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Review

Catalysts and conditions for the highly efficient, selective and stable heterogeneous oligomerisation of ethylene

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Abstract

The oligomerisation of ethylene into products in the C₄–C₂₀ range over heterogeneous nickel catalysts in a fixed-bed reactor at low temperature and high pressure (LT-HP) is reported. The catalysts were obtained by Ni(II) exchange or impregnation of two differently prepared amorphous and mesoporous silica–alumina supports. A plot of catalytic activity versus temperature at 35 bar and MHSV=2 produces a volcano-type curve with a maximum around 120°C. Experiments performed under the LT-HP reaction conditions, viz. 120°C, 35 bar and MHSV=2, give an ethylene conversion level of 99% and a 97% selectivity to products with an even number of carbon atoms. The product spectrum (C_n distribution) was dependent on the type of catalyst used, with the percentage of the C₁₀₊ oligomers lying in the range 23–41% by mass. Of practical significance, these types of catalyst were found to be extremely stable in use showing no detectable drop in conversion after 108 days on stream under the LT-HP reaction conditions employed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Ethylene; Oligomerisation; Heterogeneous nickel catalysts

1. Introduction

Propylene and other olefins of higher molecular weight can be easily oligomerised over a wide range of acid catalysts of both zeolitic and non-zeolitic type [1]. In the case of ethylene, however, only low conversions can be obtained over acidic catalysts. Transi-

tion metal catalysts, on the other hand, and particularly those based on nickel, are active for both ethylene dimerisation and oligomerisation [2–5]. In terms of heterogeneous nickel catalysts, numerous reports have already appeared in the literature which deal primarily with the dimerisation of ethylene over these catalysts [1,2,5]. Examples of such catalysts are nickel on silica [6], nickel on silica–alumina [7] and nickel on zeolites X [8] and Y [9,10]. These catalysts can be prepared by techniques such as ion-exchange, impregnation, coprecipitation and even from the decomposition of organometallics pre-deposited on the oxide system. Such studies demonstrate the versatility of nickel for ethylene activation and conversion for a large number of coordination environments and methods of catalyst preparation.

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With NiX it was shown by Diaz et al. [8] that at 250°C oligomers up to C₁₂ could be obtained. And with NiY, Venuto and Landis [9] found that C₁₂–C₃₅ oligomers could be extracted from the pores of the zeolite after the reaction had been terminated. With both of these systems, however, severe catalyst deactivation was observed and the systems appeared to be of little significance for practical application. Based on the results obtained with NiX [8] and NiY [9] and the established behaviour/use of homogeneous Ni catalysts [2–5], we decided to re-examine the use of heterogeneous nickel catalysts for the oligomerisation of ethylene into products in the C₆₊ range for use in the synthetic fuel, polymer or detergent industries [10]. Use of a nickel catalyst could, in principle, lead to products in the C₆₊ range with little or no branching [3,11]. Finally, of significance in synthetic fuel applications is the fact that the C₁₀₊ fraction would contain little or no aromatic compounds, important from both a fuel quality (cetane number) and environmental points of view.

In our previous work we had shown that catalysts based on nickel(II) supported on ion-exchangeable solid carriers such as silica–alumina [12,13] and zeolite Y [14] possessed high initial activity for the oligomerisation of ethylene. These catalysts required no pre-reduction as is necessary for example for the Ni/SiO₂ type systems [6]. However, oligomerisation over the nickel-exchanged silica–alumina (NiSA) catalysts was carried out at high temperature (300°C) and low pressure (11 bar) (HT-LP conditions) and in these circumstances rapid deactivation took place due to catalyst coking. Loss of catalytic activity with time-on-stream was also observed in our studies with the NiY catalyst under the LT-HP conditions [14], and this deactivation was ascribed to pore blockage in the zeolitic catalyst by bulky oligomer products [14,15].

In recent short communications [16,17] we reported on the type of heterogeneous nickel catalysts and the reaction conditions required for the highly efficient, stable and selective heterogeneous oligomerisation of ethylene into products in the C₄–C₂₀ range. In the present publication a full and more detailed account of this work is reported as well as further results from an extended catalytic run which lasted up to five months on-stream, along with data on the effects of reaction temperature and MHSV. The

quality of the oligomer product for use in synthetic fuels is also described.

2. Experimental

2.1. Preparation of silica–alumina (SA) supports

2.1.1. Silica–alumina type I (SA-I)

The first type of silica–alumina support used in this study, SA-I, was prepared by gelling an aqueous mixture of tetrapropylammonium aluminate and silicic acid followed by drying and calcining at 530°C [18,19]. Full details of the synthesis are given below.

The aluminate solution was obtained by precipitating Al(OH)₃ from 4.1 g AlCl₃·6H₂O and boiling it in a 2.35 M excess of tetrapropylammonium hydroxide. The silicic acid solution was prepared by diluting 123.7 g of sodium silicate with 613 g of water. While stirring, 99.6 g of a cation exchange resin in the hydrogen form (BIORAD, AG 50 W-X12) was added slowly to the silicic acid solution. After separating the resin by filtration, cation exchange was repeated with 24.0 g of fresh resin. To the silicic acid solution obtained in this way 6.0 g of tetrapropylammonium hydroxide was added immediately before addition of the aluminate solution. This mixture was reacted for four days at room temperature and for three days at 70°C. After this it was evaporated to dryness, washed free of excess tetrapropylammonium hydroxide and redried. The product was calcined at 530°C. This support had an SiO₂/Al₂O₃ ratio of 72 and a surface area of 450 m²/g.

2.1.2. Silica–alumina type II (SA-II)

The synthesis of the second type of silica–alumina support (SA-II, SiO₂/Al₂O₃=50) was carried out by the coprecipitation of freshly prepared sodium aluminate and commercially available sodium silicate solutions by the addition of nitric acid. A typical synthesis of SA-II is as follows:

(i) Preparation of sodium aluminate solution

4.5 g of Al(OH)₃, 5.0 g of NaOH and 7.5 ml of distilled water were placed in a flask equipped with a condenser and the mixture was allowed to react at reflux, with stirring, until a clear solution was obtained. 250 ml of distilled water were then added

to the flask and the solution was stirred and heated for a further 1 min.

(ii) Preparation of the silica–alumina hydrogel

To 199 ml of waterglass solution (Merck, 28% by mass SiO₂) and 1085 ml of distilled water, 228 ml of the hot sodium aluminate solution were added, followed by 430 ml of 1.4 M nitric acid under vigorous stirring. A gel is obtained within 1–2 min with a resultant pH=9. The hydrogel is then aged at 25°C for three days and it is then washed with distilled water until neutral pH is obtained in the wash water.

(iii) Preparation of the solid silica–alumina

The diluted hydrogel obtained above is filtered using a buchner funnel, to remove as much of the water as possible, and the more concentrated product is then dried at 110°C overnight followed by calcination at 550°C for 3 h. The Na⁺-form of the solid silica–alumina product thus obtained is used as such as described in Section 2.1.5.

2.1.3. Preparation of NiSA-IA

SA-I was impregnated with an aqueous solution of nickel nitrate hexahydrate and after evaporation of the solvent possessed a nickel loading of 3.84%. This catalyst is designated as NiSA-IA.

2.1.4. Preparation of NiSA-IB

The ion-exchange equivalent of NiSA-IA, i.e. NiSA-IB, was prepared by refluxing SA-I in a nickel nitrate solution for 4 h. After filtration, the solids were extensively washed with distilled water and then dried at 110°C. The product had a nickel content of 0.73%.

2.1.5. Preparation of NiSA-II

NiSA-II was obtained by ion-exchange of the Na⁺-form of the solid support SA-II with an aqueous solution of nickel chloride for 5 h at reflux, using three moles of nickel(II) for every two moles of aluminium in the silica–alumina support. The green solids were then filtered and extensively washed with distilled water until the filtrates were free of chloride ions, otherwise detected by the addition of silver nitrate. After drying at 110°C and following acid digestion of the green solids, the catalysts contained 1.56% nickel by mass as determined by AA. Other chemical and physical properties of the NiSA-II catalyst are given in Table 1.

Table 1

Chemical composition and physical properties of the NiSA-II catalyst^a

Ni content	1.56 mass (%)
Al content	1.6 mass (%)
Na content	0.68 mass (%)
BET surface area	425 m ² /g
Average pore radius	18.7 Å
Pore volume	0.75 cm ³ /g
XRD analysis	Amorphous

^a For acid strength properties of catalyst see [12] under LASA.

A NiSA-II sample with a nickel content of 0.76% was obtained by stirring the support in the nickel solution at room temperature for 18 h.

2.2. Catalytic experiments

The catalytic experiments were performed in a fixed-bed flow microreactor which has been described previously [14]. After the reactor had been charged with the catalyst (1.3 g, particle size 300–500 microns), the sample was freed from adsorbed water by heating at 300°C for 3 h under a flow of UHP nitrogen. The reactor was then allowed to cool down under a low nitrogen flow and the conversion of ethylene was carried out under the experimental conditions described in the text below. CP grade ethylene was used which was first passed over a BASF R3-11 copper catalyst and 3 Å molecular sieves (Merck). Gas flows were regulated using Brooks mass flow controllers, and Tescom back-pressure regulators were used for controlling the pressure.

2.3. Product analysis

On- and off-line analyses were carried out using Carlo Erba 4200 gas chromatographs equipped with FID detectors and a 60 m SEG OV1 or BP-1 capillary column. Liquid products were condensed with a water-cooled condenser and the volume of gaseous products was additionally quantified with a laboratory wet gas meter.

The ASTM D613 cetane number engine test as well as the other tests listed in Table 4 were performed by the fuel and physico-chemical section, Sasol 1, Sasolburg.

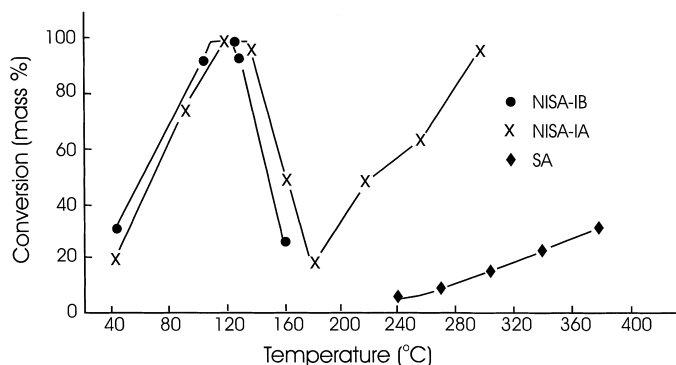


Fig. 1. Plot of catalytic activity of NiSA-IA, NiSA-IB and silica–alumina for ethylene oligomerization as a function of temperature (at 35 bar and MHSV=2).

The hydrogenation reactions were carried out in a Labortechnik autoclave using a commercial palladium catalyst (Johnson Matthey, 5% Pd/C, Type 87L). To avoid any risk of skeletal isomerisation reaction of the oligomers, temperatures below 80°C and high pressures around 30 bar were employed. The reaction was allowed to proceed (with intermittent supplementation of the hydrogen pressure) until no further hydrogen consumption was observed. The extent of reaction was further evaluated by determining the bromine number using IP test method 126. The reaction was terminated provided that a bromine number of <10 was achieved.

3. Results and discussion

The catalytic activity of the two types of NiSA-I catalyst, as well as that of the support itself, for ethylene conversion to products of higher molecular weight, as a function of reaction temperature is shown in Fig. 1. The silica–alumina shows no appreciable conversion below 230°C. With the nickel-containing catalysts, two distinct temperature regions of high catalytic activity are observed. One is at a low temperature, a volcano-type curve with a conversion maximum close to 120°C, and the other at a higher temperature around 300°C. The results also show that the contribution of the nickel to ethylene conversion in both temperature regions is definitely more significant than that of the support.

The characteristics of the oligomerisation reaction are, however, different in the two temperature regions. At the low temperature, the reaction is highly selec-

tive, resulting almost exclusively in products with an even number of carbon atoms (see Fig. 2), and can thus be considered as “true” oligomerisation, i.e. the products, C₄–C₂₀, are integral multiples of the monomer. The amounts of products with an odd number of carbon atoms were 1.1% for the NiSA-IA and 2.4% for the NiSA-IB catalysts at 97.7% and 99.3% conversion, respectively. The high-temperature region, on the other hand, is characterised by a high concentration of products with an odd number of carbon atoms, the amounts of which increase with increasing reaction temperature (see Table 2). The results in Fig. 2 also show that the product distribution obtained at

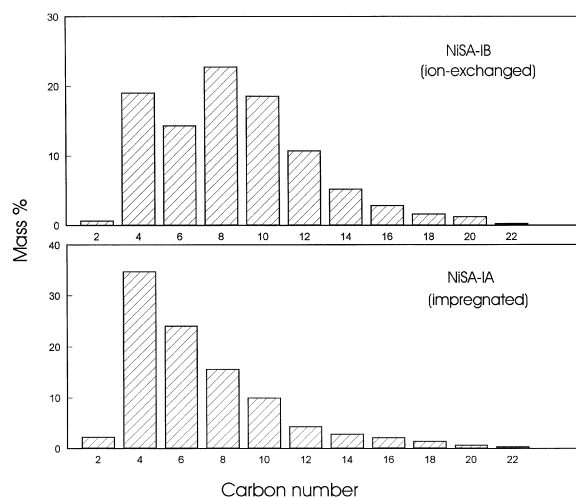


Fig. 2. Product-spectrum obtained with the NiSA-IA and NiSA-IB catalysts (at 120°C, 35 bar and ethylene MHSV=2).

Table 2

Effect of temperature on the amount of products with an odd number of carbon atoms

Temperature (°C)	Concentration (mass %)
120	1.1
218	2.6
250	9.3
300	18.2

With NiSA-IB catalyst at 35 bar and MHSV=2.

120°C is dependent on whether the nickel is incorporated by ion-exchange or impregnation. An examination of the product spectrum obtained with the impregnated catalyst shows a decrease in concentration with increasing molecular weight. With the NiSA-IB catalyst, 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 9, are obtained. The C₁₀₊ or diesel fractions were 41% and 22% for the ion-exchanged and impregnated NiSA-I catalysts, respectively. The results show therefore that the nickel is more effectively used in the ion-exchanged catalysts. It can be noted here that the nickel content of these catalysts is considerably higher than that employed in our previous studies (0.3%) under the HT-LP reaction conditions [12,13].

An important property exhibited by these catalysts is shown in Fig. 3 where percentage conversion is plotted against time-on-stream. The results show that the ion-exchanged catalyst is extremely stable when used at 35 bar, 120°C and MHSV=2, i.e. at the reaction conditions at the “top of the volcano” curve,

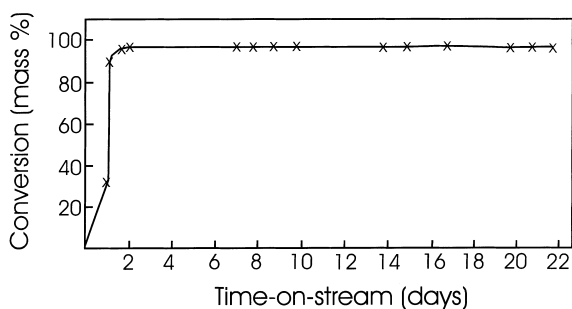


Fig. 3. Plot of percentage ethylene conversion versus time-on-stream for the NiSA-IB catalyst (at 120°C, 35 bar, and MHSV=2).

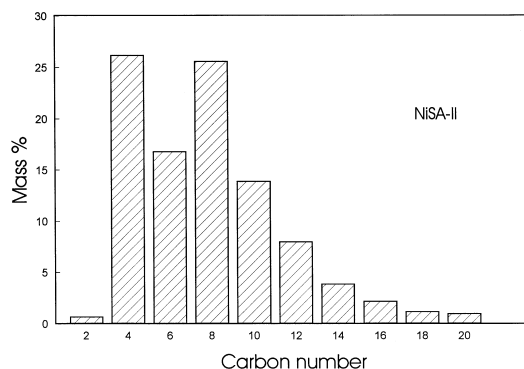


Fig. 4. Product spectrum obtained with the NiSA-II catalyst (at 120°C, 35 bar, and ethylene MHSV=2).

showing no detectable drop in conversion after 22 days on-stream.

Having thus established that the foregoing reaction conditions and catalysts allow for the highly efficient, selective and stable heterogeneous oligomerisation of ethylene, we subsequently examined the use of a silica–alumina support which could be synthesised via the use of more conventional reagents and procedures, namely from the coprecipitation of freshly prepared sodium aluminate and commercially available sodium silicate solutions (SA-II, see Section 2).

The product spectrum obtained with the nickel catalyst prepared by ion-exchange of this support, NiSA-II (1.56% nickel), is shown in Fig. 4. It can be observed that at a conversion of 99.3%, the amount of C₁₀₊ products formed (30.4%) with this catalyst is approximately 11% lower than that obtained with NiSA-IB catalyst. Using a NiSA-II sample with 0.76% nickel, a 99.6% conversion was achieved which yielded a C₁₀₊ fraction of 28.6%. The amounts C₁₀₊ obtained with the NiSA-I and NiSA-II type catalysts are in agreement with our previous conclusions [12] that the oligomerisation activity of the nickel catalysts increases with increasing acid strength of the support. The influence of the difference in the surface areas of the supports cannot, however, be entirely excluded. Further, calculation of the turnover numbers for the 0.76% and 1.56% nickel NiSA-II catalysts clearly indicate that the low loadings of metal cation result in a much more effective use of the nickel.

In a separate experiment, the stability of the NiSA-II catalyst was examined in a run which lasted over

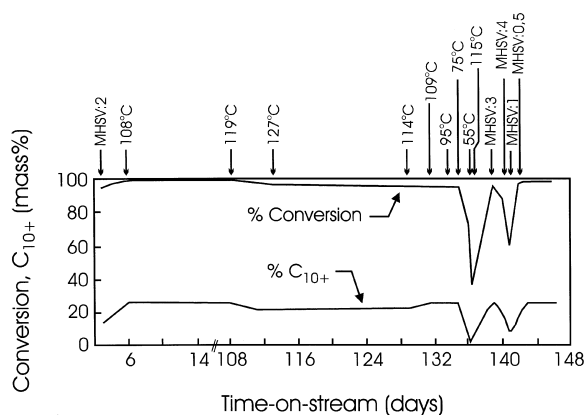


Fig. 5. Oligomerization of ethylene at 35 bar.

144 days (see Fig. 5). From day 6 until day 108, the reaction conditions were 108°C, 35 bar and MHSV=2. During this time on-stream, no catalyst deactivation was observed, the ethylene conversion remained at 99+% throughout and the cumulative amount of C_{10+} product was 26% by mass (see Table 3). These results confirm that with the amorphous and mesoporous ion-exchanged NiSA catalysts and under the specified reaction conditions of LT-HP, we can obtain the highly efficient, selective and stable heterogeneous oligomerisation of ethylene into products in the range C_4 – C_{20} . The amounts of the different carbon-number products obtained during this time-on-stream per gram of catalyst are listed in Table 3. The high selectivity to products with an even number of carbon atoms [16,17] was again observed. It can also be noted that the percentage of C_{10+} given above is lower than that reported above, 30.4%, and this difference can be ascribed to the lower reaction temperature used in this latter experiment (108° as compared with 120°C).

Table 3
Products and yields obtained over 108 days on-stream per gram of catalyst^a

Product	Yield (g)
Butenes	1662
Hexenes	1229
Octenes	940
Decenes and higher	1332
Pentenenes, heptenes etc.	55

^a With NiSA-II catalyst at 108°C, 35 bar and MHSV=2.

Table 4

Characterisation of a straight-run diesel product obtained from ethylene (cut-off point: 180°C)

Property	C_{10+} fraction	SA Standard (SABS 342)
Distillation (°C)		
20%	202	—
50%	220	—
90%	295	362 maximum
Cetane no. (engine)	60	45 minimum
Cloud point (°C)	+1	—
Cold filter plugging point (°C)	-20	-4 maximum
Carbon residues (mass %)	0.11	0.2 maximum
Viscosity at 40°C (mm^2s^{-1})	2.32	2.2–5.3
Density at 15°C (g ml^{-1})	0.8036	—
Bromine no.	84.2	—

The quality of a typical diesel-range sample produced is shown in Table 4 together with the South African Bureau of Standards Specification (SABS 342) for diesel. It can be observed that, with the exception of the bromine number, the specification is met in all the properties listed, and that the very high cetane number indicates that a synthetic diesel fuel of high quality could be obtained from our catalytic system. The high bromine number indicated is due to the fact that the sample had not been hydrogenated. As a consequence, the cetane number is an underestimate of that which would be expected from a fully hydrogenated sample [1]. We can also report that the unhydrogenated gasoline fraction, on the other hand, had a RON of 86.2. Further, from ^{13}C – NMR it can be determined that aromatics are essentially absent from the fuel samples produced under the LT-HP conditions [14].

An estimation of the amount of linear products versus the amount of branched products was obtained for the carbon number range C_6 – C_{10} . This was achieved by determining the percentage of linear alkanes and percentage branched alkanes after hydrogenation of the samples in a batch reactor using a commercial hydrogenation catalyst (see Section 2). As a result of the hydrogenation step, a simplified gas chromatogram is obtained where the n -alkanes can be readily identified (last alkane peak to elute in a C_n group, as well as being well separated from its branched counterparts due to b.p. differences). The percentage of the n -alkanes relative to the remainder of the nonlinear alkanes in a particular carbon-number

Table 5
Linearity of products in C₆–C₁₀ range

Products	Percentage of linear isomer in its C _n group	
	Ethylene oligomerization ^a	F-T synthesis ^b
<i>n</i> -Hexane	64.4	70.7
<i>n</i> -Octane	9.3	53.6
<i>n</i> -Decane	1.8	50.0

^a Over NiSA-IB catalyst under LT-HP conditions.

^b Taken from [20].

group is then easily evaluated. It can also be stated that this simple method for the determination of the linear products is facilitated by the fact that in our product streams the odd-numbered products are essentially absent and this minimises any possible overlap between the *n*-alkane of a C_n and a low b.p. species from the C_{n+1} group. The results obtained from these studies are shown in Table 5 and it can be observed that the amount of linear oligomers decreases with increasing carbon number with a particular dramatic decrease from C₆ to C₈. Also listed in Table 5 are the corresponding products obtained from Fischer–Tropsch synthesis. It can be concluded that the products obtained from ethylene oligomerisation over the NiSA catalysts at LT-HP are of lower linearity than those from Fischer–Tropsch, and this is especially true for the higher oligomers C₈ and C₁₀. An explanation for this drastic decrease in the percentage of linear products observed in the C₈ relative to the C₆ fraction is that under our reaction conditions, a high degree of butene dimerisation leading to branched products is also taking place, in parallel with pure ethylene oligomerisation, to give nonlinear oligomers [5,21]. This reasoning is supported by the fact that when the reaction is conducted at 120°C with the NiSA-II catalysts, the concentration of the octenes is higher than those of the hexenes (C₈/C₆=1.52) [16,17]. Whereas at 108°C (see Table 3) we have the reverse situation (C₈/C₆=0.76) (see also the paragraph on effect of MHSV). In the case of the butenes formed, and as expected from the mechanism of the reaction [21], only the linear isomers are obtained.

The effect of the reaction temperature on catalyst performance was determined in the time period 108–139 days (see Fig. 5). Increasing the temperature from 108°C via 119°C to 127°C resulted in a drop in the activity of the catalyst (conversion decreased to

96.5%). Returning to the lower temperatures (109°C) did not result in an increase in the catalytic activity indicating that this drop in activity with increasing reaction temperature beyond 120°C is therefore an irreversible process. On the other hand, the effect of a decrease in the reaction temperature (to lower than 108°C) resulting in lower activities, can be reversed. Thus, at 55°C the conversion is 34.7% but when the reaction temperature is allowed to rise to 115°C the resultant conversion level is 97.2%. This behaviour of the catalyst could be ascribed to the fact that beyond “the top of the volcano” in the plot of activity versus temperature for the NiSA catalysts (see Fig. 1), the surface organometallic nickel species responsible for the low temperature catalytic activity becomes unstable with increasing reaction temperature resulting in a complete loss of catalytic activity around 180°C. The activity observed above 200°C (see Fig. 1) could therefore be due to a different catalytic species and/or reaction mechanism (see below) as reflected in the type of product obtained at the higher temperatures (see Table 2). Investigations into the nature of the catalytic species are currently underway.

Further, in this high-temperature regime and as shown in Fig. 6, the reaction temperature has a decisive influence on catalyst stability. Above 300°C, catalyst deactivation is rapid, whereas at the temperature of 285°C, a more stable behaviour is observed. The diesel fraction obtained at 285°C has a cetane number of 36.6 indicating a more branched product. Thus, at the higher temperatures, acid-catalysed side reactions (skeletal isomerisation, hetero- and conjunct oligomerisation [14,22]) contribute to the product

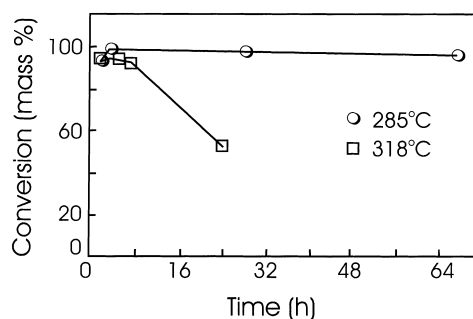


Fig. 6. Deactivation of NiSA-II catalyst at 35 bar at high reaction temperatures.

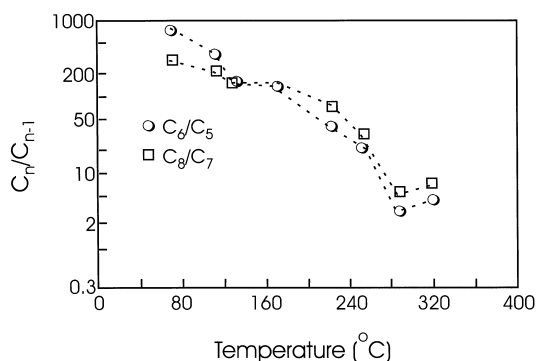


Fig. 7. Nature of product as a function of reaction temperature at 35 bar.

formation. This is clearly demonstrated by the results shown in Fig. 7 where we have plotted separately the ratio of two primary products (C_6 and C_8) to two secondary products (C_5 and C_7), i.e. C_6/C_5 and C_8/C_7 , against the reaction temperatures [14]. These ratios can therefore be taken as a measure of the degree of hetero-oligomerisation as defined by Langlois [22]. At low temperatures the reaction is selective and the odd-numbered products are practically absent. As a consequence, extremely high ratios are obtained. As the temperature is increased, the selectivity for the even-numbered products decreases as reflected by the lower ratios [14].

We have also examined the effect of MHSV on the catalytic activity as demonstrated by the results shown in Fig. 5 and Table 6 for the time period 139–146 days. Increasing the MHSV via 3 to 4 results in a decrease in ethylene conversion to 59.6%. By lowering the MHSV to 1, and then to 0.5, the high conversion levels (99.3%) are restored. In addition, as shown in Fig. 8, the maximum space–time–yield of the C_{10+} fraction is obtained at $MHSV \approx 2.0$. From the results in Table 6 it can also be observed that at

Table 6
Effect of MHSV

MHSV	Conversion (%)	C_{10+} (%)	C_8/C_6
0.5	99.3	25.2	1.26
1.0	98.2	21.2	0.90
2.0	99.0	25.5	0.76
3.0	88.9	10.7	0.67
4.0	59.6	3.9	0.64

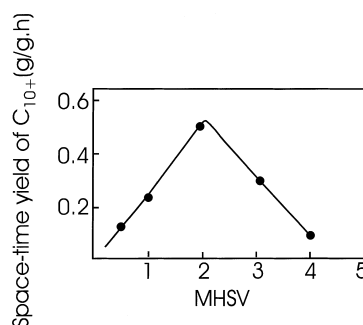


Fig. 8. Plot of space–time–yield versus MHSV.

$MHSV=0.5$, the C_8/C_6 ratio is >1 implying that with decreasing space velocities the statistical reaction sequence deviates increasingly from a growth reaction obeying the Schulz–Flory distribution. Thus, at high temperatures (see above) or low MHSVs we have a higher degree of butene dimerisation resulting in higher yields of the C_8 than of the C_6 olefins, and hence in more branched products [23]. These observations indicate therefore that products of higher linearity are favoured by low temperatures and high space velocities.

4. Conclusions

In this paper we have shown, with an ethylene oligomerization run that lasted over 144 days, that with the amorphous and mesoporous nickel-exchanged silica–alumina catalysts and when used at relatively low temperatures (100–120°C) and high pressures (35 bar) and $MHSV=2$, we can obtain

1. high catalyst stabilities,
2. high selectivities to products with an even number of carbon atoms,
3. a C_{10+} or diesel fraction having a very high cetane number and amounting up to 41% of the product stream (depending on type of catalyst used).

The results therefore constitute a major development for the utilisation of ethylene as a feedstock for the production of higher oligomers. Apart from the Fischer–Tropsch synthesis reactions, ethylene and other light olefins can also be obtained from the conversion of methanol over zeolites and molecular sieves using technologies developed by companies

such as Mobil [24] and UOP [25,26]. Another important potential source of ethylene is the methane coupling reaction which results in both ethylene and ethane [27,28], where the latter can be subsequently dehydrogenated to give additional ethylene.

References

- [1] C.T. O'Connor, M. Kojima, *Catal. Today* 6 (1990) 329.
- [2] A.M. Al-Jarallal, J.A. Anabtawi, M.A.B. Siddiqui, A.M. Aitani, A.W. Al-Sa'doun, *Catal. Today* 14 (1992) 1.
- [3] O.-T. Onsager, J.E. Johansen, in: F.R. Hartley, S. Patai (Eds.), *The Chemistry of the Metal-Carbon Bond*, vol. 3, Wiley, New York, 1985, p. 205.
- [4] W. Keim, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 235.
- [5] J. Skupinska, *Chem. Rev.* 91 (1991) 613.
- [6] F.X. Cai, C. Lepetit, M. Kermarec, D. Olivier, *J. Mol. Catal.* 43 (1987) 93.
- [7] Y. Chauvin, D. Commereuc, F. Hugues, J. Thivolle-Cazat, *Appl. Catal.* 42 (1988) 205.
- [8] G.C. Diaz, L. Ortiz, F. Villegas, Preprints, Div. of Petrol. Chem. ACS, 1978, p. 1194.
- [9] P.B. Venuto, P.S. Landis, *Adv. Catal.* 18 (1968) 259.
- [10] F.T.T. Ng, D.C. Creaser, *Appl. Catal. A* 119 (1994) 327.
- [11] S.M. Pillai, M. Ravindranathan, S. Sivaram, *Chem. Rev.* 86 (1986) 353.
- [12] R.L. Espinoza, R. Snel, C.J. Korf, C.P. Nicolaidis, *Appl. Catal.* 29 (1987) 295.
- [13] R.L. Espinoza, C.P. Nicolaidis, C.J. Korf, R. Snel, *Appl. Catal.* 31 (1987) 259.
- [14] J. Heveling, A. Van der Beek, M. De Pender, *Appl. Catal.* 42 (1988) 325.
- [15] B. Nkosi, F.T.T. Ng, G.L. Rempel, *Appl. Catal. A* 158 (1997) 225.
- [16] J. Heveling, C.P. Nicolaidis, M.S. Scurrrell, *J. Chem. Soc., Chem. Comm.* (1991) 127.
- [17] J. Heveling, C.P. Nicolaidis, M.S. Scurrrell, Preprints, Div. of Petrol. Chem., ACS, 36, 1991, p. 578; in: G.J. Stiegel, R.D. Srivastava (Eds.), *Proceedings of The Liquefaction Contractors Review Meetings*, US Department of Energy, Pittsburgh Energy Technology Center, 3–5 September, 1991, p. 113.
- [18] M.G. Howden, Report CENG 441, CSIR, Pretoria, 1982.
- [19] R.L. Espinoza, C.M. Stander, W.G.B. Mandersloot, *Appl. Catal.* 6 (1983) 11.
- [20] C.D. Frohning, H. Kölbl, M. Ralek, W. Rottig, F. Schur, H. Schulz, in: J. Falbe (Ed.), *Chemical Feedstocks from Coal*, Wiley, New York, 1982, p. 309.
- [21] W. Keim, in: D.W. Slocum, W.R. Moser (Eds.), *Catalytic Transition Metal Hydrides*, The New York Academy of Sciences, New York, 1983, p. 191.
- [22] G.E. Langlois, *Ind. Eng. Chem.* 45 (1953) 1470.
- [23] M. Peuckert, W. Keim, *J. Mol. Catal.* 22 (1984) 289.
- [24] S.A. Tabak, S. Yurchak, *Catal. Today* 6 (1990) 307.
- [25] J.N. Armor, *Appl. Catal.* 78 (1991) 141.
- [26] B.V. Vora, T.L. Marker, P.T. Barger, H.R. Nilsen, S. Kuisle, T. Fuglerud, in: M. de Pontes, R.L. Espinoza, C.P. Nicolaidis, J.H. Scholtz, M.S. Scurrrell (Eds.), *Natural Gas Conversion IV, Studies on Surface Science and Catalysis*, vol. 107, Elsevier, Amsterdam, 1997, p. 87.
- [27] E.E. Wolf (Ed.), *Methane Conversion by Oxidative Processes – Fundamental and Engineering Aspects*, Van Nostrand Reinhold, New York, 1992.
- [28] I.V. Yentekakis, Y. Jiang, M. Makri, C.G. Vagenas, in: M. de Pontes, R.L. Espinoza, C.P. Nicolaidis, J.H. Scholtz, M.S. Scurrrell (Eds.), *Natural Gas Conversion IV, Studies on Surface Science and Catalysis*, vol. 107, Elsevier, Amsterdam, 1997, p. 307.