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**Supported Chromium Oxide Catalyst
for Olefin Polymerization. XI.
Comparison between
Ethylene and Propylene Polymerization**

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ABSTRACT

It is shown that the new model of an active site of chromium oxide catalyst supported on silica-alumina, previously proposed for ethylene polymerization, is also valid for propylene polymerization. The new model involves a set of three chromium atoms with different oxidation degrees located at the border of the flat chromium oxide domains spread onto the support. The main differences between the behavior of the two monomers are caused by the much higher reducing power of the propylene and also by its mode of adsorption which is stronger. Some copolymerization experiments are described.

INTRODUCTION

The results reported in the previous paper [1] of this series suggest that the active site of supported chromium oxide catalysts might be the

same for ethylene and propylene polymerization in spite of many differences. The main argument was that optimum activity was reached after the same conditions of reducing pretreatment with hydrogen or ethylene. The purpose of this paper is to discuss the behavior of the two monomers, to show that a new model of site that we have suggested [2] for ethylene polymerization is valid also for propylene polymerization, and to explain the origin of the differences observed. A brief review of these differences is at first presented and then it is shown that, if one accepts the new model, these differences may be attributed to two main causes: a higher reducing power of the propylene and a stronger mode of adsorption of this monomer. A few experiments of copolymerization are presented that strengthen these statements.

DIFFERENCES BETWEEN ETHYLENE AND PROPYLENE POLYMERIZATION

The polymerization rate is much higher for ethylene than for propylene. The ratio of the rates is the highest at high pressure and decreases by lowering the pressure from about 100 under 50 bars to about 10 at 1 bar, and less at under atmospheric pressures.

The shapes of the kinetic curves are very different. A maximum rate is observed after a more or less long induction period in the case of ethylene and in many cases the activity remains stable, while the rate decreases continuously and rapidly in the case of propylene.

The activity vs ethylene polymerization is not dependent on the atmosphere (nitrogen or air) and on the hourly spatial velocity (HSV) used during the activation treatment or on the average oxidation degree after the activation (if it is higher than 4), while in the case of propylene the activity increases with the average oxidation degree.

The maximum activity as a function of chromium content (for the same silica-alumina support) is located at about 2% for ethylene, and between 4% at low pressure and about 6% at high pressure for propylene.

In both cases a maximum of the activity as a function of the temperature is observed, but the decrease of activity by increasing the temperature is much larger in the case of propylene. However, there is no maximum of the initial activity for the propylene after a reducing pretreatment has been carried out.

Whatever the conditions of activation and eventually of reducing pretreatment, the polymerization is always first order vs propylene pressure at all measurable ranges of temperature and pressure, while the order decreases from 1 to low values in the case of ethylene by decreasing the temperature at low pressure, and also during the polymerization. Further, the apparent activation energy

is higher in the case of propylene (10 kcal instead of 0 to 6, depending on the pretreatment conditions).

THE NEW MODEL FOR ACTIVE SITES AND MECHANISM OF POLYMERIZATION FOR ETHYLENE

The model proposed in our previous work [2] for the active sites in ethylene polymerization is formed by a set of three chromium atoms with different degrees of oxidation. These sets are located on the border line around the flat domains of chromium oxide spread on the surface of the silica-alumina carrier. After a correct activation treatment under air or nitrogen, but before contact with monomer, these sets include two Cr^{3+} and one Cr^{6+} atoms. An optimal pretreatment by hydrogen allows a maximum number of such sets to be reached which for the most active catalysts (2% chromium), corresponds to a very low percent of the chromium atoms. The last step of the formation of the sites is accomplished by the monomer itself, which probably reduces the central Cr^{6+} atom of the site to Cr^{2+} . If proper activation treatment before contact with monomer has not been carried out, the same central atom may be reduced to another oxidation state, for instance Cr^{3+} , and then does not form an active site.

An estimate of the relative number of sites may be obtained from the calculation of the probability of occurrence of sets of Cr^{3+} , Cr^{6+} , Cr^{3+} atoms. The calculation assumes that the reduction state is homogeneous [2]. Noting d , the average oxidation degree of chromium (between 3 and 6), the number of the sets is proportional to $(\frac{d}{3} - 1) (2 - \frac{d}{3})^2$. A plot of the relative number of sites vs d is illustrated in Fig. 1.

The mechanism is of the Langmuir-Hinshelwood type [3]. Ethylene is adsorbed on the whole surface of the chromium oxide domains and is mobile enough in the adsorbed layer to reach the active sites on the border line, so that the saturation conditions (zero order) may be observed rather easily at low temperature or high pressure. Moreover, the adsorption is not very strong, so that at high temperature the adsorption-desorption equilibrium may limit the polymerization rate. In the absence of a diluent the polymer formed covers the support surface, the chromium oxide domains, and progressively blocks the sites, so that the saturation conditions are approached.

The above features point out the importance of the reducing power of the monomer and also of the adsorption properties of the monomer. A comparison of ethylene and propylene was therefore made on this basis.

THE REDUCING PROPERTIES OF THE MONOMERS

The reducing power of propylene is much higher than that of ethylene. Starting from the same catalyst activated under air (chromium content

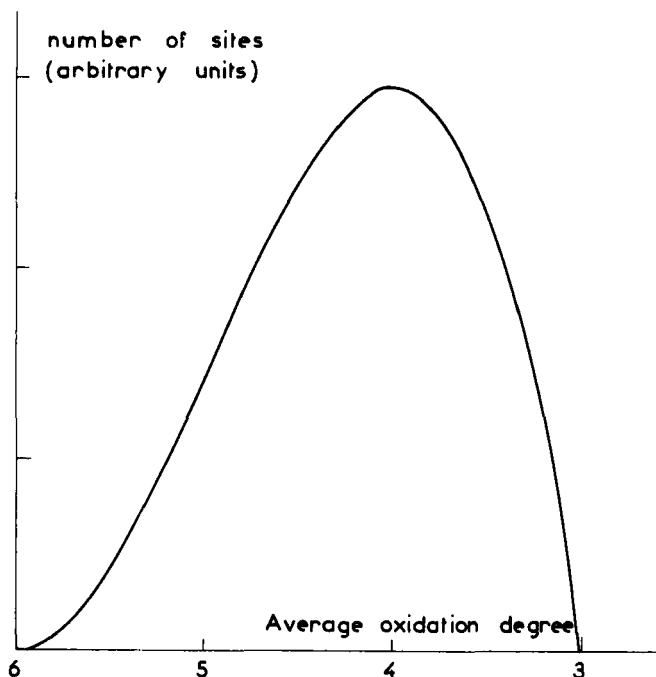


FIG. 1. Theoretical number of active sites vs average oxidation degree of chromium.

3.6%, average oxidation degree 5.6), it has been shown that no soluble (hexavalent) chromium remains after 1 min contact with propylene at 90°C compared to more than 15 min contact with ethylene at 145°C. Many of the differences between ethylene and propylene polymerization may be explained on this basis.

In the absence of a reducing pretreatment by H_2 or C_2H_4 , the reduction by propylene is very rapid and the chance of obtaining a large number of active sites is higher if the initial average oxidation degree is higher. In this case the induction period observed during ethylene polymerization, which corresponds to the time necessary to reduce the Cr^{6+} atom of the sites to the active state Cr^{2+} , disappears because the reduction by propylene is very rapid. Thus the kinetic curve shows no maximum in polymerization rate, but only a continuous decrease which is caused either by the blocking of the surface by the polymer or by a further reduction which destroys the sites. The reduction is less rapid if the chromium content increases because the reducibility of the catalyst is lower. For that reason the activity

maximum is located at a higher chromium content in the case of propylene polymerization and, because the reduction rate is dependent on the amount of monomer, i.e. the pressure, the exact location of the maximum activity is pressure dependent. Also, the reduction rate is temperature dependent and, for that reason, a dramatic decrease of the polymerization activity by increasing the temperature is observed.

Comparison between ethylene and propylene polymerizations shows other differences which may be accounted for through the reducing power of the monomers. The catalysts are more active for ethylene than for propylene polymerization, but the difference in activity is pressure dependent and increases with the pressure; at low pressures the reducing power of propylene is closer to that of ethylene, so that the ratio of activity decreases from 100 to 10 between 40 and 1 bar. At low temperature (-15°C) the catalyst has a low activity vs propylene and no activity vs ethylene. The reason is that the reducing power of ethylene at such a temperature is too weak to carry out the last step of activation. Propylene can do this step and, in spite of the low polymerization rate at such a temperature, the activity is high enough to cause a partial covering of the surface of the catalyst.

If a pretreatment with H_2 has been carried out under optimal conditions, many sites are stabilized and their destruction through reduction is not so easy. Then, at rather low temperatures (20 to 60°C) the shape of the kinetic curve for propylene polymerization is not different from that of ethylene and an induction period is observed. Also, at high temperatures (90 to 145°C) there is no decrease in the initial polymerization rate upon increasing the temperature, although there is a rapid drop in polymerization rate after a few minutes [1].

THE ADSORPTION PROPERTIES OF THE MONOMERS

No specific study of the adsorption of the monomer has been carried out. However, study of ethylene polymerization has led us to conclude that the monomer was adsorbed on the surface of the chromium oxide. The adsorption was supposed to be light, i.e., the monomer may be easily desorbed at high temperature, and it is mobile in the adsorbed layer on the surface of the chromium oxide. The adsorption of ethylene on bulk Cr_2O_3 , where no polymerization takes place, has been observed to be practically independent on the temperature in the range 0 to 150°C . It is interesting to note that, after optimal reducing pretreatment, the polymerization rate for ethylene is also independent of the temperature in a large range although the activation energy in the case of propylene polymerization is about 10 kcal in the range 20 to 90°C . This large difference shows that propylene is more strongly adsorbed on the surface. This difference in adsorption explains quite well the difference in the reaction order vs monomer

concentration, which is 1 in the case of propylene and varies between 0 and 1 for ethylene. The high mobility of the ethylene in the adsorbed layer allows the saturation condition to be reached easily if the number of sites is low or the polymerization rate is low. In the case of propylene, the monomer, strongly adsorbed, is not mobile and, after a polymerization step, the monomer which was adsorbed on the site has to be replaced by direct adsorption.

EXPERIMENTS USING BOTH MONOMERS

A few mixed experiments using both monomers could prove these concepts. These experiments are of two kinds: either simultaneous or a sequenced-type copolymerization. Propylene may be used for the reducing pretreatment before an ethylene polymerization experiment because it can form the sites at lower temperatures (for instance, 145°C instead of the 250°C used for ethylene pretreatment). After contact with propylene, the catalyst is active vs ethylene at low temperatures. This is due to the stronger reducing power of propylene. If the precontact has been carried out at low temperature (0 to 20°C) and the ethylene polymerization at higher temperatures (90 or 145°C), a very long induction period is observed which corresponds to the desorption of the products and of the propylene which remains strongly adsorbed. The activity which is finally reached is not different from that obtained without propylene adsorption. Therefore the potential sites have not been destroyed by the propylene through reduction. It is even possible to carry out the following sequence of treatments: reducing activation pretreatment by ethylene at 250°C, propylene polymerization during a few minutes at temperatures between 20 and 100°C, and ethylene polymerization at 90 or 145°C. After such a sequence the final activity vs ethylene polymerization, reached after a rather long induction period, has not been changed by the intermediate step of propylene polymerization. The final activity is reduced only if the intermediate step is done at high temperatures or for a long time.

These experiments show that the sites can resist chemical reduction by propylene if they have been stabilized by a proper activation pretreatment. Then the major phenomenon is a very strong adsorption of propylene which causes a long induction period during the final ethylene polymerization.

Practically no data have been published about ethylene-propylene copolymerization with Phillips catalysts. Hogan [4] has reported a few experiments showing that the propylene polymerization rate is increased by a factor of 10 if the concentration ratio of propylene to ethylene is 10.

We have carried out a few experiments, but the apparatus used for homopolymerization yields only the total consumption of the monomers

without distinguishing between the monomers. The results are as follows. Whenever the ratio of ethylene to propylene in the monomer feed is between 1 and 5, the shape of the kinetic curve is the same as for propylene polymerization; there is no induction period and the rapid decrease of the polymerization rate is more pronounced at higher temperatures. But if after a limited time of copolymerization a ethylene homopolymerization step is carried out, a high activity is again observed after a long induction period. Therefore, once again the propylene does not destroy the sites but blocks them through strong adsorption. It has also been noted that the total polymerization rate is never higher than the homopolymerization rate of propylene, even if the feed is rich in ethylene.

Hogan [5] and Krauss et al. [6] have shown independently that, after activation pretreatment with CO, the active sites may form complexes with nitrogen, CO, and ethylene. These complexes involve one or two molecules of gas, and it has been shown that mixed complexes with CO and ethylene were not active in polymerization. This fact implies that the active site may be blocked by strong CO adsorption on one of the two coordination positions which are available for complexation in the site. It may also imply that the polymerization activity needs the adsorption of two monomer molecules on the site. If such a situation is valid for all the active sites, it may be suggested that one molecule of propylene adsorbed on a site may inhibit the polymerization of ethylene up to the moment when that molecule is either desorbed or polymerized. Another possible explanation of the retarder power of propylene might be that its adsorption blocks more than one coordination position through a π -allyl complex formation. Further experiments are necessary to make clear the adsorption mode of propylene and its precise role in copolymerization.

CONCLUSION

It may be concluded that the model of active site previously proposed for ethylene polymerization is well supported by the facts observed during propylene polymerization if one takes in account the two major differences between the monomers: the higher reducing power and the stronger adsorption mode of propylene.

It now remains to give a more precise description of the site in terms of coordination chemistry. Further work is in progress in our laboratory in that direction.

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