Ethylene oligomerization to α-olefins or long-chain olefins over Ni-supported AlSBA-15 catalyst

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Generally, oligomerization of olefin (e.g., ethylene or propylene) has been carried out in homogeneous catalytic systems, which contained titanium, zirconium, nickel or other metals as an active metal center [1]. In the commercial Shell Higher Olefin Process (SHOP), Ni atom is an active center and $NaBH_4$ is used as an activator [2]. Ni is often applied in oligomerization because Ti- or Zr-containing homogeneous catalysts show relatively high performance on polymerization. Recently, some researchers have studied heterogeneous catalytic systems, e.g., nickel-supported catalysts [3,4]. In their works, the major product is C4 olefin, which is very different from homogeneous catalytic process to produce α-olefin (C_6 and C_8 olefin) and C_{10+} long-chain oligomers. Thus, we focused on varying the product distribution from C_4 to long-chain oligomers in ethylene oligomerization over Ni-supported AlSBA-15 catalyst that is reported to show a good catalytic performance [5]. Thus, the effects of reaction parameters, such as the reactor type, reaction time, reactant feeding rate and reaction temperature, have been investigated in order to selectively produce α-olefin (C_6 and C_8) or C_{10+} oligomers.

In this work, $NaBH_4$ has been replaced by $LiAlH_4$ because the latter showed a better productivity (data will be presented on site).

The first investigation was for the reactor type. The semi-batch reactor (maintained at 35 barg using a back-pressure regulator) exhibited a slightly higher productivity and fraction of C_{10+} oligomers compared to the batch reactor (maintained at 35 barg using a high-pressure burette). For a longer reaction time, catalyst deactivation was observed but the fraction of C_{10+} oligomers were higher than for a short reaction time.

The second reaction parameter to be studied was the feed rate of ethylene. In Fig. 1, the faster ethylene feed (580 mL min^{-1}), the higher C_{10+} fractions (48.8 wt.%). However, the major products observed at the low feeding rate (200 mL min^{-1}) were C_6 and C_8 α-olefins (58.7 wt.%).

The final reaction parameter was the reaction temperature ranging from 180 to 230 ℃. Note that ethylene consumption occurred around 180 ℃ in a batch reactor. The productivity was 14.0 $g_{oligo.}$ $g_{cat.}^{-1}$ and the fraction of C_{10+} oligomers was 62.3 wt.% at 180 ℃. When the reaction was conducted at 230 ℃, the productivity was 151.7 $g_{oligo.}$ $g_{cat.}^{-1}$ with a lower fraction of C_{10+} oligomers at 25.9 wt.% (Fig. 1).

In summary, the production of C_6 and C_8 α-olefin is favorable at a high temperature and low ethylene feed rate, whereas a low reaction temperature and fast ethylene feeding would be necessary for a higher fraction of C_{10+} oligomers (long-chain olefins).

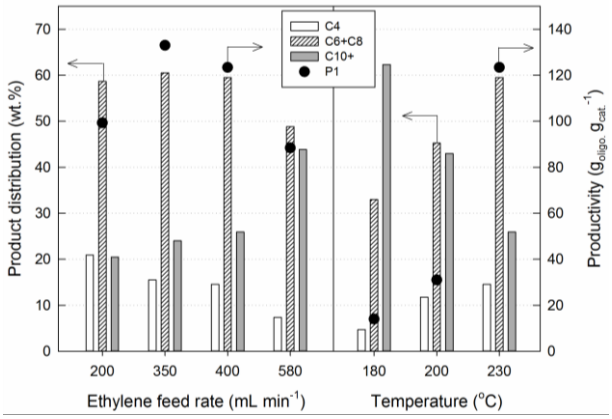

Fig.1 Productivity and product distribution obtained in ethylene oligomerization over Ni/AlSBA-15 by varying the ethylene feed rate (left) and the reaction temperature (right).

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