



Effects of External Donor on Propylene Polymerization with MgCl_2 -supported Ziegler-Natta Catalysts Based on Counting of Active Centers

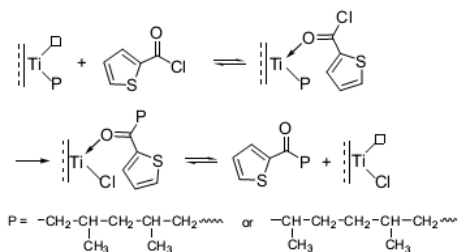
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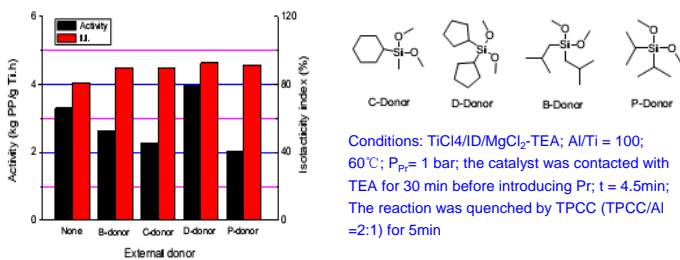
Background and purpose of the work

Electron donors have been widely applied in propylene polymerization with MgCl_2 -supported Ziegler-Natta catalysts for improving isotacticity. Extensive efforts have been devoted to disclosing the mechanism of the donor effects, but only very few such studies were based on the changes of active center distribution and k_p caused by the donors. Systematical studies based on counting of active centers can provide first-hand information of the donor's effects on the active centers, and may contribute much to the construction of a realistic mechanistic scheme. In this work, the number of active centers of a series of $\text{TiCl}_4/\text{ID}/\text{MgCl}_2\text{-Al}(\text{C}_2\text{H}_5)_3/\text{ED}$ catalysts for propylene polymerization were determined by quenching the active centers with 2-thiophenecarbonyl chloride (TPCC) in the absence and presence of hydrogen, and the influences of silane type external donors on the distribution and properties of active centers were studied.

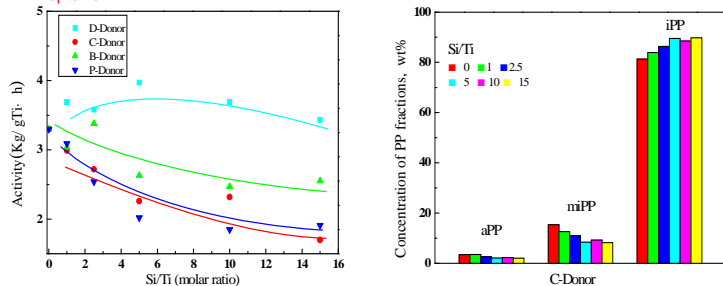
Method of active center counting



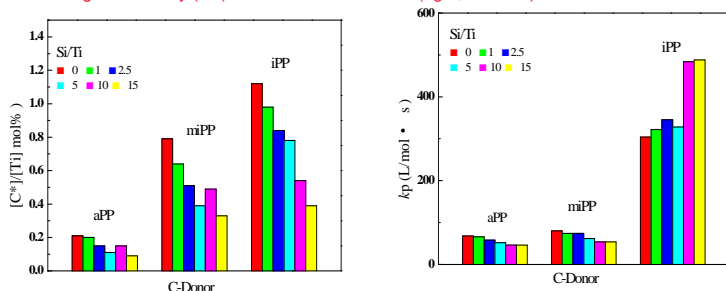
Effects of external donor on the number and reactivity of active centers in the absence of hydrogen



Activity and isotacticity of propylene polymerization in the presence of different external donors. aPP: soluble in *n*-octane at R.T.; miPP: soluble in boiling *n*-heptane; iPP: insoluble in boiling *n*-heptane.

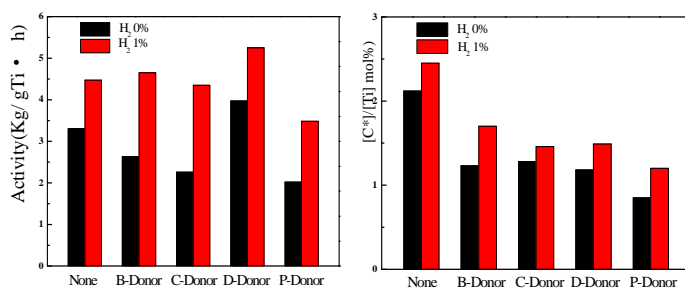


Changes of activity (left) and fraction distribution (right, C-donor) with Si/Ti.

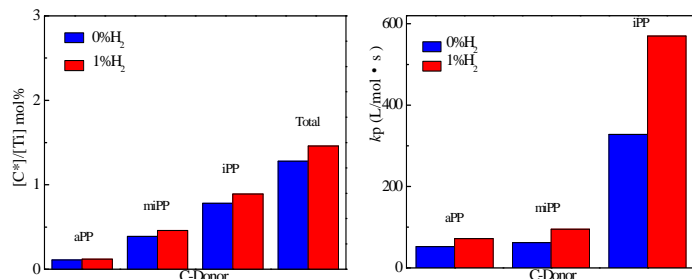


Changes of active center's number (left) and k_p (right) with Si/Ti for the fractions of PP synthesized in the presence of C-donor.

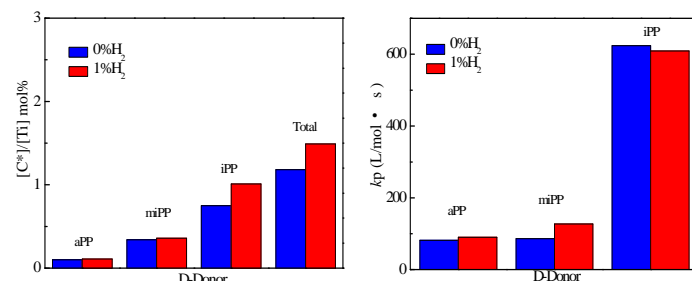
Effects of external donor on the number and reactivity of active centers in the presence of hydrogen



Effects of different external donors on activity (left) and active center's number for the propylene polymerization prepared in the presence of hydrogen.



Effects of C-Donor on changes of active center's number (left) and k_p (right) for the fractions of PP synthesized in the presence of hydrogen.



Effects of D-Donor on changes of active center's number (left) and k_p (right) for the fractions of PP synthesized in the presence of hydrogen.

Conclusions

- Silane type external donor can deactivate a part of active centers in all the three site groups (C^*_{mi} , C^*_{a} , C^*_{i}), but only the k_p value of C^*_{i} that produces isotactic PP is increased by the external donor.
- The intensity of external donor effects (deactivating a part of centers and enhancing the reactivity of the remaining centers) depends on the structure of the alkyl substituents of the silane.
- The probability of a stereo- or regioirregular insertion can be related to the structure of the alkyl substituents of the silane.