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Catalytic Dimerization of Propylene

I. A New Zerovalent Nickel Catalyst

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A new catalyst for the dimerization of lower olefins is obtained from air-stable zerovalent nickel tetrakis(triphenyl phosphite) and aluminum chloride, aluminum bromide or ethyl aluminum sesquichloride in various solvents. The dimerization activity is optimum at an Al/Ni ratio of 5–7; depending on the solvent. At higher ratios the rate of dimerization decreases, whereas the rate of polymerization increases.

INTRODUCTION

During the last decade the homogeneous dimerization of the lower olefins by complexed nickel catalysts has been extensively investigated by various groups (*1*). Divalent nickel compounds together with alkyl aluminum halides are effective dimerization and codimerization catalysts (*1–4*). Addition of free phosphines has a marked influence on the activity and selectivity of these systems (*2–4*). Ewers (*2*) postulated that alkyl aluminum halides act as reducing agents, transforming nickel to the zerovalent state.

Hata and Miyake (*5*) showed that the monovalent nickel phosphine complex, nickel chloride tris(triphenyl phosphine)–Lewis acid (aluminum chloride or boron trifluoride etherate) system is rather inactive for dimerization of propylene. Contrary to this the zerovalent phosphine complex, nickel tetrakis(triphenyl phosphine)–Lewis acid (aluminum chloride, aluminum bromide or boron trifluoride etherate) system is very active. The molar ratio of the Lewis acids to the nickel complexes was found to have a great effect on the catalytic activity of the latter system. As the molar ratios increased, the yields of hexenes increased. At a molar ratio of 5, a remarkable increase in the activity was observed. No indication, however, is given on the influence of these molar ratios on the selectivity of dimerization versus polymerization. Nickel tetrakis(triphenyl phosphine) however suffers from the disadvantage of being highly unstable to air, thereby severely limiting the industrial application of the Hata–Miyake catalyst.

We now wish to report on an air-stable zerovalent nickel complex, nickel tetrakis (triphenyl phosphite), which affords active dimerization catalysts with aluminum chloride, aluminum bromide and ethyl aluminum sesquichloride (*6*).

METHODS

Nickel tetrakis(triphenyl phosphite) is prepared from nickel nitrate by sodium borohydride reduction in the presence of excess triphenyl phosphite in ethanol, according to the method of Levison and Robinson (*7*), and is dried in air after recrystalization from benzene–acetone or benzene–methanol.

A degassed solution of 1×10^{-4} moles of the nickel compound in 75 ml solvent, which was previously distilled and dried over molecular sieve 3A, is purged with argon, and drawn into an evacuated, double walled, thermostated reactor, which has been purged with propylene (*8*) and contains a Teflon-sealed magnetic stirring bar as well as a glass ampoule containing the

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aluminum chloride (*9*). After refilling the reactor with propylene, and allowing the solvent to become saturated with the gas, the glass ampoule is broken and the magnetic stirrer is started. The propylene uptake during the reaction is measured at short intervals by means of a set of calibrated capillary flowmeters.

After a chosen period the reaction is stopped by injection of 200 ml water. The yield of hexenes is established by gc analysis, using a 4 m × 3 mm column packed with 3% OV1 on 80–100 mesh Chromosorb P. Normal heptane is used as internal standard.

RESULTS

The aluminum chloride reacts with the nickel compound to form a yellow complex. The time necessary for the yellow complex to form is dependent on the temperature of the solvent as well as the concentration of the aluminim chloride; its formation coincides with a sharp rise in the uptake of propylene. The excess aluminum chloride dissolves slowly and reacts with the propylene to form a reddish product which precipitates in the form of a red sludge in the case where toluene is used as a solvent, but remains in solution when either chlorobenzene or methylene chloride are used as solvents.

The Al/Ni ratio appears to be very important. The reaction rate and yield of hexenes (*10*) increases with increasing ratio, with a sharp rise between molar ratios 4.5 and 5.5 in the case of chlorobenzene (see Fig. 1) and between 5 and 6 in the case of methylene chloride. A more gradual increase was found with increasing ratio up to a maximum of approximately 7 in the case of toluene. In a typical experiment [aluminum chloride, nickel tetrakis(triphenyl phosphite), chlorobenzene as solvent, 30°C, 790 mm Hg, 1 hr reaction period], the conversion of propylene per mole nickel was 940 and 2410 moles at molar ratios of 4.6 and 5.6, respectively. With further increasing molar ratios, the increase in reaction rate (i.e., total absorption of propylene) gradually slows down. Analysis of the reaction products shows that above an optimum ratio of 5–7 (depending on the solvent) the yields of hexenes suffer an undesirable drop whereas the polymer formation increases (*11*).

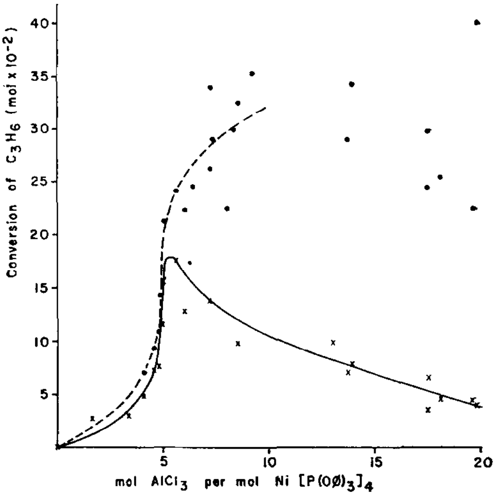

FIG. 1. Propylene conversion in chlorobenzene at 30°C for 1 hr. (×) Influence of Al/Ni ratio on propylene dimerization; (○) influence of Al/Ni ratio on total propylene conversion.

At higher Al/Ni ratios the polymerization reaction is found to become increasingly dependent on the particle size of the aluminum chloride. This is of course due to the fact that the larger particles dissolve more slowly and that they become coated with a layer of insoluble high polymers. Particle size has very little influence on the dimerization reaction.

The propylene uptake profile (see Fig. 2), is highly dependent on the Al/Ni molar ratio, even at values below 5, where polymer formation is minor.

Premixing of nickel tetrakis(triphenyl phosphite) and aluminum chloride in chlorobenzene at 30°C under argon in the absence of propylene leads to a catalytically active system, but the activity drops with the length of the premixing period as illustrated in Fig. 3. This indicates that the nickel tetrakis(triphenyl phosphite)–aluminum chloride–solvent system is unstable. Therefore the rapid decline in activity shown by this catalyst system, as illustrated in Fig. 2, is, apart from poisoning by feed gas impurities, probably mainly

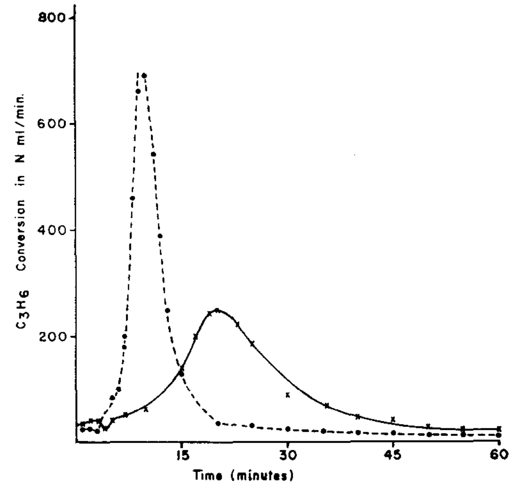

FIG. 2. Influence of Al/Ni ratio [(×) 5.1; (○) 6.4] on the profile of propylene uptake in chlorobenzene at 30°C.

due to thermal instability of the catalytic system itself. This is further borne out by the fact that the conversion to hexenes in chlorobenzene at an Al/Ni ratio of 6, could be increased by about 50% by lowering the reaction temperature from 30 to −10°C as soon as the dimerization reaction starts, instead of running the reaction at 30°C as described in the Methods section.

In addition it is found that boron trifluoride etherate, boron trifluoride and triethyl aluminum lead to catalytically inactive systems with nickel tetrakis(triphenyl phosphite).

DISCUSSION

Our results lead to the following conclusions:

i. The nickel in the active dimerization catalyst is presumably in the zerovalent state as indicated by the following experimental observations:

a. Divalent nickel compounds such as nickel acetylacetonate and bis(triphenyl phosphine)nickel dichloride were found to form active dimerization catalysts with alkyl aluminum halides (known to be reducing agents) but not with aluminum chloride.

b. Nickel tetrakis(triphenyl phosphite) affords an active dimerization catalyst with aluminum chloride. After addition of an oxidant, such as mercuric chloride, all dimerization activity ceases.

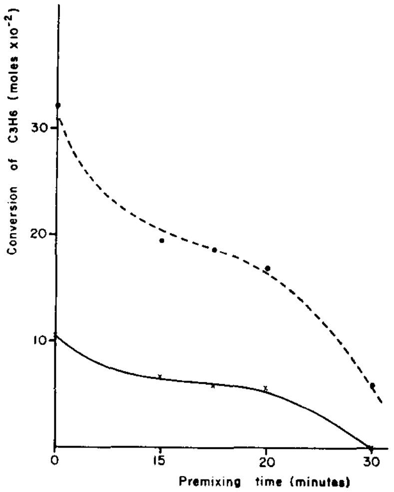

FIG. 3. Influence of the premixing period (at 30°C in chlorobenzene under argon atmosphere) on the activity of a catalytic system with Al/Ni ratio of 10. (×) Propylene dimerization; (○) total propylene conversion.

ii. The function of the Lewis acid is assumed to be the removal of ligands from the nickel to leave free coordination sites.

iii. At Al/Ni ratios exceeding the optimum values for the various solvents, the competing polymerization reaction, caused by free aluminum chloride, increases rapidly at the expense of the slower dimerization reaction.

iv. The "active" dimerization catalyst is thermally unstable. For optimum conversion the "active" catalyst should be developed at room temperature, but the dimerization temperature should be kept as low as possible. The more polar the solvent, the lower the temperature necessary for developing the active catalyst in a reasonably short time—ca. 30°C for toluene, ca. 10°C for chlorobenzene and 0–5°C for methylene chloride. This obvious relation to the polarity of the solvents indicates that the dimerization catalyst is a highly polar species.

v. When ethyl aluminum sesquichloride

was used as cocatalyst at a Al/Ni ratio of 100:1 and at reaction temperatures of 30 and 10°C, the catalyst solution still showed considerable activity after 7 and 11 hr, respectively. In the former case the total conversion was 13,000 moles propylene/mole nickel and in the latter case, 30,000 moles propylene/mole nickel. The conversion to dimers was 3600 and 15,000 moles/mole nickel, respectively. These results indicate once more the influence of temperature on the overall activity as well as on the dimerization activity of the system.

The prolonged activity found when using such a large excess of cocatalyst, could be due to the ethyl aluminum sesquichloride either regenerating spent catalyst or acting as a scavenger (*12*) to remove impurities (i.e., small amounts of water or sulfur compounds) which are present in the feed gas. The fact that ethyl aluminum sesquichloride is a milder Lewis acid than aluminum chloride itself, probably accounts for the fact that even at such a high Al/Ni ratio, considerable amounts of dimers are still formed. In contrast to this, when using aluminum chloride as a cocatalyst at a Al/Ni ratio of 20:1, which was the highest ratio tested, the system lost virtually all activity within 20 min and only small amount of dimers were formed (see Fig. 1).

ACKNOWLEDGMENT

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8. Polymerization grade propylene was obtained from SASOL and used directly without further purification.

9. Anhydrous, granular aluminum chloride obtained from B. D. H. The purity was determined by dissolving a sample in ether, addition of distilled water and titration with standardized 0.5 *N* NaOH, using methyl red as indicator.

10. Capillary gc analyses (UCON 550X, 100 m × 0.5 mm i.d.) show a *n*-hexene:isohexene ratio of approximately 3:7. The complete composition and factors influencing this composition, will be dealt with in a further publication.

11. We are presently investigating the effect of added free phosphines and phosphites.

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