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CHEMISTRY

SELECTIVELY INCREASING THE STABILITY OF A NICKEL-ALUMINA CATALYST BY PRESSING (E)

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It was shown earlier /1/ that aluminum oxide subjected to a pressure of 20,000 atm was twice as stable with respect to the reaction of the dehydration of alcohol than material not so pressed. The reduction in the activity of the catalyst in this process is due to the blocking of its surface by a film of polymerized unsaturated reaction products. This is confirmed by the fact that aluminum oxide left in an atmosphere of the reaction products of alcohol dehydration rapidly loses its activity, while in a nitrogen atmosphere the activity is entirely preserved. We kh may therefore well suppose that the increase in the stability of the aluminum oxide after pressing is associated with a reduction in the rate of forming the polymer film, resulting from a change in the macrostructure of the catalyst /2/.

It is well known that the polymerization of unsaturated hydrocarbons usually takes place by a chain mechanism /3/. Naturally the change in the number, size, and shape of the catalyst pores after pressing should lead to a change in the rates of generation and breaking of the chains responsible for the formation of the polymer film on the surface of contact. On the other hand, we may suppose that the stability of the catalyst ~~afterxprs~~ will be unaffected by pressing if the blocking process on its surface ~~if~~ is not created by a chain mechanism.

In order to verify this point we studied the effect of representatives of two types of organic substances on the stability of a nickel-alumina catalyst before and after pressing. The nickel in this catalyst is distributed over a vast area of aluminum oxide pores. Hence any change in the stability of the nickel-alumina catalyst after pressing should also be associated with the mechanism of the formation of a blocking film on its surface.

We judged the relative stability of the pressed and unpressed catalyst samples * by reference to the changes in their activity with time in the ~~dehydration~~ dehydrogenation of cyclohexane and a narrow fraction of Maikop gasoline. As poison impurities we took cyclopentene and thiophene. The choice of cyclopentene as poison was made because, as shown by N. I. Shuikin,~~xnd~~ S. S. Novikov,et al. /4/, a nickel-alumina catalyst, (as well as Pt and Pd in charcoal or silicagel)

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* Without regeneration of the catalyst.

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is rapidly deactivated during the ~~dehydration~~ dehydrogenation (at 300°) of cyclohex-

ane containing 10% of 1-ethylcyclopentene-1. The authors consid-

er that the reason for the poisoning of the catalysts in this pro-

cess is the intermediate formation of an easily-polymerizing cy-

clopentadiene. As a second type of poison we took thiophene. The

cyclohexane had a ~~kxpx~~ bp of 80.7° (751 mm) and refractive index

..... . The gasoline contained considerable quantities of hydro-

aromatic hydrocarbons ; it boiled between 96 and 107° and had a

refractive index ~~xf~~ and density of.....; it contained no sulfur or

unsaturated compounds. It was natural to expect that the stability

of the nickel-alumina catalyst in the course of the ~~dehydration~~ dehydrogenation of

this gasoline (not containing impurities in the form of five-mem-

bered cyclenes) should not depend on ~~khx~~ any change in the porosity

of the catalysts after pressing.

A catalyst containing 30 wt.% nickel and 70 wt.% alumina was

prepared by the method described in /5/.

After forming, the catalyst was treated with hydrogen at

350° for 25 h. The hydrogen was passed over 50 ml of catalyst

dried at 125° at a rate of 5 to 6 liters/h. Part of the reduced

catalyst was subjected to pressing at 10,000 and 20,000 atm in a

special booster. The catalyst was pressed in aluminum ampoules

50 mm long, with outer diameter 10 mm and inner diameter 9.6 mm,

in accordance with the method given in /1/.

In all the our experiments we used samples of the same catalyst,

250 ml of which were prepared in one process. The specific vol-

ume of the catalyst fell by 35% after pressing at 10,000 atm and by 50% after pressing at 20,000 atm.

The dehydrogenation was carried out at 300° in a feeble current of hydrogen at a volume rate of 0.3. The degree of dehydrogenation of the cyclohexane was determined refarctometrically /6/ and that of the gasoline by the sulfuric acid method.

Fig. 1. Effect of thiophene impurity in the dehydrogenation of cyclohexane on the stability of a nickel-alumina catalyst.

Key

1) Degree of cyclohexane dehydrogenation

2) h

Figures 1, 2, and 3 show the variation in the activity of various catalyst samples with time (characterizing their stability). The y axis gives the degree of dehydrogenation in percents of the theoretical value, and the x axis gives the time in hours.

We see from the figures that at the beginning of the experiment the unpressed sample (curve I) had the same activity as the pressed ones (curves II and III). Hence the size of the active surface was also unchanged. This is confirmed by the fact that the denser (pressed) catalyst sample was poisoned by thiophene at the same rate as the unpressed one (Fig. 1).

Stability of Catalyst Samples in the Dehydrogenation of Cyclohexane with Thiophene Impurity. Some 6 ml of pure cyclohexane were first passed over 20 ml of unpressed catalyst (13.9 g). The resultant catalyzate had a refractive index of....., i.e.,

the degree of dehydrogenation was 73.2%. During the next 11 h work, 68 ml of cyclohexane,containing 0.034 g of the thiophene sulfur, were passed over the catalyst. The last sample of catalyst had....., i.e., the degree of dehydrogenation had been reduced to 33.0%.

Some 6 ml of pure cyclohexane were also initially passed over 20 ml (29.4 g) of catalysts pressed at 20,000 atm. The resultant catalyzate had a refractive index of....., i.e., the degree of dehydrogenation was 73.0%. During the next 11 h, another 68 ml of cyclohexane, containing 0.033 g of thiophene sulfur, were passed over the catalyst. The last sample of catalyzate had....., i.e., the degree of dehydrogenation was 31.6%.

It follows from Fig. 1 that both catalyst samples, the unpressed (curve 1) and the pressed (curve 2), showed almost identical stability in respect of poisoning by thiophene.

Stability of Catalyst Samples in the Dehydrogenation of Cyclohexane with Cyclopentene Impurity.   After the passage of a mixture containing 10% cyclopentene, the catalyst was only poisoned very slowly ; we therefore used a mixture containing 30% cyclopentene.

Fig..2.   Effect of cyclopentene impurity (in the dehydrogenation of cyclohexane) on the stability of a nickel-alumina catalyst.
    Key
    1) Degree of cyclohexane dehydrogenation
    2) h

We see from Fig. 2 that the degree of dehydrogenation of the cyclohexane in the presence of the unpressed catalyst sample

(curve I) after 27 h has fallen from 70 to 20%. With the sample pressed at 20,000 atm, the degree of dehydrogenation after 48 h has fallen from 70 to 48% (curve II). The degree of cyclohexane dehydrogenation with the sample pressed at 10,000 atm has fallen from 70 to 30% in 29 h (curve III). Thus the stability of the sample pressed at 10,000 atm was greater than that of the unpressed sample and less than that of the sample pressed at 20,000 atm.

Stability of Catalyst Samples in the Dehydrogenation of the 96-to-107° Fraction of Maikop Gasoline. Figure 3 shows the time variation in the activity of a catalyst samples during the dehydrogenation of gasoline by reference to the degree of dehydrogenation of the cyclohexane after every 10 h of passing gasoline.

Fig. 3. Stability of a nickel-alumina catalysts in the reaction of the aromatization of the 96-to-107° fraction of Maikop gasoline.

    Key
1) Degree of cyclohexane dehydrogenation
2) h

We see from Fig. 3 that in an experiment lasting more than 220 h the unpressed sample (curve I) had about the same stability as that pressed at 20,000 atm (curve II).

The results of all these experiments show that the stability of a nickel-alumina catalyst in the dehydrograntion of hydroaromatic hydrocarbons in the presence of a five-membered cyclene poison may

be raised by pressing.   In the case of thiophene poisoning, which probably involves a different mechanism, pressing had no effect on the stability of the catalyst.   Thus it would certainly appear that the increase in the stability of the catalyst ~~as a result of~~ *resulting from* pressing is selectively associated with the mechanism underlying the formation of the blocking film.

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