Cocatalyst for metallocene polymerization

Methylaluminoxane (MAO)

TOSOH FINECHEM CORPORATION

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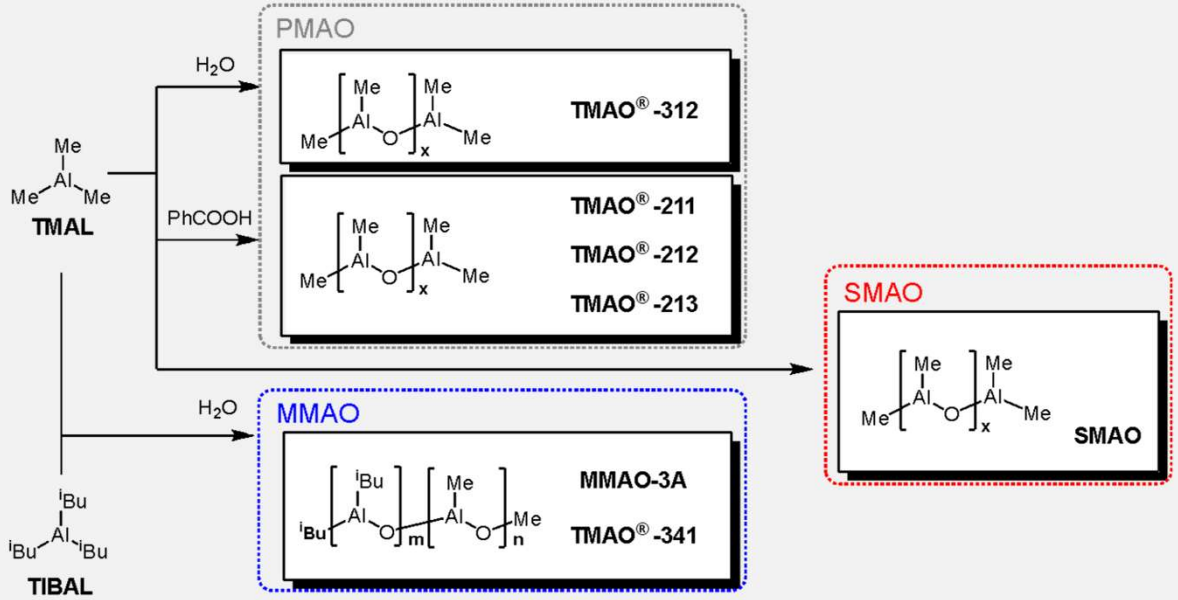
Tosoh Finechem MAO Products

Polymethylaluminoxane (PMAO): Cocatalyst for silica support (gas phase and slurry polymerization)
Modified methylaluminoxane (MMAO): Hydrocarbon soluble cocatalyst (solution polymerization)
Solid methylaluminoxane (SMAO): Supported composite-type cocatalyst (slurry polymerization)



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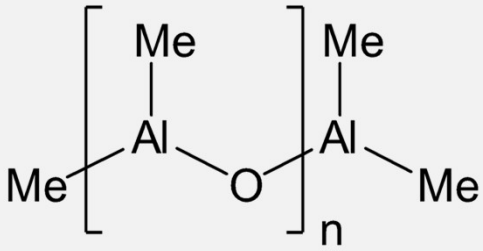
TFC MAO lineup

Product	Molecular formula	Forms	Solvent	Notes
TMAO®-312	$[MeAlO]_x$	Solution (liquid)	Toluene	Standard MAO products
MMAO-3A	$[Me_miBu_nAlO]_x$	Solution (liquid)	Hexane	Standard MMAO products
TMAO®-341	$[Me_miBu_nAlO]_x$	Solution (liquid)	Hexane	High Me-group ratio MMAO products
SMAO	$[MeAlO]_x$	Solid (slurry)	Toluene or decane-hexane mixture	Small particle size d(0.5): 4.5 ~ 8μm Medium particle size d(0.5): 8 ~ 12μm

TMAO®-312/Toluene

- Highly active PMAO products synthesized using the hydrolysis method
- Stable storage for 1 year at -20°C



MAO

Al concentration (wt%): 13 – 14
Me/Al (mr): 1.5 – 1.8
TMAL (wt%): 3.7 – 5.3



TMAO®-312

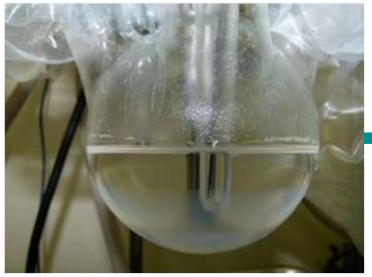
TMAO®-312/Toluene

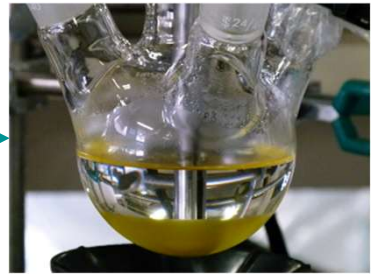
- Highly active PMAO products synthesized using the hydrolysis method
- Stable storage for 1 year at -20°C

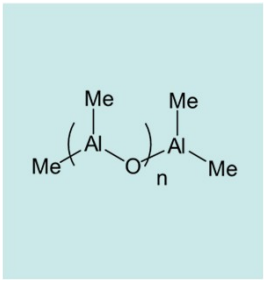
Polymerization coverage

Applicable for gas-phase/slurry polymerization with carrier support

Support example)





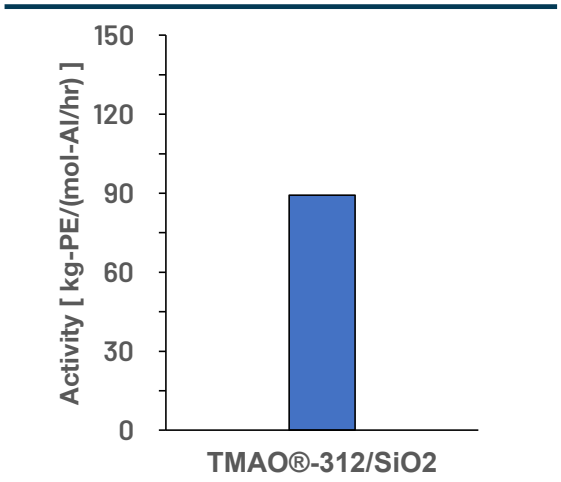


MAO/SiO_2 support

Catalyst support

Polymerization activity*

Fig. 1: Polymerization activity (silica-supported MAO)



Catalyst: Metallocene catalyst
Polymerization conditions: Al/Zr =2 00, 1.0 MPa -80°C, 2 hrs.
*** TFC internal testing**

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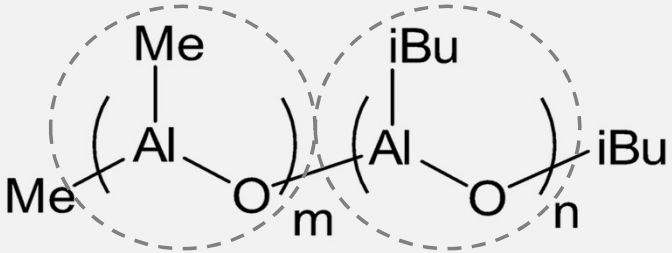
MMAO-3A/Hexane

- MMAO products composed of PMAO and PBAO(Polyisobutylaluminoxane)
- Suitable for polyolefin elastomers (POE), ethylene propylene diene monomers (EPDM), and solution polymerization processes
- In addition to its catalytic activity, MMAO-3A/Hexane is soluble in aliphatic hydrocarbons and stable at room temperature



PMAO — High activity

PBAO — Solubility, Stability

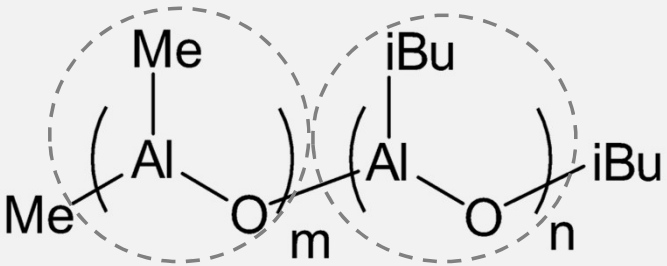
Al concentration (wt%): 5.0 – 6.4
Me/iBu ratio (mr): 2.0 – 3.5
(Me+iBu)/Al ratio (mr): 1.4 – 1.8



MMAO-3A

TMAO®-341/Hexane

- MMAO product with higher PMAO percentage than MMAO-3A
- High activity while maintaining hydrocarbons solubility



PMAO > **PBAO**

Al concentration (wt%): 11 – 13
Me/iBu ratio (mr): ≧ 3.5
Me (PMAO) (mol%): 64 – 70

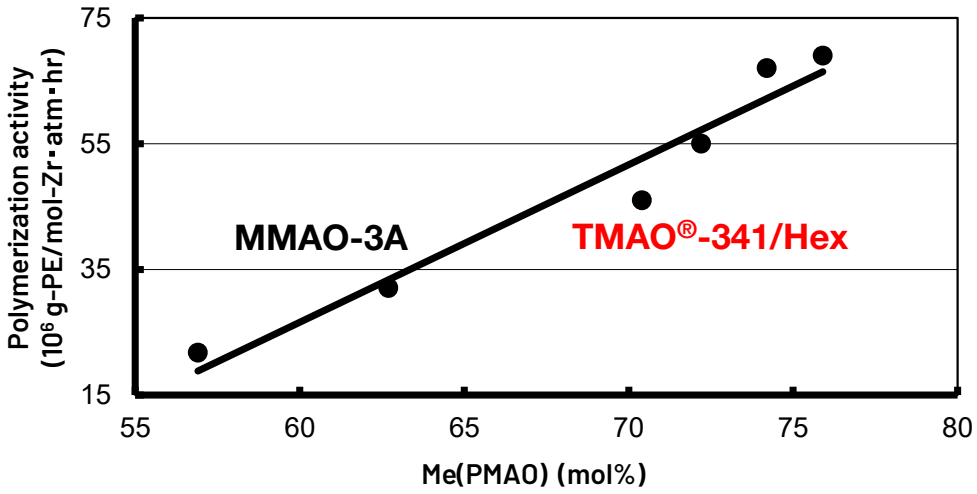


TMAO®-341

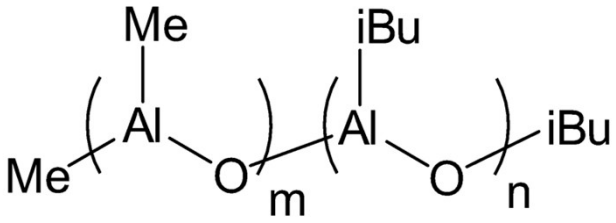
TMAO®-341/Hexane

Polymerization activity

Higher activity than MMAO-3A, with polymerization activity equivalent to PMAO



Me (PMAO): Mole fraction of Me-group derived from PMAO



Polymerization activity

Catalyst: Metallocene catalyst
Polymerization conditions: Al/Zr = 5000, Ethylene: 1 atm
Solvent: 250mL toluene; Polymerization time: 10 min;
Polymerization temperature: 40°C

Tosoh Corporation,*"Tosoh Research & Technology Review"*, 2003, *47*, 55 - 60.

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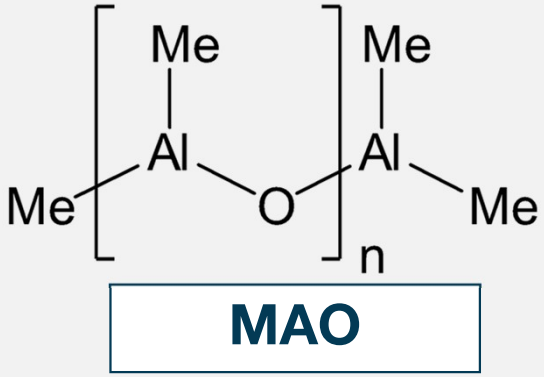
SMAO (carrier complex methylaluminoxane)

- ○ Suitable for High-density polyethylene (HDPE) and other slurry processes
- ○ Solid and acts as carrier as is, so no carrier is required
- ○ Particle size controllable



MAO

New cocatalyst for metallocene catalysts for polyolefins



SMAO (SEM images)

Features of SMAO

Uniform particle size, with no coarse or fine particles

→ Enables stable plant control
→ Reduces fouling and other capacity loss

High specific activity

→ SMAO can be expected to be more active than silica-supported MAO (TFC internal testing)

Fig. 1: Particle size distribution and SEM images of SMAO

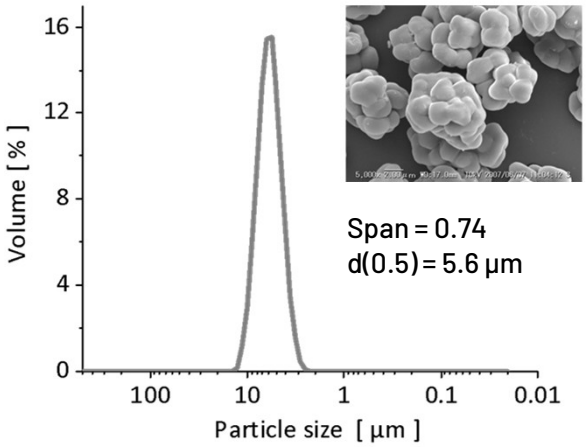
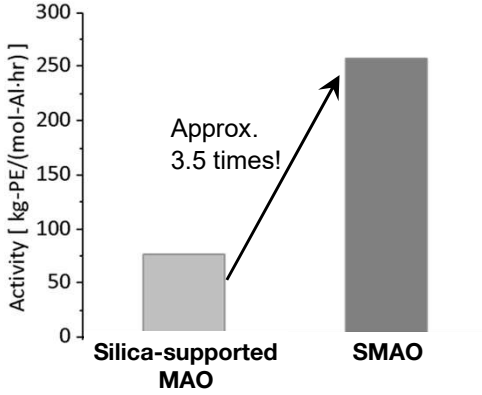


Fig. 2: Comparison of polymerization activity (silica-supported MAO vs. SMAO)



Catalyst: Metallocene catalyst
Polymerization conditions: Al /Zr = 200, 1.0MPa-80°C・2 hrs.

TOSOH FINECHEM CORPORATION

Tosoh Finechem Corporation

Location

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Business

Organometallic compounds: Aluminum alkyls, aluminoxanes, organometallics
Bromine compounds: NaSS, styrene derivatives, alkyl bromides
Fluorine compounds: TFEA, CF_3I, fluorine compounds