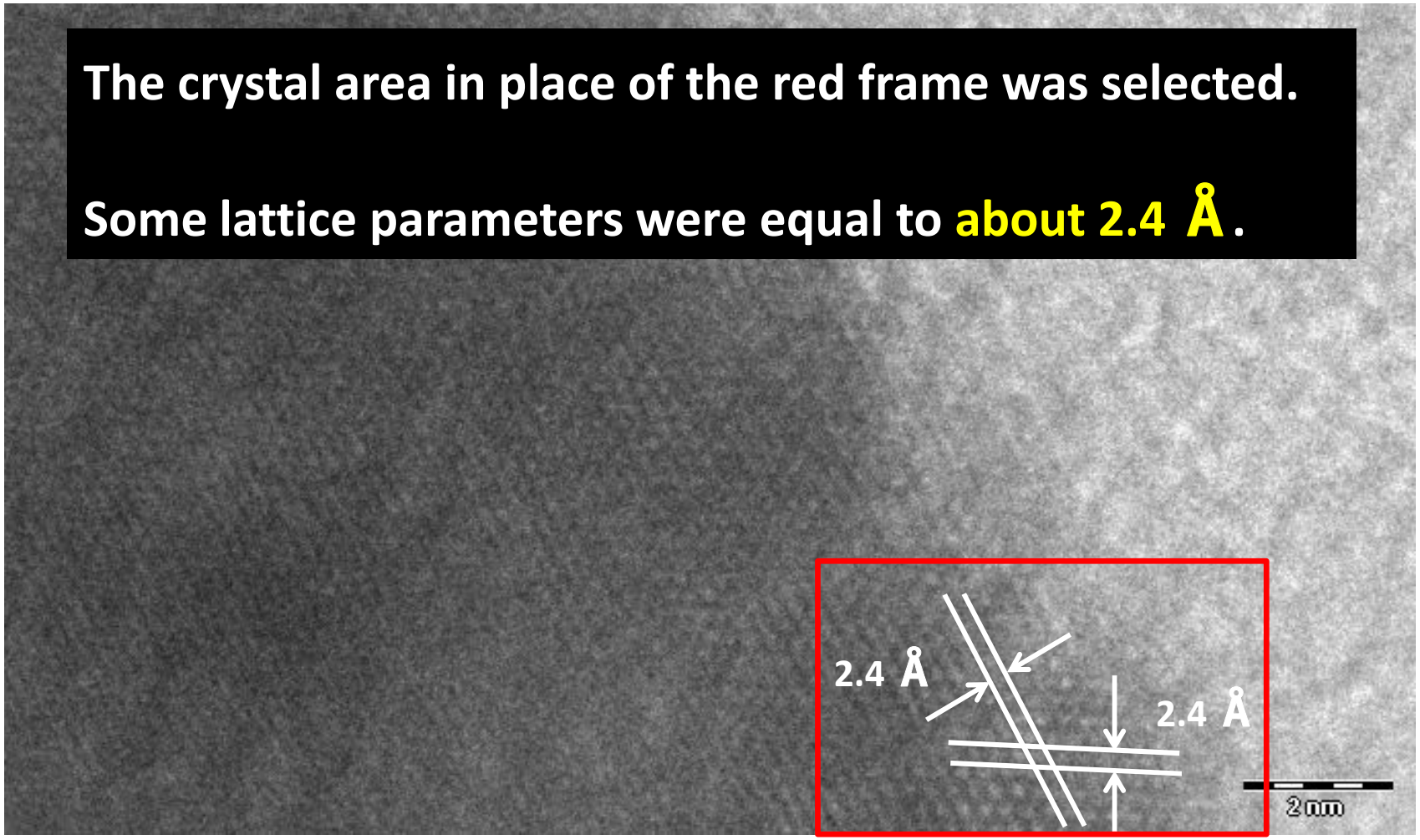
1) **Electron diffraction(ED) pattern simulated from crystal lattice pattern of Solid MAO :**

   ReciPro software(http://pmsl.planet.sci.kobe-u.ac.jp/~seto/)

2) **ED pattern of Solid MAO with those of known crystal compounds**

3) **Crystal lattice pattern of Solid MAO with that of known crystal compound :** VESTA software(http://jp-minerals.org/vesta/)

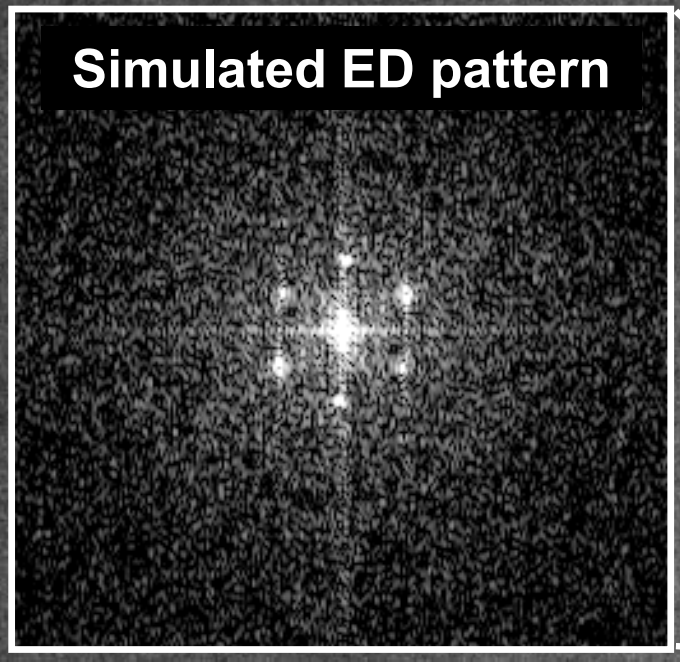
Lattice Image of Solid MAO from TEM Observation

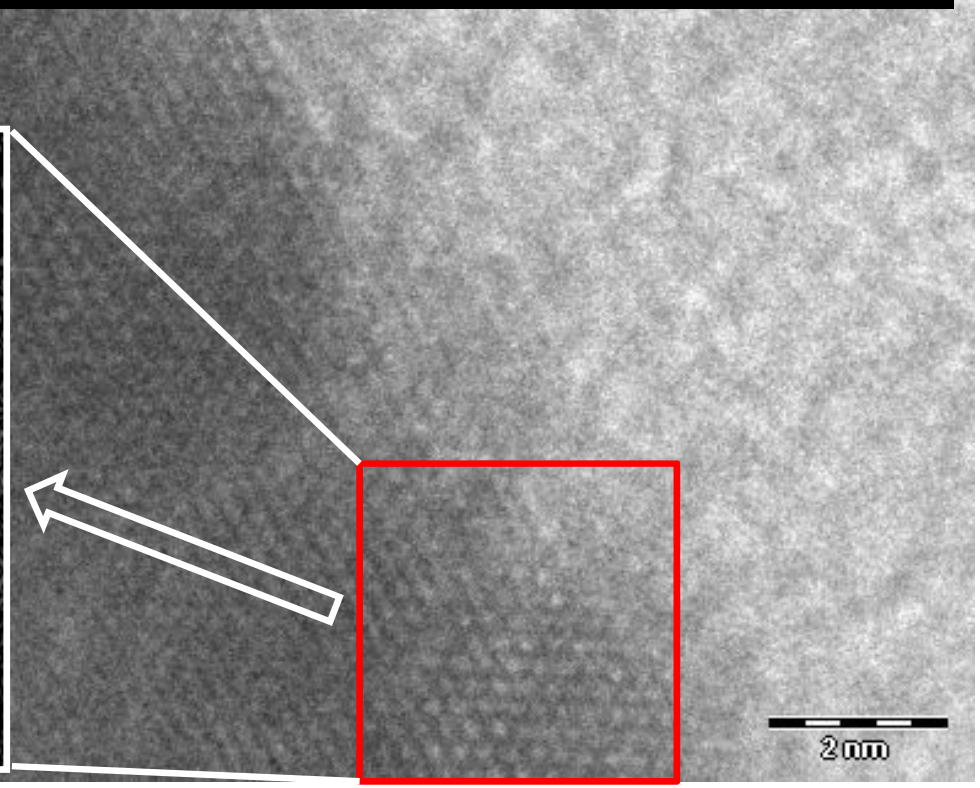


Lattice Image & ED Pattern of Solid MAO

The information of the crystal lattice pattern (figure data used) was used to simulate to this ED pattern.

Simulation to ED pattern was used by ReciPro software.



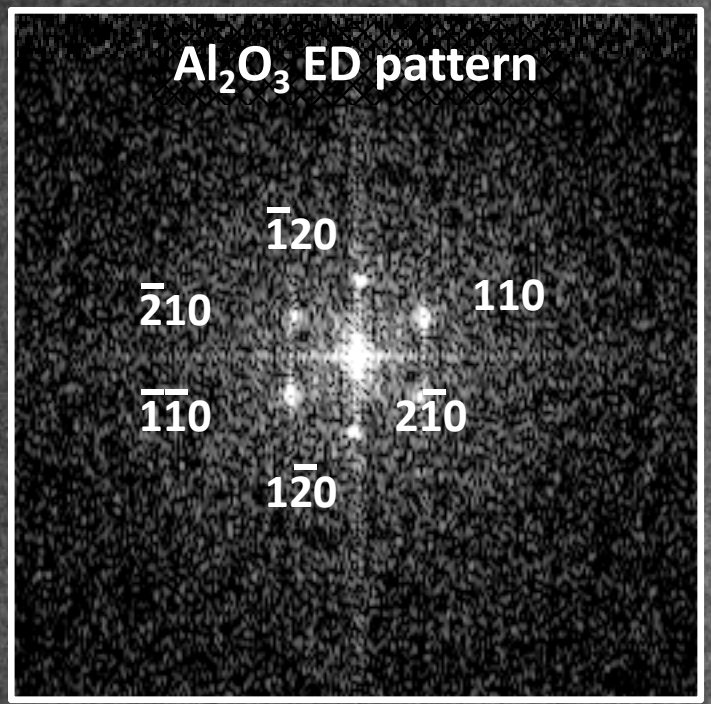


Simulation Result of Solid MAO

Unit-cell parameter of Al_2O_3 [Acta Crystallographica A38 (1982) 733]:

- $a = b = 4.7602$ Å, $c = 12.9933$ Å
- $\alpha = \beta = 90°$, $\gamma = 120°$

The ED pattern of Al_2O_3 with corundum structure was identified as simulated ED pattern of crystal phase in Solid MAO.



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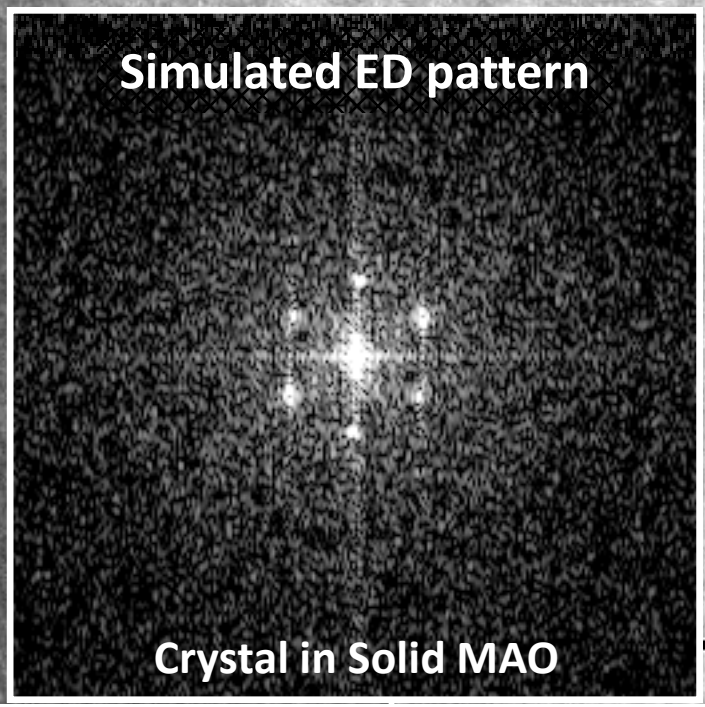
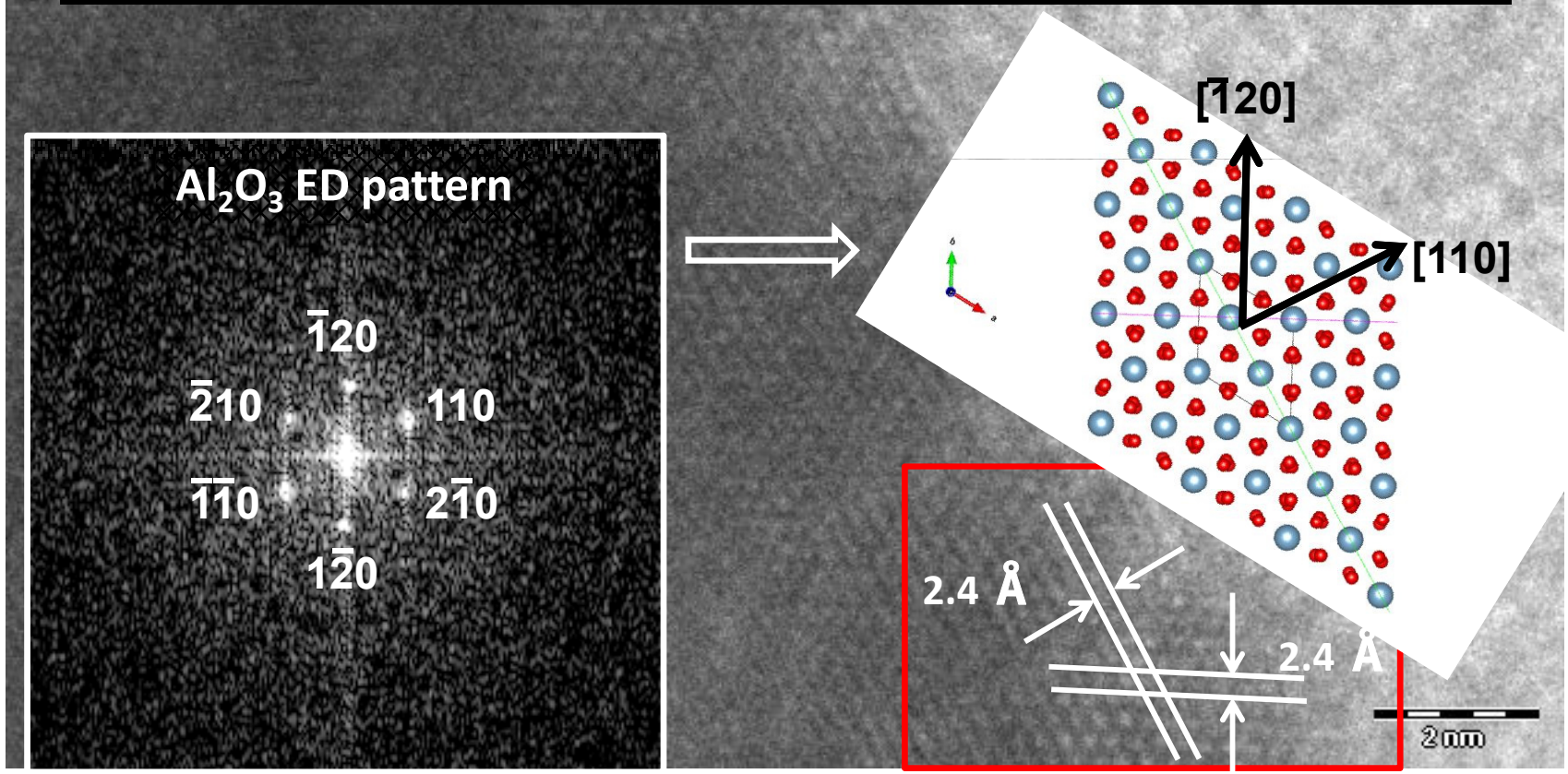


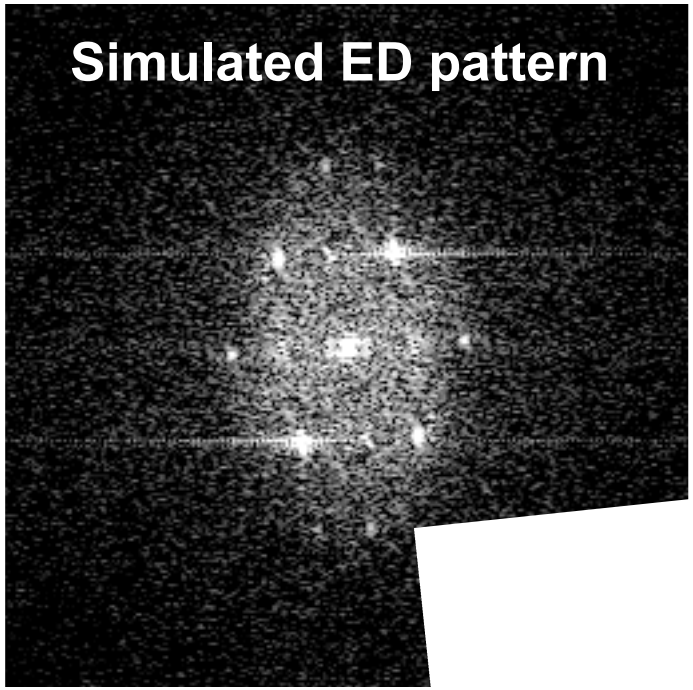
Simulation Result of Solid MAO

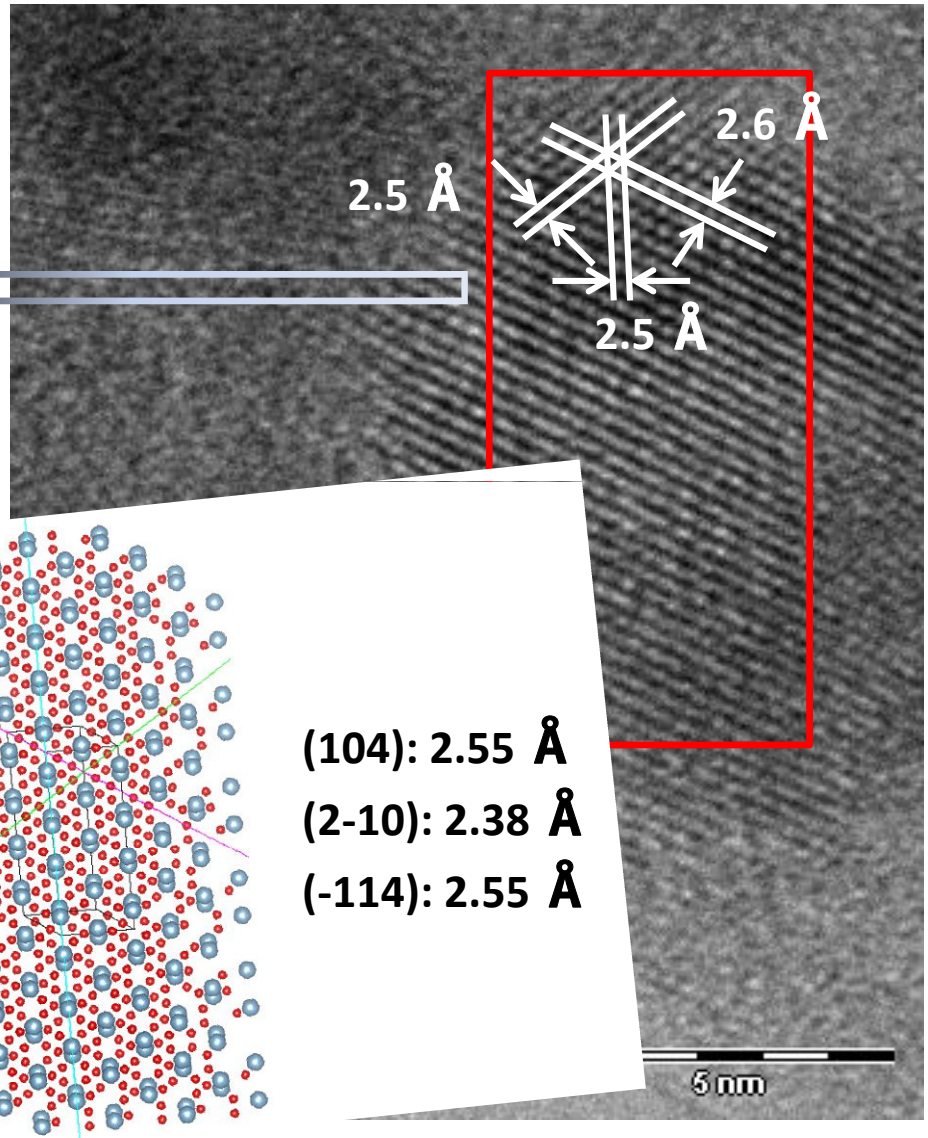
Arrangement of atoms & lattice pattern of Al_2O_3 were good agreement with crystal phase of Solid MAO.

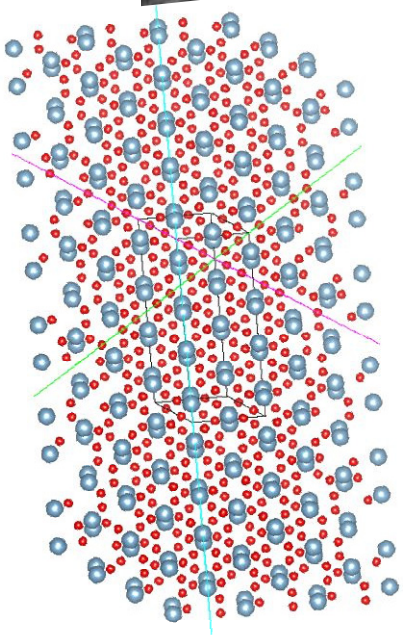
Observed crystal was Al_2O_3 with corundum structure.



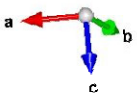
Lattice Image & ED pattern of Solid MAO







(104): 2.55 Å
(2-10): 2.38 Å
(-114): 2.55 Å

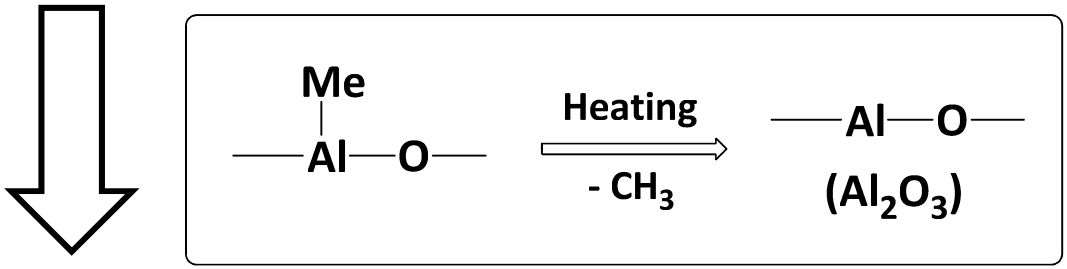


Formation of Al_2O_3

- **Al_2O_3 Formation**

  · It is necessary to remove Me-group from MAO chain in order to form Al_2O_3 structure in Solid MAO.

  · The amount of Al_2O_3 crystal could not be determined.

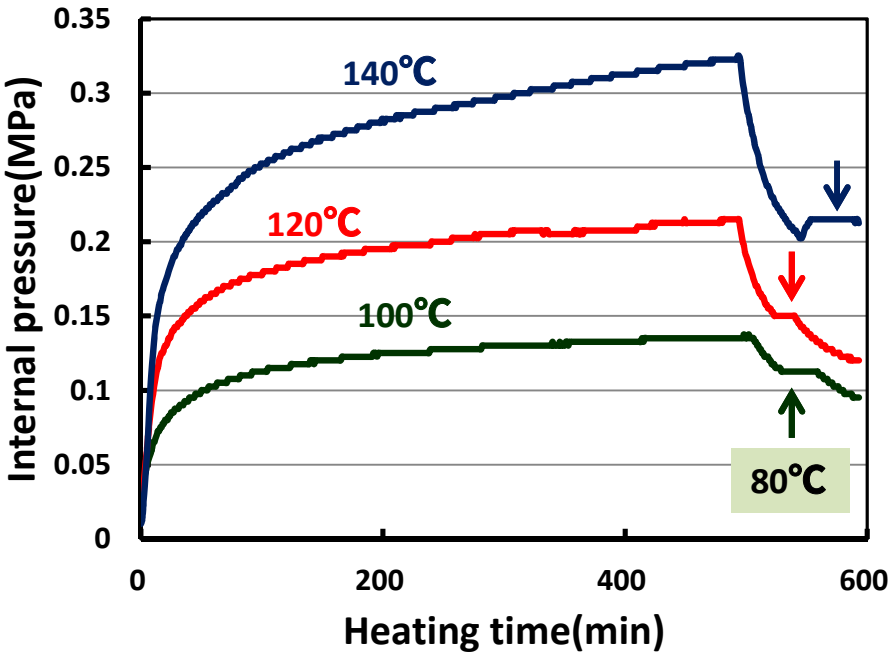


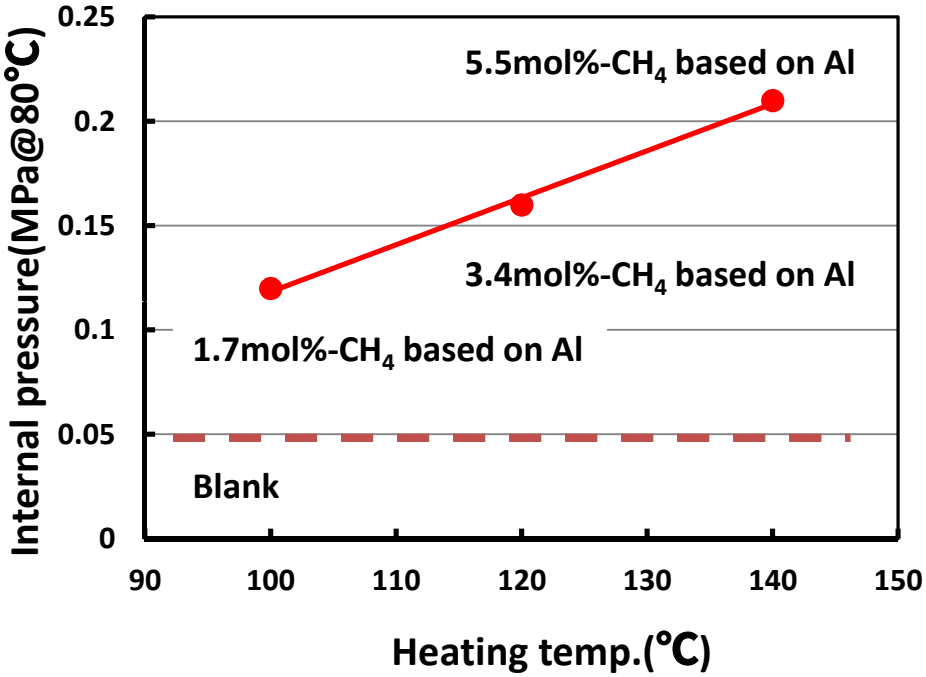
- **The amount of total Al_2O_3 (crystal & amorphous)**

  The amount of Me-group removed would be related to total Al_2O_3 formation.

Effect of Solidification Temperature

MAO solution(-AlMe-O-/Me_3Al) ⇒ Heating - CH_4↑ ⇒ Sold MAO・Al_2O_3

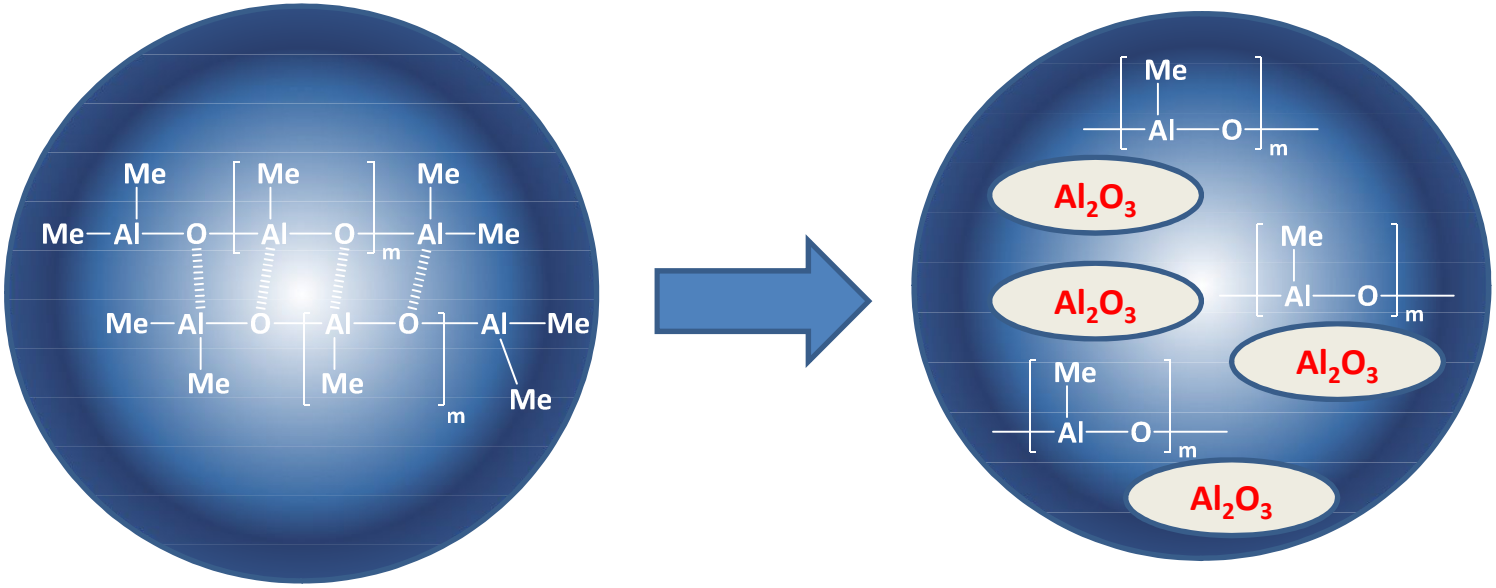




- **The amount of CH_4 removed increased according to solidification temperature elevation.**

Summary

- Solid MAO has been prepared by a self aggregation procedure.
- Solid MAO showed high activity and gave high BD of polymer in ethylene polymerization.
- A difference was found between Solid MAO and SiO_2/MAO in ^{27}Al MAS NMR spectrum.
- The existence of Al_2O_3 crystal which made by an in situ production has been found by structure analysis of Solid MAO.



Coworkers

- Kentaro Sakai (Miyazaki Univ.)
- Etsuo Yoshioka
- Takeo Yamane
- Minoru Oshima
- Yujin Takemoto
- Tomoyuki Kinoshita