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Chain-length distributions obtained over nickel(II)-exchanged or impregnated silica–alumina catalysts for the oligomerization of lower alkenes

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In the oligomerization of ethene, the chain-length distributions obtained over heterogeneous nickel catalysts at a low reaction temperature (ca. 110 °C) depend on the acidity of the silica–alumina support, the nickel loading and the olefin feed. Most significantly, ion-exchanged catalysts based on a silica–alumina of high acidity (ca. 0.7 mass% Ni), and those based on a highly-exchanged medium-acidity support (ca. 1.6% Ni), show a distinct superimposed activity for the dimerization of the intermediate butenes. This causes a desirable shift to higher hydrocarbon products, and it is possible to obtain 41 mass% C_{10+} oligomers, while the corresponding value predicted from Schulz–Flory statistics is only 24 mass%. No such deviation from Schulz–Flory statistics is observed in propene oligomerization.

KEY WORDS: nickel-exchanged; silica–alumina; heterogeneous; oligomerization; Schulz–Flory; ethene; propene.

1. Introduction

In previous publications we have reported on the oligomerization of ethene, propene, and 1-butene into distillate-range products using nickel(II)-exchanged zeolite Y [1] and amorphous nickel-supported silica–alumina catalysts [2,3]. One of the remarkable features of these catalysts is the activity pattern observed when the conversion is plotted against the reaction temperature. Both systems show two pronounced activity maxima, one at low and one at high reaction temperature. From the results obtained at a low reaction temperature and elevated pressures, i.e. at 120 °C, 3.5 MPa and a MHSV of 2.0 $g_{feed}\ g^{-1}_{cat}\ h^{-1}$, the most important characteristics can be summarized as follows: > 99% conversion of ethene to oligomers in the C_4–C_{22} range, > 97% selectivity to oligomers containing an even number of carbon atoms, and a high linearity of the product oligomers up to C_6.

With increasing reaction temperature, the mode of oligomerization changes from *true oligomerization* (that is the formation of oligomers composed of integral multiples of the monomer) to *hetero-oligomerization* (that is the simultaneous formation of oligomers composed of integral and non-integral multiples of the monomer). The selectivity patterns observed were discussed in a recent communication [4]. If high selectivity (*true oligomerization*) and stable catalyst performance are required, the reaction should be performed at low temperatures (ca. 100–120 °C).

Another concern in this subject area is the chain-length distribution observed when the catalyst operates in the mode of true oligomerization at low temperatures. This is of particular importance when a certain carbon-number cut (e.g. diesel fuel) is the target product. In this article, we describe the limitations involved and the potential strategies to overcome them.

2. Experimental

The supports and the catalysts used in this paper were chosen from those employed previously [2–4] (see table 1), and the experimental procedures were as reported earlier [2]. The oligomerization reactions were performed in fixed-bed micro-reactors at a mass hourly space velocity (MHSV) of 2.0 $g_{feed}\ g_{cat}^{-1}\ h^{-1}$, and, if not otherwise indicated, a pressure of 3.5 MPa was employed. For each experiment, the product distribution described was obtained at the reaction temperature of the low temperature activity maximum (T_{max}).

3. Results

In table 2, we list the conversions and turnover frequencies (TOF) obtained with selected nickel catalysts at the reaction temperature of the low temperature maximum (T_{max}). The positions of these maxima were

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Table 1
Amorphous silica–alumina supports and nickel catalysts used

Sample	Support	Ni content (mass%)	SiO_2/Al_2O_3 (mol ratio)	Specific surface area (m^2/g)	Acidity [5]
SA-I	type I		70	450	high
SA-II	type II		50	420	medium
NiSA-IA (3.84)[a]	type I	3.84	70		
NiSA-IB (0.73)	type I	0.73	70		
NiSA-II (0.76)	type II	0.76	50		
NiSA-II (1.56)	type II	1.56	50		

[a] All catalysts were prepared by ion-exchange, except NiSA-IA, which was prepared by impregnation [2].

Table 2
Feed conversions and turnover frequencies (TOF) over the various catalysts at the low-temperature maximum (MHSV $= 2.0\ g_{feed}\ g_{cat}^{-1}\ h^{-1}$)

Catalyst	Feed	T_{max} (°C)	P (MPa)	Conv. (mass%)	TOF ($mol_{feed}\ mol_{Ni}^{-1}\ h^{-1}$)
NiSA-IA (3.84)	ethene	120	3.50	97.7	106
NiSA-IB (0.73)	ethene	115	3.50	99.3	569
NiSA-II (0.76)	ethene	100	3.50	99.6	548
NiSA-II (1.56)	ethene	110	3.50	99.3	266
NiSA-IA (3.84)	propene	90	0.75	12.2	9
NiSA-IB (0.73)	propene	85	0.75	27.0	103

determined in our previous studies by plotting the conversion against the reaction temperature (see [1–3] for examples). For ethene and propene at a high pressure (3.5 MPa), the maxima are typically found between 100 and 120 °C. For a propene feed at low pressure (0.75 MPa), the maximum is found at somewhat lower temperatures, typically at 85–90 °C. Figure 1 shows the corresponding product distributions obtained from ethene oligomerization over the catalysts listed in table 2. These catalysts are based on two different silica–alumina supports [2]: SA-I is a silica–alumina of high acidity, while SA-II is of medium-acidity. Two of the catalysts are supported on SA-I, where NiSA-IA was obtained by impregnation (3.84% Ni), and NiSA-IB by ion-exchange (0.73% Ni). The SA-II support, on the other hand, was ion-exchanged to a low and to a high degree (0.76 and 1.56% Ni, respectively); the corresponding catalysts are named NiSA-II (0.76) and NiSA-II (1.56). Under the indicated reaction conditions (figure 1), the oligomers obtained over the impregnated NiSA-IA catalyst and over NiSA-II (0.76) follow, over the whole product range, a statistical chain-length distribution as described by Schulz and Flory [6–8]. However, with the catalysts NiSA-IB (0.73) and NiSA-II (1.56), higher concentrations of the octenes than of the hexenes are observed, indicating deviations from a regular Schulz–Flory growth pattern. Over the latter two catalysts, a distinct activity for the dimerization of the butene intermediates to the octenes is found. But also in these cases, the carbon-number distribution of the higher olefins ($>C_6$) correlates well with Schulz–Flory statistics, as shown in table 3, and further stepwise growth of the octenes with ethene leads to comparatively high amounts of C_{10+} products in the total product spectrum.

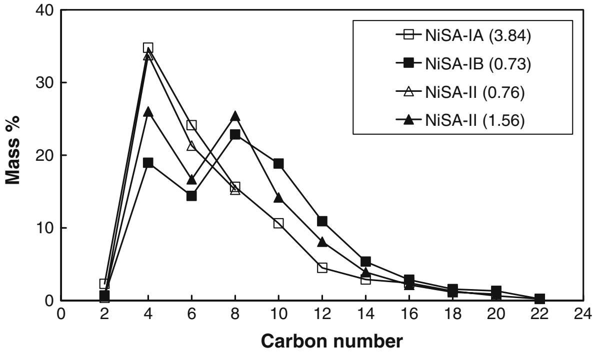

Figure 1. Oligomerization of ethene: exit stream composition obtained over the various catalysts at T_{max} (100–120 °C), 3.5 MPa and MHSV $= 2.0\ g_{ethene}\ g_{cat}^{-1}\ h^{-1}$.

For our calculations, the following form of the Schulz–Flory equation was used [8]:

$$\log(W_n/n) = n \log \alpha + \log((1-\alpha)^2/\alpha),$$

where n is the number of monomer units in the oligomer, W_n is the mass fraction of the nth oligomer, and α is the chain growth probability (growth factor). The growth factors α, the correlation coefficients, and the corresponding mass% of the C_{10+} hydrocarbon cuts (distillate-range products) are given in table 3.

The Schulz–Flory distribution places a significant limitation on the maximum yield of the various carbon number fractions that can be obtained. For ethene as feed and at 100% conversion, the product distribution as a function of the growth factor α is shown in figure 2.

Table 3
Growth factors α (for the carbon-number range indicated), correlation coefficients (r^2), and the resulting C_{10+} product cut obtained at T_{max} (100–120 °C) and 3.5 MPa over various catalysts

Catalyst	Feed	C_n range	α	r^2	C_{10+} (mass%)
NiSA-IA (3.84)	ethene	C_4–C_{22}	0.49	0.993	22.6
NiSA-IB (0.73)	ethene	C_8–C_{22}	0.49	0.997	41.1
NiSA-II (0.76)	ethene	C_4–C_{22}	0.50	0.997	28.6
NiSA-II (1.56)	ethene	C_8–C_{20}	0.48	0.993	30.4
NiSA-II (1.56)	propene	C_6–C_{21}	0.30	0.927	25.8

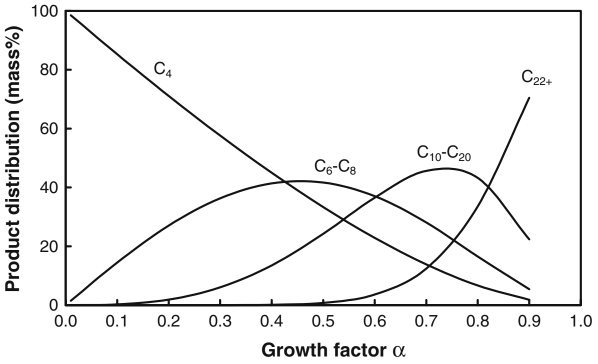

Figure 2. Oligomerization of ethene: product distribution according to Schulz–Flory statistics as a function of the growth factor α.

For example, a maximum of 45% C_{10}–C_{20} hydrocarbons can theoretically be produced in a straight run. Controlling the growth pattern is therefore important, as it allows influencing the selectivity of the oligomerization process. As was shown above (table 3), the high dimerization activity for the intermediate butenes shown by the catalyst system NiSA-IB (0.73), allowed us to obtain 41% C_{10+} hydrocarbons while the value of α (for C_8–C_{22}) was only 0.49. Thus, 17 mass% higher C_{10+} yields than predicted by Schulz–Flory were produced.

The distillate range products theoretically obtainable from propene and butene at 100% conversion are shown in figure 3. The product distributions attained with ethene and propene (separately) over the NiSA-II (1.56) catalyst under similar reaction conditions can be seen in figure 4. While the dimerization of the butene intermediates is clearly evident in the case of ethene oligomerization, the analogous dimerization activity is absent with propene as feed (i.e. in the latter case, dimerization of the hexenes to produce higher than expected C_{12} yields is not observed). The growth factor α, the correlation coefficient, and the C_{10+} hydrocarbons obtained from propene are also included in table 3.

4. Discussion

From the results listed in table 2 (for ethene as well as for propene), it is clear that the ion-exchanged catalyst NiSA-IB (0.73) is superior in terms of conversion and turnover frequencies as compared to the impregnated catalyst NiSA-IA (3.84). By ion-exchange, the formation of highly active isolated nickel species can be expected [9], and the metal is much more efficiently utilized than in the impregnated catalysts [2,3]. A further consequence is the high dimerization activity for the intermediate butenes formed from ethene, which is not seen with NiSA-IA, but is clearly evident over NiSA-IB (see figure 1). Therefore, the oligomerization with NiSA-IA follows Schulz–Flory statistics over the whole product range, and the amount of C_{10+} oligomers obtainable is much lower than those observed over the

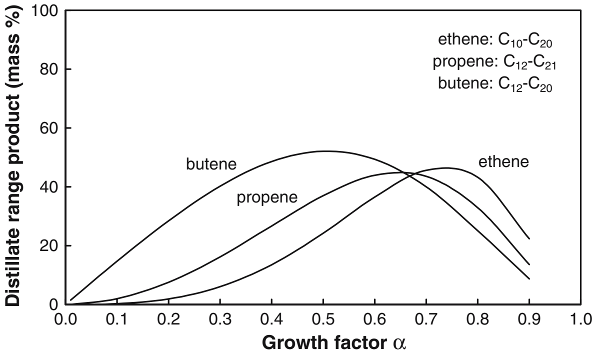

Figure 3. Distillate-range products obtainable from ethene, propene and butene according to Schulz–Flory statistics as a function of the growth factor α.

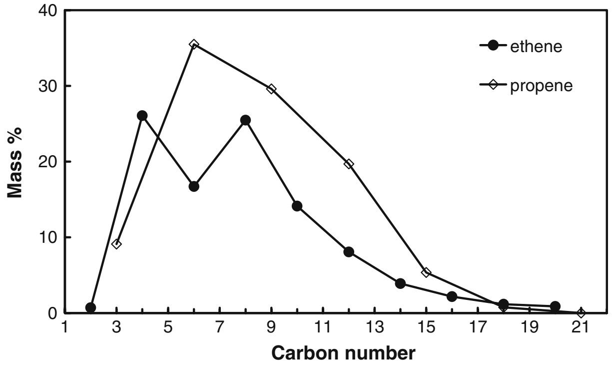

Figure 4. Oligomerization of ethene and propene: exit stream composition obtained over the catalyst NiSA-II (1.56) at T_{max} (110–120 °C), 3.5 MPa and MHSV = 2.0 $g_{ethene}\ g_{cat}^{-1}\ h^{-1}$.

ion-exchanged NiSA-IB catalyst (23% versus 41%, see table 3).

It was established earlier that, at least at high reaction temperatures [5], the oligomerization activity of silica–alumina supported nickel catalysts depends on the acidity of the support. In contrast to NiSA-IB (0.73), the ion-exchanged catalyst NiSA-II (0.76) prepared from a silica–alumina of lower acidity, does not show any obvious dimerization activity for the C_4 olefins; the total product composition is described by a Schulz–Flory distribution (see figure 1 and table 3). However, when more nickel is introduced, as in NiSA-II (1.56), the ethene supply under the prevailing reaction conditions becomes limited, and again a considerable amount of the butenes is directly converted to octenes. This is in agreement with the kinetic model proposed for this catalyst by Heydenrych *et al.* [10]. In that work, the observed rate of ethene conversion and the product distribution obtained in a slurry reactor was correlated using three second-order reactions: ethene–ethene dimerization, ethene–oligomer reaction, and butene–butene dimerization.

That model does not allow for the dimerization of hexenes (the dimers obtained from propene); therefore, the product distribution obtained from propene oligomerization over NiSA-II (1.56) follows a Schulz–Flory growth pattern, while this is not the case for ethene (see figure 4). Consequently, the amount of oligomers produced from propene with carbon numbers >10 is comparatively low (26%), corresponding to an α-value of only 0.30 (table 3). This is also a reflection of the generally lower reactivity of propene and of higher alkenes in coordinative transition metal-catalyzed oligomerization [3,11].

However, chain growth is not only influenced by the catalyst and the feed composition, but also by other parameters which have an influence on carbon–carbon bond formation, namely, temperature, pressure, and MHSV [1,2,8]. For example, figure 5 shows the dependence of the chain growth probability α on the reaction temperature for the catalyst NiSA-IA. The maximum α-value is found at ca. 120 °C, which is at the temperature of maximum feed conversion as shown in tables 2 and 3.

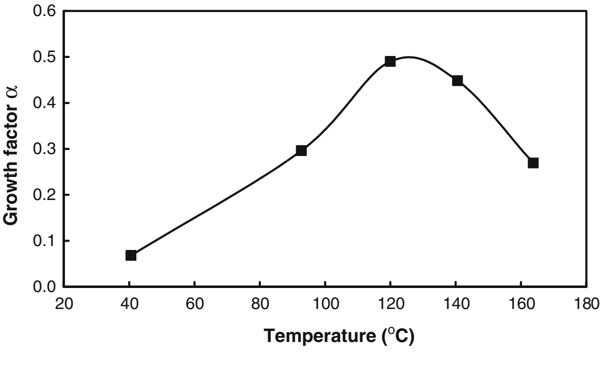

Figure 5. Oligomerization of ethene over the catalyst NiSA-IA (3.84): growth factor α as a function of the reaction temperature.

5. Conclusions

It is well established that the product distribution obtained over *homogeneous* nickel catalysts for the oligomerization of ethene can be described by Schulz–Flory statistics [12]. Our own results show that alkene oligomerization over *heterogeneous* nickel-exchanged silica–alumina catalysts at low reaction temperatures follows similar growth patterns. These results render further support to our earlier conclusion [1,2] that the low-temperature oligomerization reaction over these catalysts follows a coordinative transition metal-catalyzed mechanism.

The Schulz–Flory distribution places restrictions on the maximum yield of various carbon number fractions that can be obtained. However, with highly nickel-exchanged silica–aluminas of appropriate acidity satisfactory yields of the C_{10}–C_{20} hydrocarbons are obtained from ethene. Over these catalysts, the limitation imposed by the Schulz–Flory distribution is partially overcome, since a significant amount of the intermediate butenes is directly converted to octenes. As a result, Schulz–Flory statistics are only applicable to the further growth reaction of the octenes with ethene, and up to 41% C_{10+} hydrocarbons can be obtained in a single pass over the catalyst bed. This value is approximately 17 mass% higher than that predicted by the Schulz–Flory equation.

Another option in attempts to overcome Schulz–Flory limitations would be the addition of *n*-butenes to an ethene feed. However, if *linear* higher olefins are the target product, then the incorporation of already desorbed or added butenes into the growing chain should be avoided, as this will invariably lead to additional chain branching [11,13].

No deviation from Schulz–Flory statistics was observed in propene oligomerization ($\alpha = 0.30$), and the maximum amount of C_{10+} products obtainable is considerably lower (26 mass%).

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