Ethylene polymerization over $TiCl_4/MgCl_2$ catalysts with different titanium content

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Introduction

Ziegler-Natta catalyst, especially the supported titanium-magnesium catalysts (TMCs), were the main type of catalytic systems for polyolefin production in the past 50 years. Although the structure of the catalysts, as well as the polymerization mechanism, were widely studied in recent years, many questions still remain a subject of debate. Because the active center was a small portion of Ti species supported on the $MgCl_2$ support (less than 10%). It is difficult to characterize the chemical structure of the active species directly in these catalysts. Therefore, it is necessary to develop a simple model catalytic system to study the composition and structure of active sites and the polymerization mechanism of the TMCs.

Experimental

Two TMCs were synthesized by loading $TiCl_4$ on $MgCl_2$ particles prepared via reaction of metallic magnesium powder with 1-chlorobutane, which contained 0.1 wt% (TMC-0.1) and 1.0 wt% (TMC-1.0) of Ti, respectively. Ethylene slurry polymerization with the TMCs activated by TEA was conducted, and the number of active centers ([C*]/[Ti]) was determined by quenching-labeling the propagation chains with 2-thiophenecarbonyl chloride.

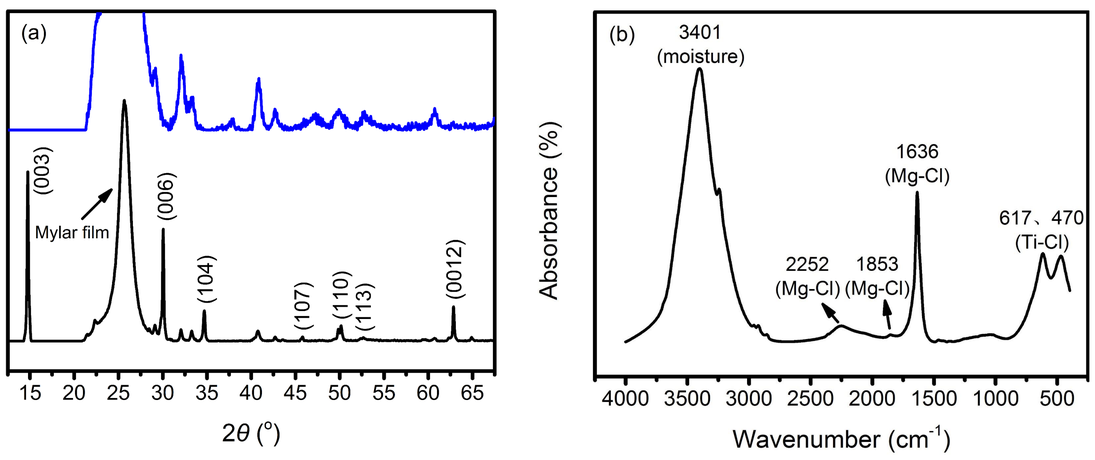
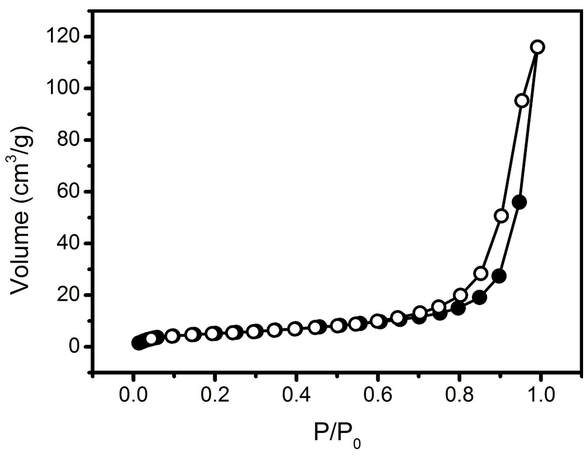


Fig. 1 (a) PXRD patterns of α-$MgCl_2$ (black bottom curve) and $MgCl_2$-containing support (blue top curve). (b) FT-IR spectrum of supported titanium-magnesium catalyst (TMC-1.0). The absorption peaks at 2252, 1853 and 1636 cm^{-1} indicate Mg-Cl bands. The absorption peaks at 617 and 470 cm^{-1} indicate Ti-Cl bands. The absorption at 3401 cm^{-1} indicate moisture adsorption.



The adsorption isotherm is of IUPAC Type IV, and is characterized by a pronounced hysteresis loop, which reveals the presence of mesoporous structures. The specific surface area, evaluated by means of the BET model, is 32.1 m^2/g, and the pore volume is of 0.30 cm^3/g.

Fig.2 N_2 physisorption isotherm collected at 77K for $MgCl_2$-containing support. Adsorption and desorption data were shown with filled and empty symbols, respectively.

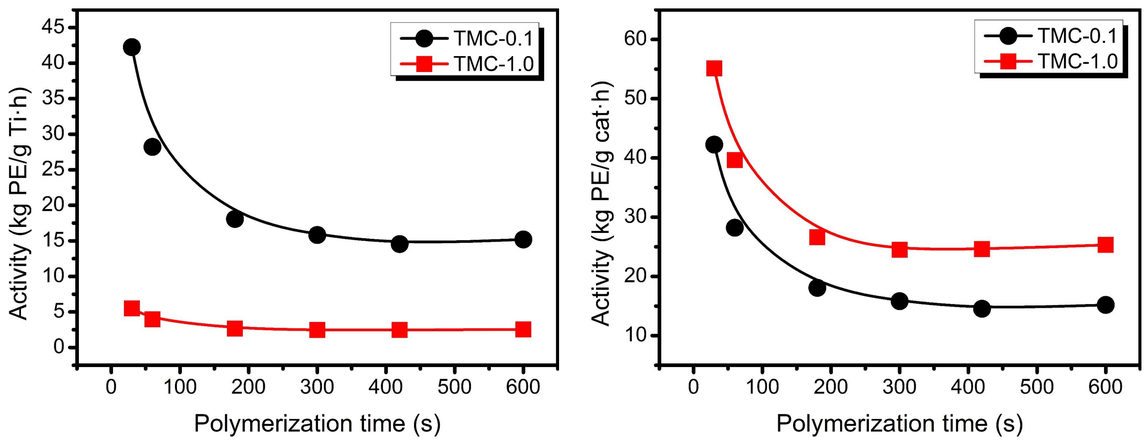


Fig. 3 Ethylene catalytic activity of TMCs with different Ti content. TMC-0.1 (0.1 wt% of Ti) was prepared by depositing a calculated amount of $TiCl_4$. TMC-1.0 (1.0 wt% of Ti) was prepared by the treatment of $MgCl_2$-containing with excessive $TiCl_4$. Polymerization conditions: [Catalyst] = 4 g/L, cocatalyst = $AlEt_3$, [$AlEt_3$] = 125 mmol/L, ethylene pressure = 1 atm, n-heptane = 50 mL, polymerization temperature = 60 °C.

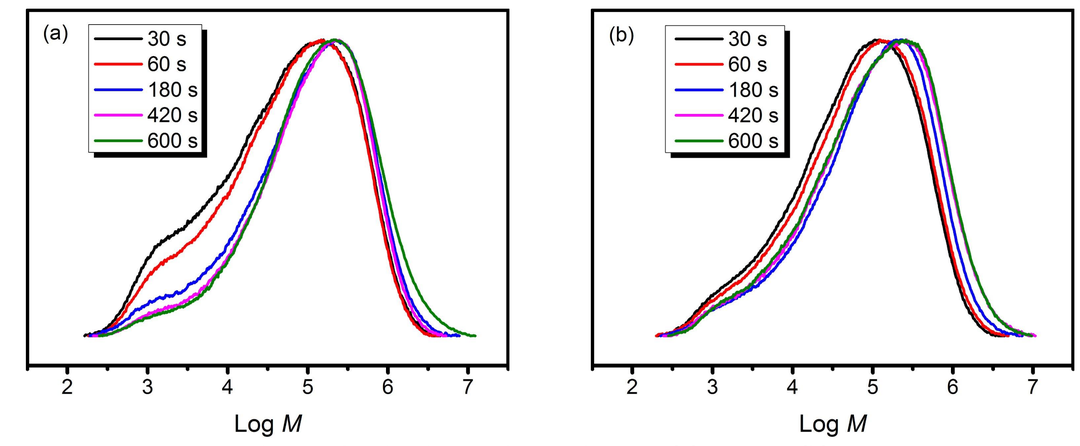


Fig. 4 Time evolution of molecular weight distributions: (a) TMC-0.1; (b) TMC-1.0.

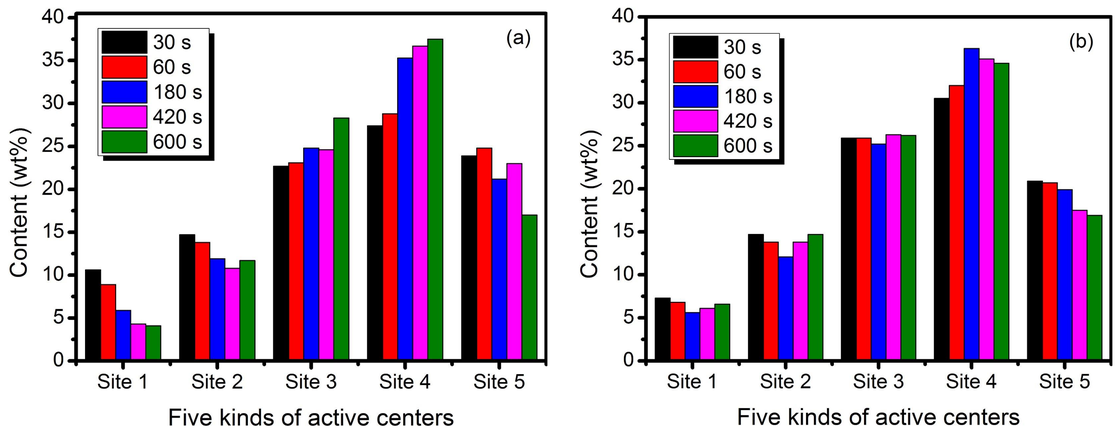


Fig. 5 Effect of polymerization time on content of the Flory components: (a) TMC-0.1, (b) TMC-1.0.

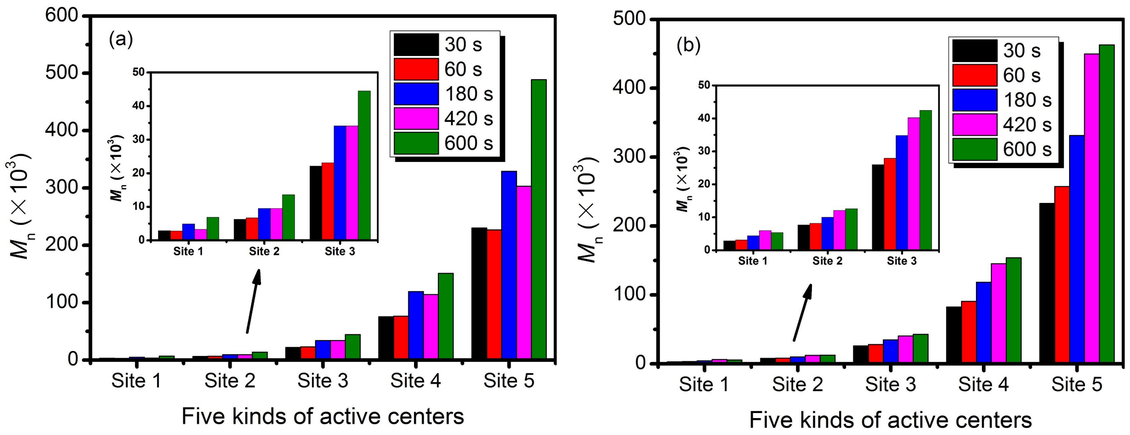


Fig. 6 Effect of polymerization time on molecular weight of the Flory components: (a) TMC-0.1, (b) TMC-1.0.

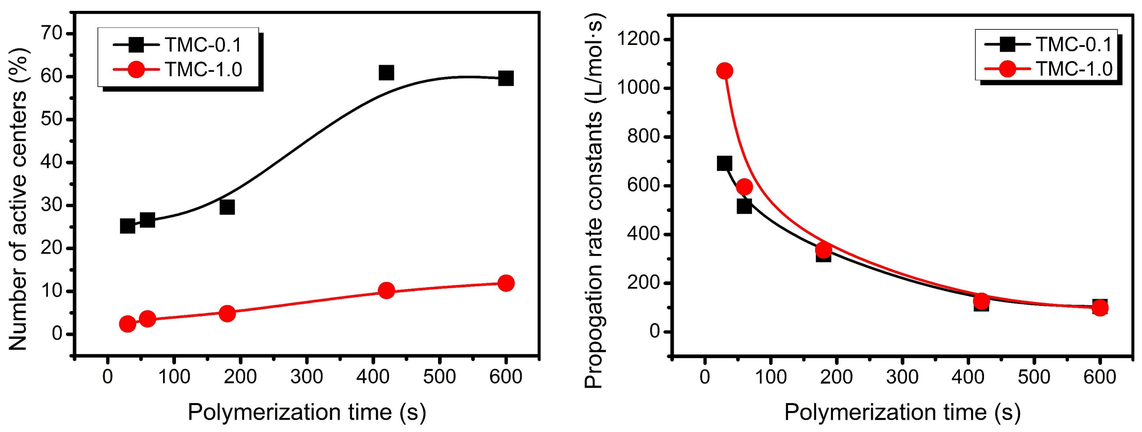


Fig. 7 Kinetic profile of ethylene polymerization over TMCs with different Ti content.

Conclusions

- **The sites forming low MW PE could be easily activated by $AlEt_3$ in the initial stage of polymerization, and it deactivated faster than those forming high MW PE.**
- **The super-high activity of the TMC with low titanium content (0.1 wt%) was attributed to an increased content of active sites.**

Acknowledgement

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References

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