

## CATALYSTS AND CONDITIONS FOR THE HIGHLY EFFICIENT AND STABLE HETEROGENEOUS OLIGOMERIZATION OF ETHYLENE

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### ABSTRACT

The oligomerization of ethylene into gasoline- and diesel-range products over nickel catalysts at high pressure (35 bar) and low temperature (120 °C) is described. The catalysts used were obtained by nickel(II)-exchange or impregnation of two differently prepared silica-alumina supports. Under the above reaction conditions and at an MHSV = 2, conversion levels between 98 - 99% were obtained with the products formed having almost exclusively an even number of carbon atoms, C<sub>4</sub> - C<sub>20</sub>. The percentage of C<sub>10+</sub> products varied from 22 - 41% by mass, depending on the type of catalyst used. Most significantly, the catalysts are extremely stable in use, showing no detectable drop in conversion after 40+ days on stream. The work has been extended to include propylene as feed for the oligomerization reaction over these catalysts.

### INTRODUCTION

Propylene and other olefins of higher molecular weight can be easily oligomerized over a wide range of acid catalysts, both zeolitic and non-zeolitic (1). In the case of ethylene, however, only very low conversions can be obtained over this class of catalysts. In contrast to the situation found with acid catalysts, the study of supported nickel catalysts for the dimerization of ethylene, where use is made of amorphous or crystalline aluminosilicates and silica as supports, is well documented (1-3). Of interest to us was the mobilization of ethylene as an additional source of automotive fuel by taking the reaction beyond the dimerization step. Avoidance of the acid-catalyzed route would also result in a less-branched product, as anticipated from the reaction mechanism of ethylene oligomerization over nickel catalysts. In our previous work (3,4) we have shown that nickel(II), supported on ion-exchangeable carriers such as silica-alumina and zeolite Y, leads to highly active catalysts for the oligomerization of ethylene into gasoline- and diesel-range products. It was found

that for these catalysts no pre-reduction is necessary as required for the Ni/SiO<sub>2</sub>-type catalysts (5-7). The reactions over the nickel-exchanged silica-alumina catalysts, carried out at low pressure (11 bar) and high temperature (300 °C) (3,8), were, however, characterized by rapid deactivation of the catalysts. Similar deactivation patterns were observed with the NiX system studied by Diaz et al. (9). Our studies on the oligomerization of ethylene over NiY at low temperatures showed that this system also deactivated rapidly (4).

In this paper we will report on a novel heterogeneous nickel-based system (catalyst composition and reaction conditions) under which ethylene oligomerization into products in the gasoline- and diesel-ranges can be carried out over extended periods of time without catalyst deactivation. Furthermore, having shown previously (3) that the oligomerization activity is a function of the acid strength of the support, we examined in this study the use of two different silica-aluminas as support material. One was a specially prepared high-acid-strength silica-alumina (SAI), as determined using a catalytic test reaction (3), and the other was prepared via conventional procedures and reagents to give a material of low acid strength (SAII). Also included will be some of our results on the oligomerization of propylene over these nickel catalysts.

## **EXPERIMENTAL**

### **Preparation of the silica-alumina supports**

The first type of silica-alumina, SAI, was prepared by gelling an aqueous mixture of tetrapropylammonium aluminate and silicic acid followed by drying and calcining at 530 °C (3). This support had a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 72 and a surface area of 450 m<sup>2</sup>/g.

The second type, SAII, was obtained by the co-precipitation of sodium aluminate and sodium silicate solutions through the addition of 1 M nitric acid (3). After gelation, the material was thoroughly washed with distilled water until the filtrates had a sodium concentration of not more than 10 ppm. This was followed by drying at 110 °C and calcination at 550 °C.

### **Incorporation of the nickel ions**

SAI was impregnated with an aqueous solution of nickel nitrate which, after evaporation of the solvent, resulted in a nickel loading of 3.84% by mass. This catalyst will be designated as NiSA-IA. The ion-exchange equivalent of this catalyst, NiSA-IB, was prepared by refluxing SAI in a nickel nitrate solution for four hours. 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%.

SAlI was ion-exchanged with an aqueous solution containing a 3-molar excess of nickel chloride hexahydrate, based on the number of theoretically exchangeable aluminium sites. The mixture was stirred for five hours at reflux. The solids were then filtered and extensively washed with distilled water until the filtrates were free of chloride ions, as detected by the addition of silver nitrate. After drying at 110 °C, the catalyst had a nickel content of 1.56% by mass.

### Catalytic experiments

The catalytic experiments were performed in a fixed-bed flow reactor which has been 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 three hours under a flow of UHP nitrogen. The reactor was then allowed to cool down under a low nitrogen flow. In the experiments in which catalyst activity was measured as a function of reaction temperature, the reactor was heated incrementally and it was maintained 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 an MHSV = 2.

### 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 around 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 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<sub>4</sub> - C<sub>20</sub>, are integral multiples of the monomer. The amount of products with an odd number of carbon atoms was 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 characterized by a high concentration of products with an odd number of carbon atoms, the amounts of which

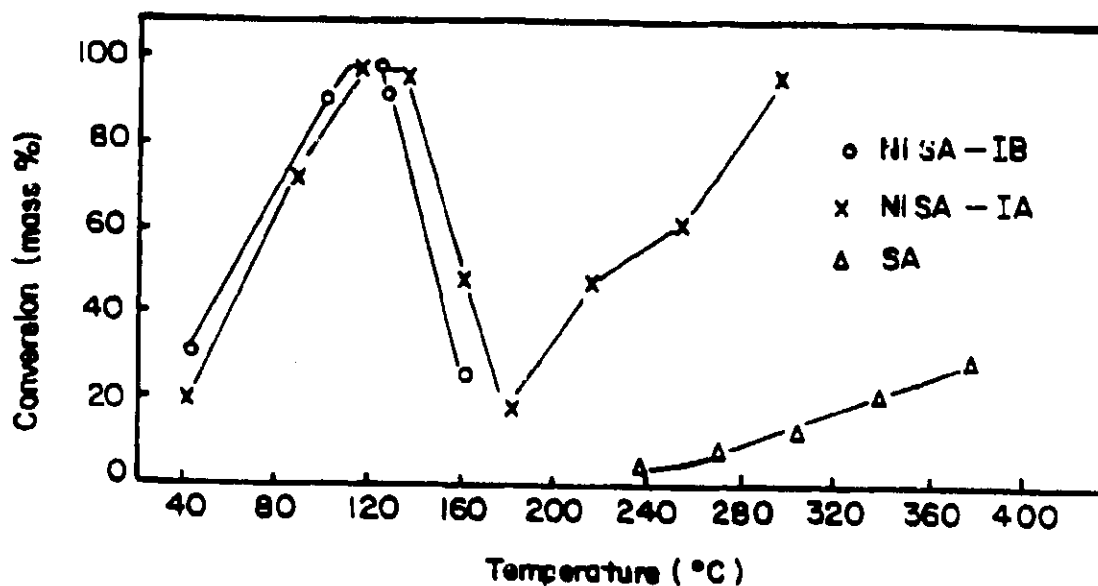


Figure 1. Plot of catalytic activity of NiSA-IA, NiSA-IB and silica-alumina for ethylene oligomerization as a function of temperature (at 35 bar and MHSV = 2).

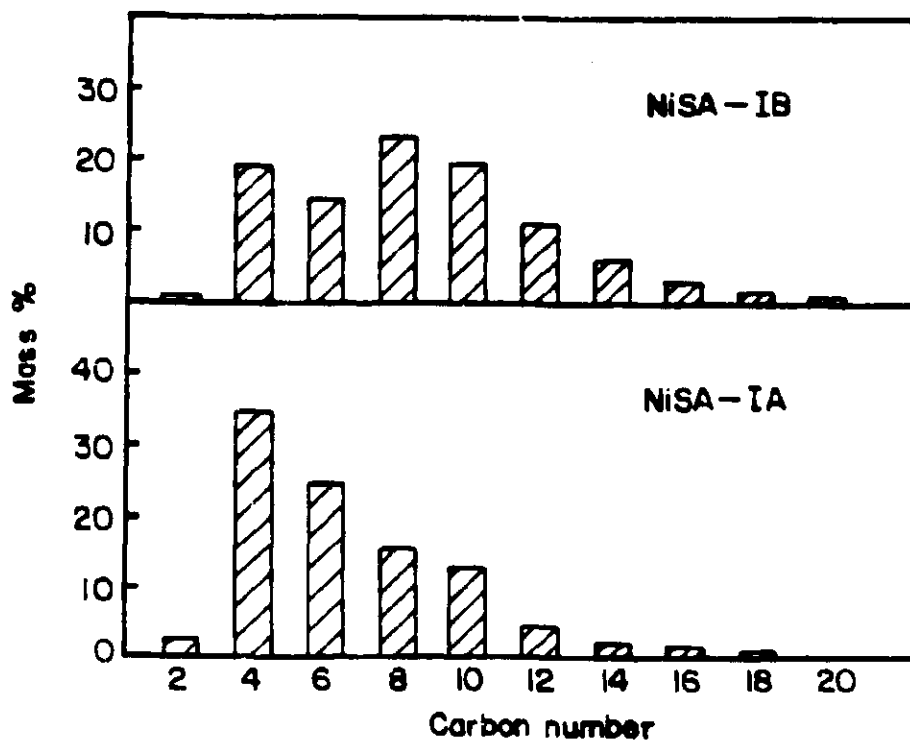


Figure 2. Product spectrum obtained with the NiSA-IA and NiSA-IB catalysts at 35 bar, 120 °C and ethylene MHSV = 2.

increase with increasing temperature (see Table 1). 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. 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 nine are obtained. The C<sub>10+</sub> or diesel fractions were 41.1 and 22.1% for the ion-exchanged and impregnated NiSA-I catalysts respectively. It thus appears that the nickel is more effectively used in the ion-exchanged catalysts. Also, the nickel content of these catalysts is considerably higher than that employed in our previous studies, 0.3% (8).

The most significant property in terms of industrial importance 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 in use (at 35 bar, 120 °C and MHSV = 2), showing no detectable drop in conversion after 22 days on-stream.

Having established therefore that the above reaction conditions (and catalysts) allow for the highly efficient and stable heterogeneous oligomerization of ethylene, we subsequently examined the use of a silica-alumina which could be synthesized via the use of more conventional reagents and procedures (SAII, see Experimental). The product spectrum obtained with the nickel catalyst prepared from 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 C<sub>10+</sub> products formed (30.4%) with this catalyst is approximately 11% lower than that obtained with the NiSA-IB catalyst. Using a NiSA-II sample with 0.76% nickel, a 99.6% conversion was achieved which yielded a C<sub>10+</sub> fraction of 28.6%. The amounts of C<sub>10+</sub> obtained with the NiSA-I and NiSA-II catalysts are in agreement with our previous conclusions (3) that the oligomerization 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 excluded.

The stability of the NiSA-II catalyst was also examined as a function of time-on-stream (see Fig. 5) and it was found that, under the above-specified reaction conditions, the catalyst showed no apparent loss in activity after 44 days on-stream.

Experiments on the conversion of propylene over the NiSA-II catalysts have also been conducted. Under the same reaction conditions as for ethylene, 90.7% of the propylene was converted

TABLE 1

EFFECT OF TEMPERATURE ON THE AMOUNT OF PRODUCTS WITH AN ODD NUMBER OF CARBONS

TEMPERATURE (°C)	CONCENTRATION (mass %)
120	1.1
218	2.6
250	9.3
300	18.2

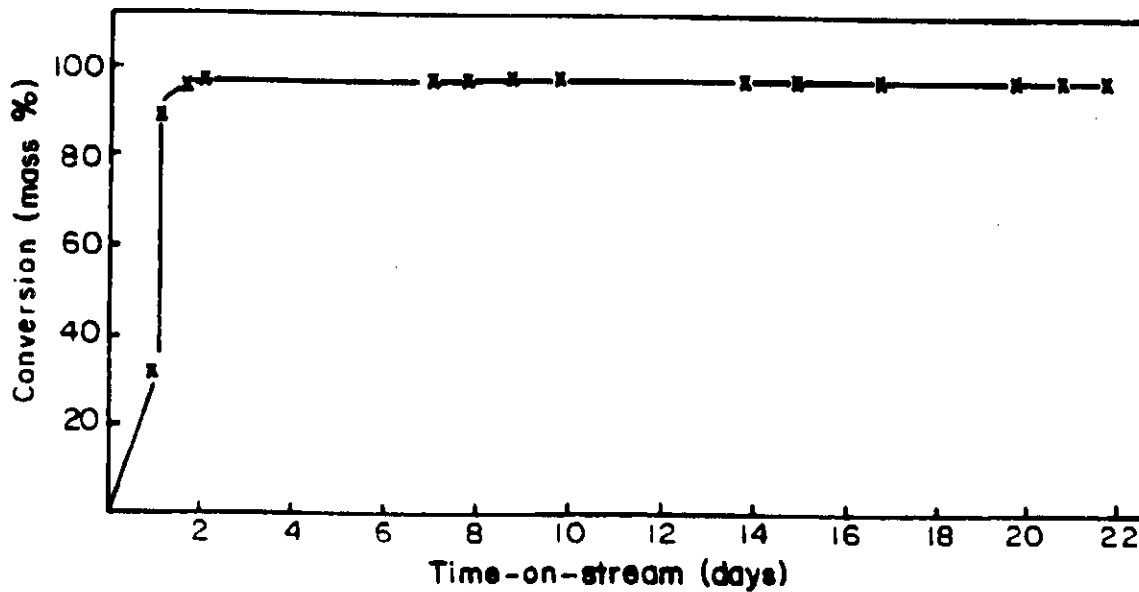


Figure 3.

Plot of % ethylene conversion versus time-on-stream for the NiSA-1B catalyst: (at 35 bar, 120 °C and MHSV = 2).

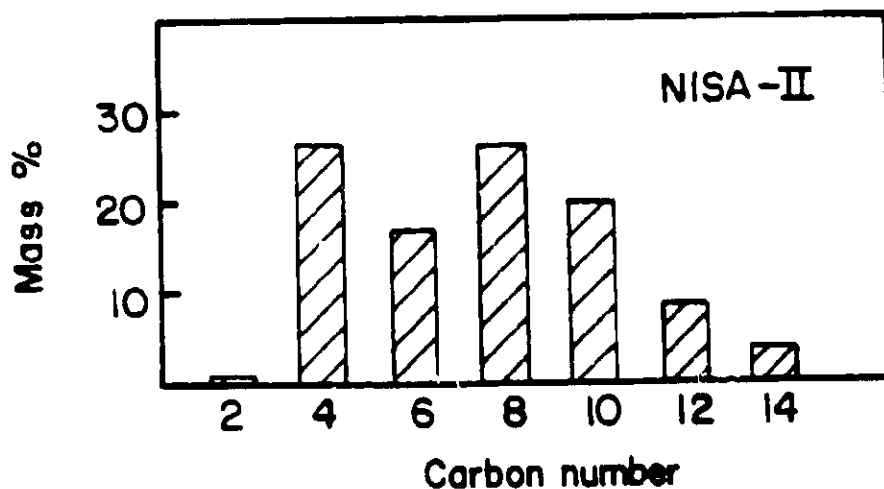


Figure 4. Product spectrum obtained with the NiSA-II catalyst at 35 bar, 120 °C and ethylene MHSV = 2.

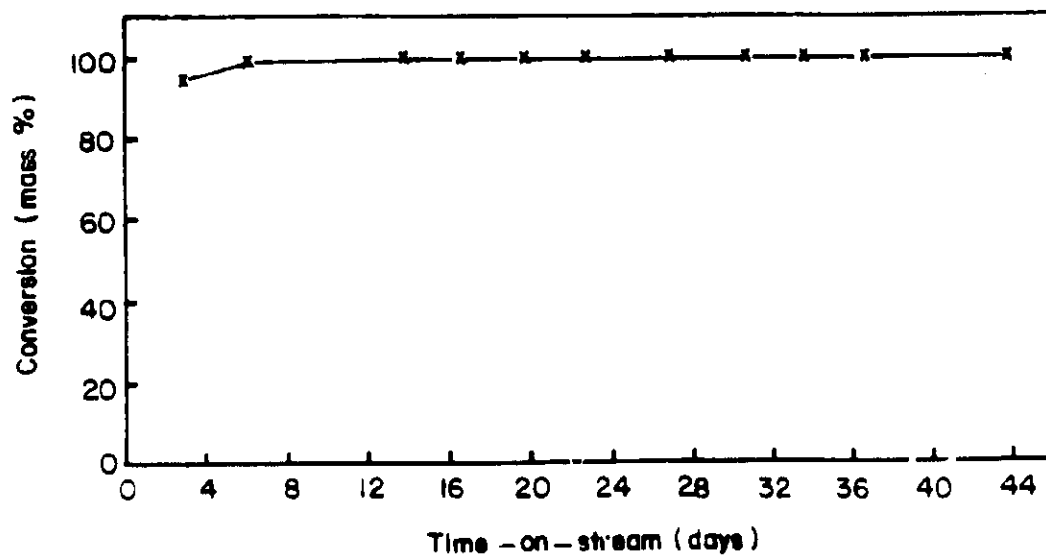


Figure 5. Plot of % ethylene conversion versus time-on-stream for the NiSA-II catalyst (at 35 bar, 120 °C and MHSV = 2).

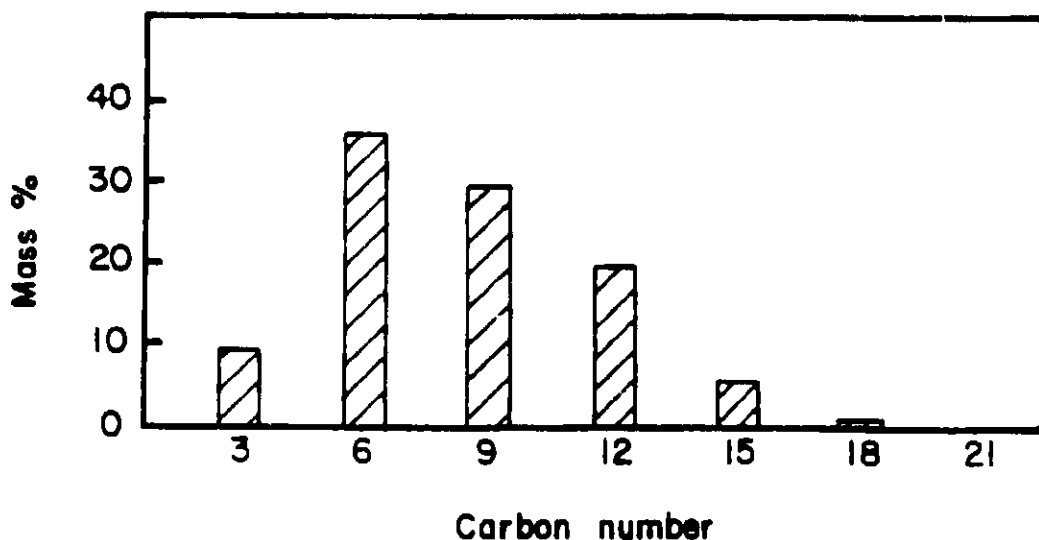


Figure 6. Product spectrum obtained with the NiSA-II catalyst at 35 bar, 120 °C and propylene MHSV = 2.

to dimers and other higher oligomers, with the  $C_{10+}$  fraction amounting to 24.8% (see Fig. 6). Catalyst stabilities were similar to those observed in ethylene oligomerization. Further details of our work on propylene conversion will be given in a later paper.

## CONCLUSIONS

We have therefore shown for the first time that silica-alumina-based nickel catalysts (of relatively high nickel contents) can be used at low temperatures and high pressures for the highly efficient and stable heterogeneous oligomerization of ethylene. The amount of  $C_{10+}$  products formed varies from 22 - 41% by mass depending on the type of catalyst used; this therefore offers some flexibility in the type of product that can be obtained via the judicious choice of support and method of catalyst preparation. The long catalyst lifetimes observed for both types of catalyst indicate that the reaction conditions are more crucial for catalyst stability than the choice of silica-alumina support. Our results also show that the catalysts can be used successfully for the conversion of propylene.

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Financial support from the Foundation of Research and Development, CSIR and the National Energy Council is gratefully acknowledged.