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Inhibition of Silica-Alumina-Chromia Polymerization Catalysts

Controlled amounts of water, oxygen, acetaldehyde, trimethylmonochlorosilane and argon have been added from the gas phase to the catalyst and its activity determined. With water and oxygen inhibition proved reversible. The results could be explained by assuming that inhibition occurred by adsorption and above a critical partial pressure of inhibitor also by reaction at the active site. Activation of the catalyst increased the number of active sites rather than their specific activity. The rate of polymerization was not diffusion controlled under the prevailing conditions.

Silica-alumina-chromia catalysts for ethylene polymerization are known to be sensitive to traces of foreign substances, notably water, oxygen, and oxygenated hydrocarbons. Most previous work on the action of poisons has been performed in the presence of solvents (*1*, *2*, *3*) which might modify poison activity. Recently Kazanski and Turkevich discussed the influence of oxygen and water (*4*) on the activity of the catalyst when polymerization was carried out in the gas phase.

In this work the action of inhibitors was studied quantitatively by adding minute controlled amounts which caused only slight reduction in the activity of the catalyst. The dose of the inhibitor was then increased in successive runs until the catalyst became completely inactivated. The inhibition curves thus obtained show significant differences between the various poisons. The results are consistent with the hypothesis that Cr^{IV} is the active species (*5*).

EXPERIMENTAL

The method for preparing the catalyst and for measuring activity were the same as reported before (*5*). The amount of inhibitor to be added was determined by reading the pressure when the gaseous inhibitor was contained in a vessel the (small) volume of which was exactly known. The gas was then transferred to the reaction vessel, containing the catalyst which adsorbed the inhibitor.

RESULTS

The first poisons to be investigated were oxygen and water. As can be seen from Fig. 1, small amounts of both had a strong inhibiting effect. But while additional amounts of oxygen depressed the activity of the catalyst further, the activity curve for water inhibition showed a shoulder.

The effect of oxygen and of water was reversible; evacuation at 300° restored the original activity of the catalyst. However, when after poisoning with oxygen evacuation was carried out at 200°, only about 60% of the original activity could be restored and at 100° evacuation did not restore activity at all.

Experiments were carried out with two catalysts prepared in identical ways except that Catalyst A was treated with 10 mg of ethylene per gram of catalyst at 100° and evacuated at 300° while Catalyst B re-

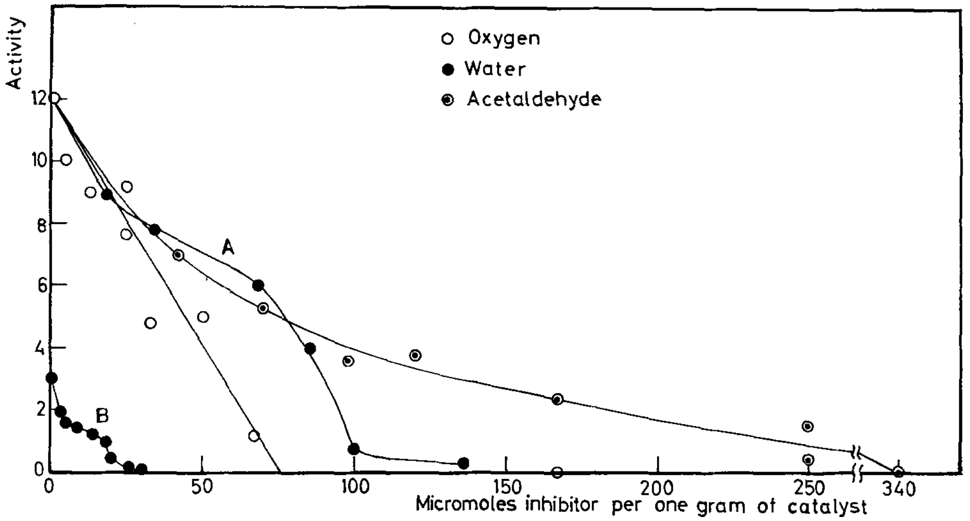

FIG. 1. Effect of addition of controlled amounts of inhibitor on the activity of the catalyst. The upper curves were obtained with the more active Catalyst A, the lower one with Catalyst B.

mained untreated. Catalyst A was about four times as active as Catalyst B. On comparing the influence of water on these two catalysts, it was seen (Fig. 1) that much less water was needed to inactivate the less active Catalyst B than the more active Catalyst A. The shape of the two curves was, however, essentially the same.

The curve for acetaldehyde poisoning was quite similar to that of water, except that the second steep decline was absent. An additional difference should be noted: The activity of a catalyst poisoned with acetaldehyde could not be restored. As with water and oxygen, evacuation at room temperature did not change the activity of the catalyst. At higher temperatures, however, evacuation decreased the activity of the catalyst, possibly due to reduction of the active centers.

Addition of 340 μmole of argon to 1 g of Catalyst A did not change the activity within the experimental error. Ethylene is apparently far more readily adsorbed on the active sites than argon.

Since it was known that the absence of water was essential for good activity it was attempted to improve the catalyst by attacking its hydroxyl groups chemically. As reagent for this purpose trimethylmonochlorosilane was chosen

$$(CH_3)_3SiCl + HOX \rightarrow CH_3SiO\text{-}X + HCl$$

However, this treatment, whether at room temperature or at 150°, only reduced activity; nor did it prove possible to regenerate the catalyst by evacuation at room temperature or at 300° (Table 1).

TABLE 1
INFLUENCE OF TRIMETHYLMONOCHLOROSILANE ON CATALYST ACTIVITY

μmoles added to 1 g catalyst	Evacuation Duration (min)	Evacuation Temp.	Activity
0.0	20	Room	4.4
3.3	5	Room	3.1
5.0[a]	20	Room	3.2
8.3	5	Room	2.3
8.3	50	300°C	2.0
16.7	5	Room	1.6

[a] Trimethylmonochlorosilane was added in this experiment at 150°, in all the others at room temperature.

DISCUSSION

Three different types of behavior could be observed on adding increasing amounts of inhibitors to the catalyst (Fig. 1). The first, exemplified by oxygen, was characterized by a steep fall in activity down to zero. The other extreme was encountered with acetaldehyde; in this case additional portions of the poison decreased activity less and less. An intermediate role was played by water which, when small amounts were added, behaved similarly to acetaldehyde; after a certain critical amount had been added, small additional amounts brought the activity down to zero.

The different effects on addition of inhibitor were probably caused by different phenomena. It has been shown before (*5*) that addition of oxygen caused an increase in the ESR signal due to Cr^{V}. The sharp drop in activity on addition of oxygen could therefore be associated with oxidation of active Cr^{IV} to inactive Cr^{V}. Simultaneously, adsorption of oxygen or oxygenated products might have reduced the number of sites available for ethylene adsorption.

The inhibition of polymerization on addition of acetaldehyde might be due to competition between acetaldehyde and ethylene for the active sites. It was reasonable to suppose that acetaldehyde was adsorbed more strongly than ethylene but that nevertheless the much higher pressure of ethylene caused an adsorption equilibrium in which a fraction of the active sites remained available for ethylene polymerization.

Quite similar in principle was the effect of argon. However, the competition between ethylene and argon was all in favor of ethylene and no inhibiting effect could be detected. The lack of inhibition also proved that the rate of polymerization of ethylene was not determined by the rate of diffusion through the pores of the catalyst. Had this been the case the pores would soon have been filled mainly by argon with consequent decrease of partial pressure of ethylene at the active sites resulting in a lower rate of polymerization in the presence of argon than in its absence.

Further conclusions could be drawn by comparing the influence of water on two catalysts with different activity. Catalyst A was treated with ethylene at 300° and evacuated before use and was therefore more active than Catalyst B. Inspection of Fig. 1 showed that the behavior of the two catalysts was similar. But whereas with Catalyst A the sharp decline in activity appeared on addition of about 90 μmole of water per gram of catalyst, 20 μmole of water sufficed for the less active Catalyst B.

Had the number of active sites of the two catalysts been equal and the difference in activity been due to different activity of the active sites, the expected result would have been an equal proportional decrease of activity for both catalysts on addition of equal amounts of water. The experiments showed instead that the greater activity was due to the greater number of active sites in the Catalyst A. In addition, in order to explain the experimental result it had to be assumed that the active centers of the catalyst were preferentially attacked by water, and this in spite of their low concentration. Had the support taken up most of the water the partial pressure of water over the catalyst surface would have been controlled by the adsorption equilibrium of the support and would therefore have been the same for both Catalysts A and B when the same amounts of water had been added. At the same partial pressure of water the same fraction of active sites would have been deactivated, resulting in the same proportional decrease in activity for both catalyst. This did not prove to be the case.

Instead, the experimental results were consistent with the following scheme: Water was preferentially taken up by the active sites. Catalyst A contained more active sites than Catalyst B. On addition of small amounts of water, the water was held lightly in an adsorption equilibrium. This still allowed ethylene to be adsorbed on some active sites, the number of which was reduced as the amount of water was increased, resulting in some deactivation. As a certain critical pressure of water was reached, hydration of the active site occurred, and the previously active site became inactive. Since little water was taken up by the support and the amount of water in the gas phase was negligible compared to that adsorbed by the active center, the critical vapor pressure for hydration was reached with less water added to Catalyst B (containing a smaller number of active sites) than to Catalyst A. Once the critical pressure was reached every additional amount of water would cause hydration, were the active sites exactly identical. It was therefore possible to estimate the upper limit of number of active sites contained in each catalyst by calculating the amount of water necessary to reduce the original activity to zero, had the decrement of activity been equal to that of the maximum slope of the activity in the region of hydration. For a stoichiometry of 1:1 this value proved to be 30 μmole of active sites per gram of Catalyst A (i.e., 10% of the chromium content) and 8 μmole per gram of Catalyst B. These estimates were consistent with Ermakov's results (*3*) of 4 μmole of active sites per gram of catalyst, considering the higher polymerization temperatures he had to use in order to obtain similar reaction rates.

Similarly the oxidation of the catalyst by oxygen might also be preceded by adsorption, both processes resulting in deactivation. In that case the inception of oxidation occurred with smaller portions of added oxygen than added water and could not clearly be distinguished by inspection of Fig. 1. Such a hypothesis would find support from the previously published observations (*5*) that on addition of small amounts of oxygen the increase in the ESR signal, indicating oxidation to $\mathrm{Cr^{V}}$ was slight but increased considerably on further additions of oxygen.

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X-Ray Diffraction Studies of Mixed Oxide Catalysts

The importance of surface configuration in catalysis is recognized. The possibility of correlating surface catalysis with readily obtainable data such as lattice spacings in the solid has not been fully explored. To this end an X-ray diffraction (XRD) apparatus which allows measurements to be made under reaction conditions has been set up in our laboratory (*1*). Preliminary studies have indicated a possible relation between catalytic properties and XRD data (*1–3*). The work reported here represents qualitative studies of a large family of catalysts, the aim being to generalize on the relation of XRD data to catalytic properties.

The isomorphic family of compounds containing the molybdates, tungstates, and vanadates has been investigated. These catalysts have attracted considerable attention in the past due to their effectiveness in the selective oxidation of hydrocarbons. Detailed studies have determined the kinetics of catalytic oxidation (*4*), and postulated the reaction intermediate and the nature of the catalytic site (*5*) in one member of this family, bismuth molybdate. These studies do not, however, permit an