Identification of Novel Catalysts and Conditions for the Highly Efficient and Stable *Heterogeneous* Oligomerization of Ethylene

Josef Heveling, Christakis P. Nicolaides* and Michael S. Scurrell

Catalysis Programme, Division of Energy Technology, CSIR, PO Box 395, Pretoria 0001, Republic of South Africa

The catalyst prepared by nickel(II) exchange of silica–alumina shows high catalytic activity and long-term stability for ethylene oligomerization at 35 bar, mass hourly space velocity = 2, and 120 °C.

Nickel supported on amorphous or crystalline aluminosilicates and on silica has been widely studied as an ethylene dimerization catalyst.[1,2] In previous communications from our laboratories,[3,4] we have reported on our work on the oligomerization of ethylene into gasoline and diesel range products over supported nickel catalysts in fixed-bed flow reactors. These studies showed that nickel(II) supported on ion-exchangeable solid carriers such as amorphous silica–alumina and zeolite Y leads to highly active catalysts for ethylene oligomerization (beyond the dimerization step). Furthermore, it was found that for these catalysts no pre-reduction is necessary as required for the Ni/SiO_2 type catalysts.[5–7] The reactions over the amorphous catalysts, carried out at low pressure (11 bar) and high temperature (300 °C),[3,8] were, however, characterized by rapid deactivation of the catalyst. Similar deactivation patterns were observed with the NiNaY catalyst[4] and the NiX system studied by Diaz *et al.*[9] In this paper we report on a novel heterogeneous nickel-based catalytic system (catalyst composition *and* reaction conditions) under which ethylene oligomerization can be carried out over extended periods of time without catalyst deactivation.

The nickel catalysts were obtained by either ion-exchange or impregnation of a silica–alumina with a SiO_2/Al_2O_3 ratio of 72 and a surface area of 450 $m^2 g^{-1}$. The support was prepared by gelling an aqueous mixture of tetrapropylammonium aluminate and silicic acid followed by drying and calcining.[3] For the synthesis of the ion-exchanged catalyst, Ni–SiO_2–Al_2O_3, 15 g of the support was refluxed for 4 h in 150 ml of a 0.5 mol dm^{-3} nickel(II) nitrate solution. After filtration, the solids were thoroughly washed with distilled water and then dried at 70 °C. The product had a nickel content of 0.73% by mass, whereas for the impregnated catalyst, Ni/SiO_2–Al_2O_3, the amount of nickel was 3.84%. These nickel contents are considerably higher than those employed in our previous studies (0.3%).[8]

The catalytic experiments were performed in a flow reactor described previously.[4] After the reactor had been charged with the catalyst (1.3 g), the sample was freed from adsorbed water at 300 °C for 3 h under a flow of ultra-high purity nitrogen. The reactor was then allowed to cool down under a low flow of nitrogen. Catalyst activity was measured as a function of reaction temperature by heating the reactor in steps and maintaining it at each temperature for at least 45 minutes before a sample was taken for analysis by gas chromatography (FID, BP-1 capillary column). All oligomerization reactions were carried out at 35 bar and a mass hourly space velocity (MHSV) of 2.

The activities of the two types of nickel catalysts, as well as that of the silica–alumina itself, for ethylene conversion over a wide temperature range is shown in Fig. 1. With SiO_2–Al_2O_3, no appreciable conversion occurs below 230 °C. When nickel is present, however, two distinct temperature regions of high catalytic activity are observed for both nickel catalysts: one at low temperatures (a volcano-type curve around 120 °C) and the other at high temperatures (300 °C). The results also show that the contribution of the nickel to ethylene conversion in *both* temperature regions is more significant than that of the support. The characteristics of the reactions are, however, different in the two temperature regions. At the low temperature, the reaction is highly selective resulting almost exclusively in products with an even number of carbon atoms (see Fig. 2), and can thus be considered as 'true' oligomerization, *i.e.* the products, C_4–C_{22}, are integral multiples of the monomer. The amount of products with an odd number of carbon atoms were 1.1 and 2.3% by mass for the Ni/SiO_2–Al_2O_3 and Ni–SiO_2–Al_2O_3 catalysts respectively, both at ~100% conversion. The high temperature region is characterized by a low C_6/C_5 ratio, where the ratio of the primary product (C_6) to the secondary product (C_5) is taken as a measure of the degree of hetero-oligomerization as defined by Langlois.[10] This ratio varies from 105 at 120 °C to 5 at 300 °C for the catalyst prepared by ion-exchange, similar to the trend observed with NiNaY.[4]

The results in Fig. 2 also show that the product distribution obtained at 120 °C is dependent on whether the nickel is incorporated by ion-exchange or impregnation. With Ni–SiO_2–Al_2O_3, both a higher concentration of octenes relative to the butenes and hexenes and also a higher amount of products with a carbon number greater than nine are obtained; the C_{10+} or diesel fraction was 41.1 and 22.6% for the exchanged and impregnated catalysts respectively. These results indicate that the ion-exchanged catalyst is more active in terms of overall oligomerization activity than the impregnated catalyst, even though the amount of nickel in the latter is considerably higher.

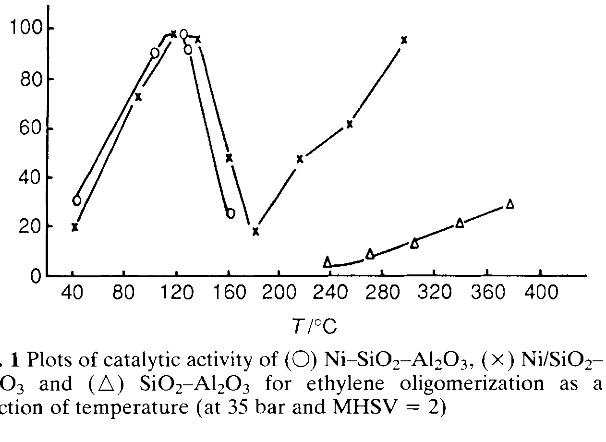

Fig. 1 Plots of catalytic activity of (○) Ni–SiO_2–Al_2O_3, (×) Ni/SiO_2–Al_2O_3 and (△) SiO_2–Al_2O_3 for ethylene oligomerization as a function of temperature (at 35 bar and MHSV = 2)

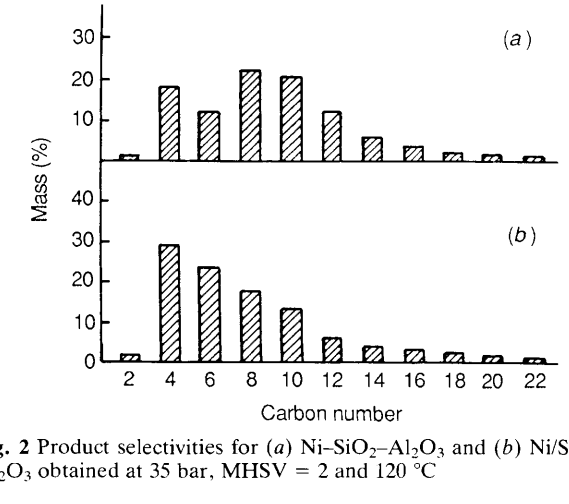

Fig. 2 Product selectivities for (*a*) Ni–SiO_2–Al_2O_3 and (*b*) Ni/SiO_2–Al_2O_3 obtained at 35 bar, MHSV = 2 and 120 °C

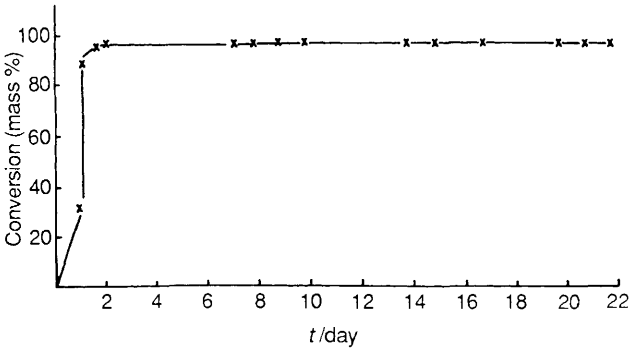

Fig. 3 Plot of % conversion *vs.* time-on-stream for Ni–SiO_2–Al_2O_3 (at 35 bar, MHSV = 2 and 120 °C)

The most significant property in terms of industrial importance exhibited by these catalysts is shown in Fig. 3 where the % conversion is plotted against time-on-stream. The results show that the Ni–SiO_2–Al_2O_3 catalyst is extremely stable in use at 120 °C showing no detectable drop in conversion (99.3% by mass) after 22 days on stream.

In this communication therefore we have shown for the first time that silica-alumina-based nickel catalysts (of high Ni content) can be used at high pressures and low temperatures for the highly efficient and stable heterogeneous oligomerization of ethylene. Further details on these catalytic systems will be given shortly in a full report.

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