ETHYLENE AND CYCLOHEXENE HYDROGENATION ON ACIDIC OR BASIC ERIONITE ACTIVATED BY DOUBLE SPILLOVER OF OXYGEN AND HYDROGEN

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Two types of erionite were submitted to a double spillover treatment: O_2 first then H_2 at 430 °C. The first type was acidic erionite while the second one was basic erionite (Na, K-erionite). Blank tests were also performed using only O_2-H_2 thermal activation procedures. Ethylene was hydrogenated at 180 °C only on basic erionite activated by spillover. The double O_2-H_2 thermal treatment was unable to convert either acidic or basic erionite into a ethylene hydrogenation catalyst. Cyclohexene was converted to cyclohexane exclusively on acidic erionite activated either by double spillover or thermally, the latter activation being less efficient than the former. It is the first time that hydrogenating sites have been created by spillover on a basic form of zeolite.

1. Introduction

Hydrogen spillover, and to a less extent O_2 spillover, is now recognized as an efficient means to activate many kinds of so-called inert oxide supports [1] and also as a dynamic species able to control the state of oxidation of a specific cation in mixed oxides (remote control concept) [2] or able to prevent deactivation [1–3] when it is continuously supplied by a donor system during the catalytic reaction. The concept of Spillover Assisted Catalytic Reaction (SACR) was recently developed and proposed during the Second International Conference on Spillover [4] in order to account for the dynamic aspect of spillover.

Erionite in the acidic form was recently activated by a double spillover procedure: first O_2 spillover, and then H_2 spillover to develop very active catalytic sites for the selective hydroconversion of n-heptane [5–7] in this laboratory. Erionite is a shape selective zeolite accessible only to molecules not larger than n-alkanes. It was checked in this laboratory that simple O_2 or H_2 spillover treatments were less efficient towards acidic erionite (for instance) in order to increase its activity in the hydroconversion of n-heptane [5,7].

As pure acidic erionite showed a dual catalytic sites network (acidic and hydrogenating ones) it seems interesting to attempt at the discrimination of these sites by the comparative testing of acidic and basic type of erionite activated thermally or by spillover.

It was already shown in this laboratory that spillover of H_2 was able to develop acidic as well as hydrogenating active sites on silica and only hydrogenation active centers on alumina [1,8] in the conversion of n-heptane.

In this paper the pure hydrogenating properties of erionite were tested towards the conversions of ethylene in ethane and cyclohexene in cyclohexane respectively.

2. Experimental

A sample of synthetic Na, K-erionite and a sample of 0.93 NH_4-erionite prepared by a repeated ion exchange of the first sample thermally treated were used in this work. The basic form was supplied by VEB Chemikombinat, Bitterfeld GDR and its SiO_2/Al_2O_3 ratio was 6. The acidic form was prepared in this laboratory by ion exchange with a NH_4NO_3 solution followed by an O_2 treatment operated in situ in the reactor [5]. The spillover oxygen and hydrogen was obtained from a Pt-Al_2O_3 catalyst (donor). The batch spillover reactor was fully described elsewhere [1] and the O_2/H_2 double spillover treatments were always performed at 430 ° C, the Pt-Al_2O_3 being removed from the reactor at the reaction temperature of 180 ° C [5]. A summary of the activation is shown on fig. 1. For each run one gram of catalyst was placed in the batch reactor. The analysis of the reaction partners was carried out by gas chromatography [7]. Ethylene was introduced in the reactor under a partial pressure of 60 Torr and cyclohexene

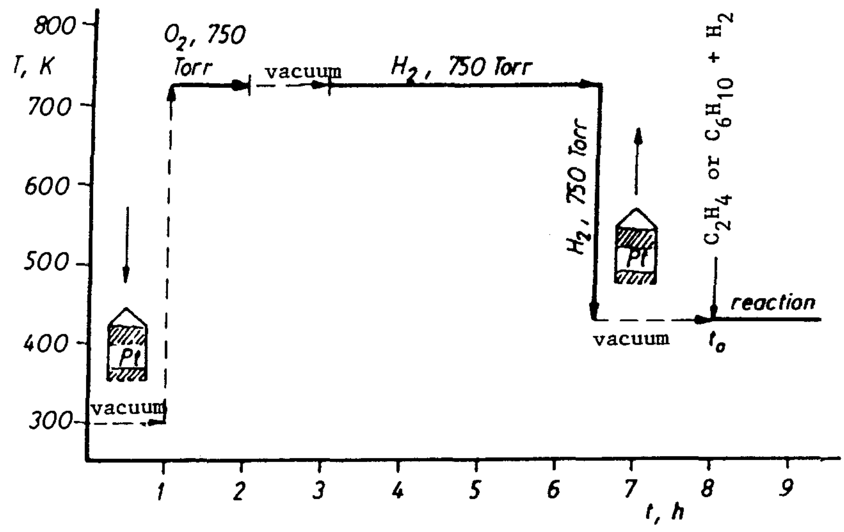

Fig. 1. Stepwise activation diagram.

under a partial pressure of 6 Torr. Helium completed the pressure to the atmospheric one.

The surface are of each form of erionite was determined by BET with N_2 at 77 K, the acidic form showed a surface area of 254 m^2/g and the basic erionite 150 m^2/g. There is a strong decrease of the specific area representing the basic erionite with comparison to that of the acidic form probably due to the large difference in the ionic radii of H^+, K^+ and Na^+ ions.

3. Results and discussion

ACIDIC ERIONITE-ETHYLENE HYDROGENATION

When H-erionite was activated by the double spillover as described above or only thermally by O_2 and H_2 (i.e. in the absence of the Pt-Al_2O_3 donor) a small conversion of ethylene at 180 °C was recorded on both types of activated zeolite, the conversions being in the vicinity of 10% in both cases. After the runs it was observed that the H-erionite had turned black indicating coke formation [7]. It was checked that 26% in weight of C was missing at the end of the run (mass balance confirmed by quantitative C analysis of the sample). Thus it seems that the strong acidic centers of erionite are the sole kind of sites developed or maintained despite the spillover treatment. These sites are not able to hydrogenate ethylene, beside no hydrogenating centers have been created by the spillover activation contrary to what was observed for simple oxides such as silica or alumina [8]. The assumption of a long induction period for the sample treated by spillover cannot be retained here as it was the case for simple oxides such as alumina [1].

BASIC ERIONITE-ETHYLENE HYDROGENATION

The situation observed in this case, with Na, K-erionite was totally different from that related to the acidic form of the zeolite.

When Na, K-erionite was activated by the double spillover a rapid transformation of ethylene into ethane was recorded as depicted on fig. 2 (curve a). Curve b of the same diagram shows that a second dose of C_2H_4 was also quickly hydrogenated, in both cases within two hours without any induction period [1].

The double thermal activation (blank test) of the Na, K-erionite resulted in a very small activity compared to the one registered when spillover activation operated as shown on curve c of fig. 2. One may notice that this last behavior is very similar to that obtained with the acidic form of the zeolite activated either by the double spillover or by the double thermal procedures.

Thus, concerning the basic erionite, the double spillover mode of activation is necessary to develop hydrogenating catalyic sites at the surface of the zeolite since the thermal procedure alone is not efficient.

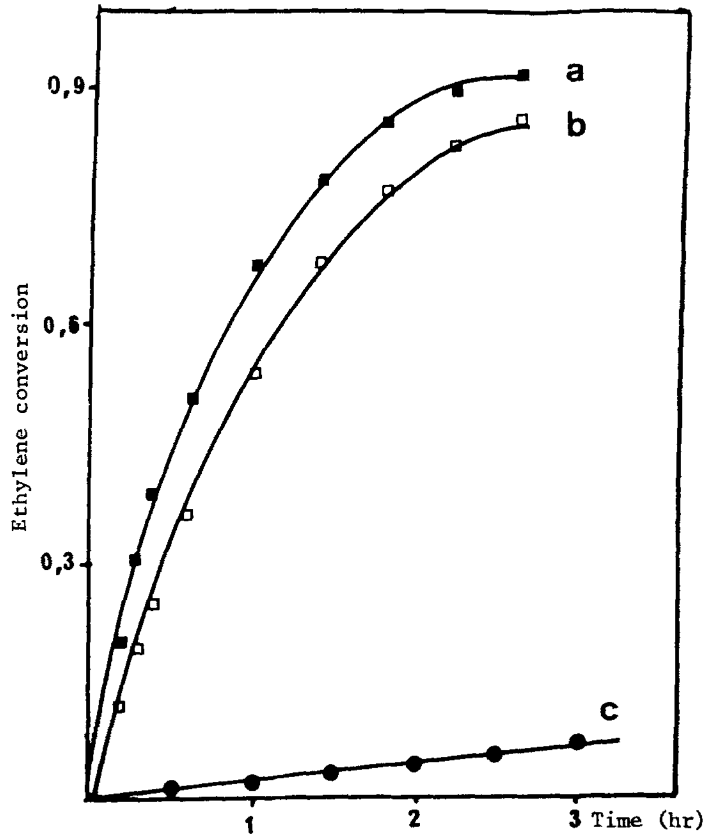

Fig. 2. Hydrogenation of ethylene at 180 °C on Na, K-erionite. a - Na, K-erionite activated by spillover, first dose, b - same as a but second dose, c - blank test (Na, K-erionite activated thermally by O_2, H_2 only).

Moreover when the spillover catalyst was treated by O_2 at 180 °C after a run, it showed no deactivation as one can see it on curve b of fig. 3 obtained after a first run (curve a) followed immediately by an evacuation and the introduction of O_2. This result clearly indicates that a spilt over hydrogen species is not necessary to convert ethylene into ethane.

The same result was also registered when O_2 was replaced with NH_3 in a sequence of runs identical to the one just described above showing that no acidic active site eventually created by spillover was involved. In these experiments it seems that the spillover activation procedure creates hydrogenating sites for ethylene hydrogenation which are missing on the basic form of erionite only thermally treated. The hypothesis that the sites so developed might perhaps have neutralized the basicity (since the pure basic erioniote is inactive) cannot be involved because NH_3 did not inhibit the activity and consequently new hydrogenating centers must have been created in a very specific way due to the spillover activation.

ACIDIC ERIONITE-CYCLOHEXENE HYDROGENATION

H-erionite activated by double spillover was able to transform cyclohexene into cyclohexane (selectivity $\simeq 100\%$) at 180 ° C with a moderate rate as shown on fig. 4 (curve a). The conversion reached the value of 33% at the end of 5 hrs of run. Traces of ethane and benzene were also detected in the gas effluents. It was also checked by a carbon mass balance calculation that an amount of 19% (weight) of C remained on the catalyst. This quantity was confirmed by elemental quantitative analysis for C [7]. It is possible that a cyclohexyl radical generated by interaction with a hydrogen spilt over species adsorbs strongly at the erionite surface on the acid sites as proposed by Lacroix et al. [9] for silica activated by hydrogen spillover in the presence of cyclohexene and hydrogen.

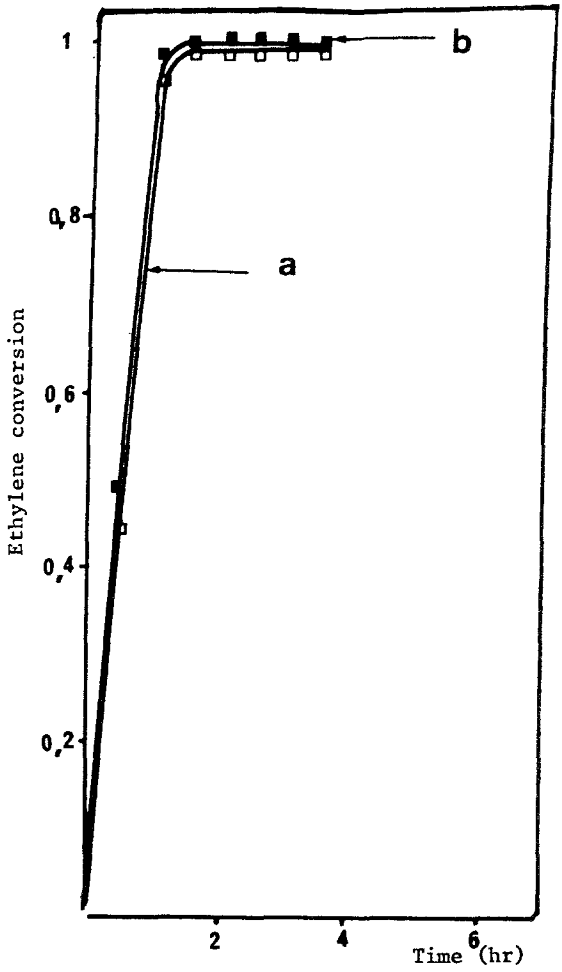

Fig. 3. Hydrogenation of ethylene at 180 ° C on Na, K-erionite. a - First dose of C_2H_4 on Na, K-erionite activated by spillover, b - Second dose, same as a but after O_2 treatment at 180 ° C.

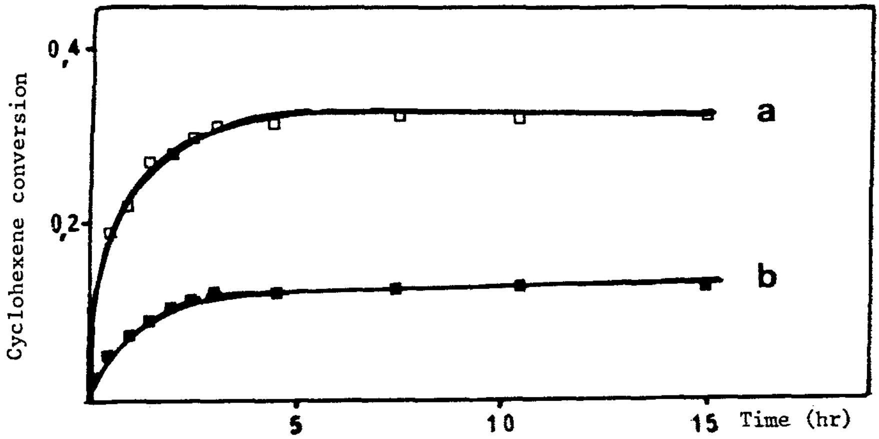

Fig. 4. Hydrogenation of cyclohexene at 180 °C on H-erionite. a - H-erionite activated by spillover, first run, b - Evacuation and second run.

A second dose of cyclohexene introduced after the evacuation of the partners of the first run was again converted but to a less extent as shown by curve b of fig. 4. The blank test carried out with the thermally activated erionite behave similarly and as indicated by curve b of fig. 4 [7]. Consequently it seems that spilt over hydrogen species is beneficial for the hydrogenation of cyclohexene. In this case cyclohexene reacts in two ways: hydrogenation into cyclohexane and cracking products but to a less extent than when ethylene is the reactant in similar conditions.

BASIC ERIONITE-CYCLOHEXENE HYDROGENATION

A very small conversion of cyclohexene in cyclohexane was registered, around 4% in the first run with Na, K-erionite activated by spillover and up to 7% in the following experiment. Thus spillover hydrogen seems detrimental to the formation of cyclohexane. This result can be explained by the need of acidic sites for adsorption of a cyclohexyl species which is lacking in the case of the Na, K-erionite, or by the shape selectivity exhibited by the basic form of the erionite. Indeed a theoretical model shows that cyclohexene may just penetrate erionite in its H form.

4. Conclusions

Acidic or basic forms of erionite activated by thermal means O_2 and H_2 show very poor catalytic activity for the hydrogenation of ethylene or cyclohexene.

It is only, by activation involving double spillover of O_2 and H_2 that the basic form of the erionite is converted into a fairly good catalyst for ethylene hydrogenation capable of withstanding poisoning by O_2 or NH_3. The acidic form which is very prone to coking has only a very small hydrogenation activity.

Acidic erionite activated by the double spillover treatment exhibits a rather low activity towards cyclohexene hydrogenation.

The major result of this study is that once again a new type of hydrogenation sites for ethylene can be induced on erionite and to our knowledge for the first time on a basic form of a zeolite by using a spillover treatment, while on the acidic form it seems that the same spillover procedure cannot overcome the strong acid sites responsible for the coking reactions. As a general rule, the sites created by the spillover method are resistant both to NH_3 or O_2 interactions and are likely of the same nature as those developed separately by spillover on SiO_2 or Al_2O_3 for ethylene hydrogenation.

Acknowledgements

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