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Conversion of Butane over the Solid Superacid ZrO_2/SO_4^{2-} in the Presence of Hydrogen

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The conversion of n – butane to isobutane on the solid superacid ZrO_2/SO_4^{2-} has been studied in a microflow reactor in a helium/hydrogen stream at constant hydrocarbon pressure under kinetic-controlled conditions. The effect of the partial pressure of hydrogen indicates a dual role for this component, namely that it is an inhibitor at high partial pressure, but is essential for maintaining the catalyst activity. The presence of platinum to maintain the catalyst activity is not necessary if the hydrogen pressure is high enough.

INTRODUCTION

The industrial importance of the isomerization reaction of linear paraffins to the branched (higher octane-grade) isomers is still increasing due to environmental constraints. As the equilibrium product distribution is the most favorable at lower temperatures, the use of very strong acids and superacids (*1*) has been suggested. The separation problems related to liquid acids have stimulated research in the field of solid superacids and the early claims based on the H_0 values of less than – 16 for sulfate-treated zirconium oxide (*2a, 2b*) have raised much interest. Recently this catalyst has been claimed to be comparable in activity to HZSM-5 in the methanol to hydrocarbon conversion (*2c*) and platinum-loaded ZrO_2/SO_4^{2-} catalyst has been proven useful for the RON improvement of straight run naphtha (*3*). Other solid superacids such as SbF_5 intercalated graphite (*4*), various SbF_5-treated oxides (*5*), and polymer-supported superacids (*6*) are known to be very active for room temperature hydrocarbon conversions, but also to deactivate rapidly due to the production of polymeric material on the catalyst surface (*7*) and physical loss of the superacid.

Despite the large number of papers devoted to the ability of sulfate-treated zirconium oxide (*2*) and other related oxides (*8*) to convert n-butane into isobutane, the question of the rapid deactivation of these catalysts under the usual experimental conditions has not been stressed. In this article we show the interesting and ambiguous influence of hydrogen on the activity and stability of this solid superacid and the implications for mechanistic aspects.

Among the small alkanes able to undergo acid-catalyzed conversion, butane has been selected on the basis of the industrial interest such as alkylation of olefins with isobutane. Moreover, butane is a convenient model compound because its conversion is the slowest from a mechanistic point of view and it also yields a quite simple product distribution. Two mechanistic approaches, by different authors and using different catalysts, have been proposed for the conversion of butane to isobutane.

1. The isomerization via the energetically very unfavorable primary carbocation

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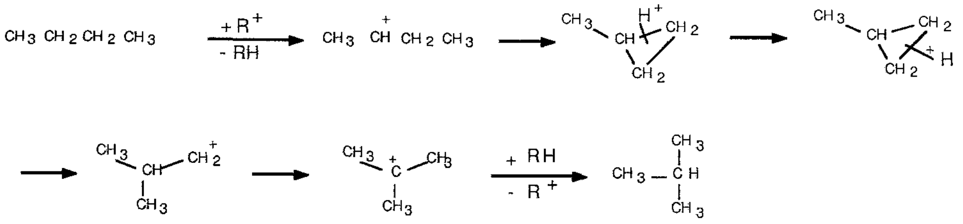
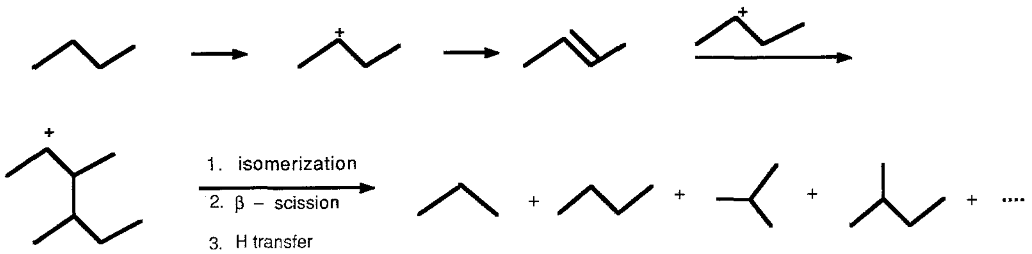


2. The energetically more favorable disproportionation reaction: alkylation–cracking via a C_8 intermediate



Whereas the probability of the deprotonation step is very low on SbF_5-based solid superacids (*9*), this pathway is probably predominant on the other solid (and weaker) superacids and most often improperly designated as an isomerization reaction. The bimolecular mechanism for *n*-butane conversion on H-mordenite has been proposed on the basis of kinetic and ^{13}C labeling experiments (*10*) and also by comparison of the product distribution of C_4 and C_8 hydrocarbons on dealuminated mordenite (*11*). The relationship between the nature of the reaction pathway and the deactivation process itself must be very close. Recently, the addition of Pt (0.5% weight) has been recommended (*3*) to increase the life-time of ZrO_2/SO_4^{2-} in the presence of hydrogen under a pressure of 10–30 kg/cm^2.

EXPERIMENTAL

Materials. Hydrocarbons (Fluka puriss grade) were used without further purification. Hydrogen and hydrogen–helium mixtures were purchased from Air Liquide (purity 4N).

Catalyst preparation. ZrO_2/SO_2^{2-} and Pt/ZrO_2/SO_4^{2-} were previously described in the literature (*2b, 2d, 3a*). We have slightly modified their preparation as follows:

ZrO_2/SO_4^{2-}: An aqueous solution of $ZrOCl_2, 8H_2O$ was hydrolyzed with an aqueous solution of ammonia (33%) at room temperature. After washing the hydroxide with deionized water and drying at 110°C for 15 h, 5 g of hydroxide were immersed in 30 ml of 1 *N* H_2SO_4 for 1 h at room temperature. After filtration, drying at 110°C (10 h) and calcination in air at 600°C (3 h) the catalyst ZrO_2/SO_4^{2-} was stored under dry N_2 in scaled Pyrex tubes.

Pt/ZrO_2/SO_4^{2-}: This catalyst was prepared by impregnation of ZrO_2/SO_4^{2-} as follows: 2.5 g of ZrO_2/SO_4^{2-} was immersed in 4 ml of H_2PtCl_6 solution (0.3% weight of Pt). After filtration, drying at 110°C and calcination at 600° (3 h) the catalyst was stored as described above.

Apparatus and Procedure

The catalytic reactions were carried out in an all-glass grease-free flow system already described (*12*). The system works as a differential flow reactor. In each run *n*-butane was introduced into the gas flow of helium, or hydrogen + helium, at constant hydrocarbon partial pressure. The pressure vs time curve as recorded by a catharometer inserted in the flow line closely approximates a square-wave pulse. From this curve the hydrocarbon pressure and hydrocarbon flow rate can be determined. In this way all the kinetic parameters can be controlled during the catalytic reaction.

Gas Chromatography

Analysis of the effluent gas from the reactor was made with the help of a 2-m Porapak Q column with a flame ionization detector and the temperature of the oven was programmed to rise from 100 to 250°C at the rate of 10°C/min.

RESULTS AND DISCUSSION

In a first series of experiments at atmospheric pressure, we have checked the stabilizing effect of platinum at low hydrogen pressure in the butane–isobutane conversion reaction over ZrO_2/SO_4^{2-}. A mixture of butane : hydrogen : helium (10 Torr : 60 Torr : 690 Torr) was fed at a rate of 10^{-7} mol s^{-1} of butane during 10 h (see Fig. 1).

The catalyst initially very active in both cases is stabilized at a lower level in the presence of Pt whereas in absence of Pt it deactivates completely after 5–6 h.

We have, however, compared the activity and stability of the sulfate-treated zirconium oxide ZrO_2/SO_4^{2-} on the butane isomerization reaction in the presence and absence of Pt using either pure helium or hydrogen as carrier gas.

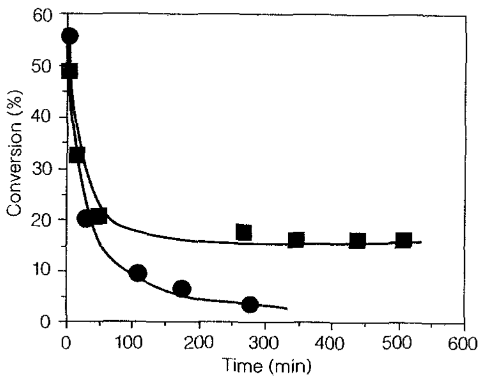


FIG. 1. Influence of Pt on ZrO_2/SO_4^{2-} deactivation at 250°C (hydrocarbon feed rate = 10^{-7} mol s^{-1}; P_{H2} = 60 Torr; P_{C_4} = 10 Torr; P_{He} = 690 Torr; catalyst 200 mg; (■) with Pt; (●) without Pt).

When the carrier gas helium is replaced by hydrogen with the same partial pressure of butane (10 Torr) we note that the presence of Pt has no influence on the catalyst activity and stability (Fig. 2). Both catalysts show at the start under helium a high activity which decreases rapidly whereas under hydrogen their activity, low at the start, increases and stabilizes after 1 or 2 h on stream.

The stabilizing effect of hydrogen is obvious. The main origin of the deactivation of acidic catalysts is the cracking polymerization–dehydrogenation process which leaves on the surface a polymeric layer with higher C/H ratio. When hydrogen is present, catalytic reduction of the surface carbocations and of the olefinic compounds occurs. We know from independent experiments that isobutene is rapidly hydrogenated on ZrO_2/SO_4^{2-} at temperatures as low as 60°C (*13*), but also that, despite the presence of excess hydrogen, deactivation of the catalyst occurs rapidly even at this temperature. Starting with *n*-butane, however, should minimize the formation of olefins in the presence of superacidic catalyst. It is indeed known that the deprotonation equilibrium of a cation such as *t*-butyl ion lies far to the left ($R = 10^{-16}$) under superacidic conditions (*13*). As the deprotonation leads to olefins which will be alkylated and cracked we felt it also of interest to use the *n*-butane conversion reaction as a test reaction to evaluate the relative superacid character of ZrO_2/SO_4^{2-} in comparison with H-mordenite as both catalysts have been claimed as superacids. We found that at 250°C under the same experimental conditions under which sulfated zirconium oxide led to 20% conversion with 95% selectivity in isomerization, H-mordenite was totally inactive. In order to observe a conversion of 20% with this catalyst the temperature of 350°C was necessary; however, the observed selectivity in isomerization was only 55%. We feel that this obser-

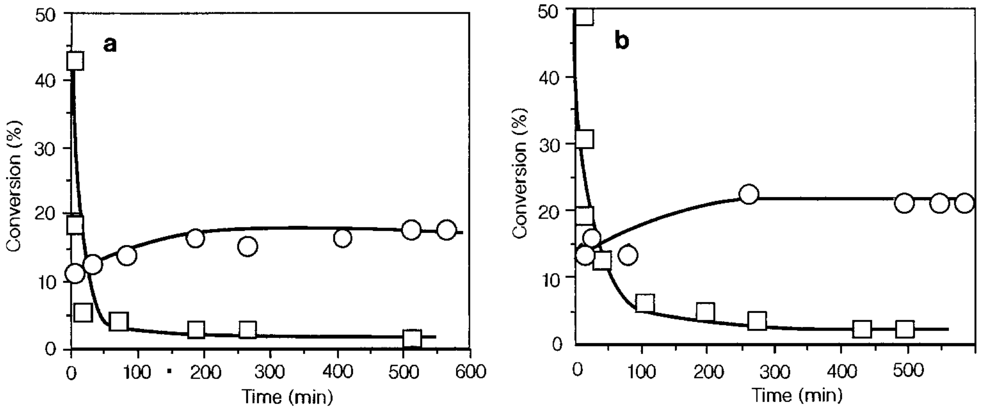


FIG. 2. Influence of the nature of the carrier gas in presence (a) and absence of Pt (b) on ZrO_2/SO_4^{2-} (hydrocarbon feed rate = 10^{-7} mol s^{-1}; P_{C_4} = 10 Torr; P_{H_2} or P_{He} = 750 Torr; catalyst: 200 mg; (○) hydrogen; (□) helium).

vation is in accord with the pronounced superacidic character of the sulfated zirconium oxide catalyst. The superacid character of the sulfate-treated zirconium oxide in comparison with H-mordenite (*10*) is also supported by the selectivity in isomerization observed (less dismutation) and the much lower temperature at which the selectivity in isomerization is the highest (250°C instead of 350°C). In a third series of experiments we have kept the hydrogen/hydrocarbon ratio at 6/1 at atmospheric pressure but running the reaction at low (60 Torr) and high (650 Torr) hydrogen partial pressure. The curves in Fig. 3 show that the presence of hydrogen, even at a ratio of 6/1, is not a guarantee of high activity and stability for the zirconium oxide catalyst, but that the hydrogen concentration at the surface of the catalyst should be at a high enough level.

Here again we note a strong increase in activity after the initial induction period when enough hydrogen is present. In order to optimize this point we have checked the influence of the H_2/C_4 ratio, keeping the hydrogen partial pressure above 500 Torr to limit the deactivation of the catalyst. These results are collected in Fig. 4 which shows

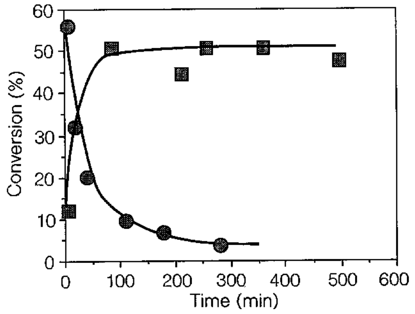


FIG. 3. Influence of the partial pressure of hydrogen ($H_2:C_4$ ratio = 6:1; catalyst ZrO_2/SO_4^{2-} without Pt, (●) p_{H_2} = 60 torr; (■) p_{H_2} = 650 Torr).

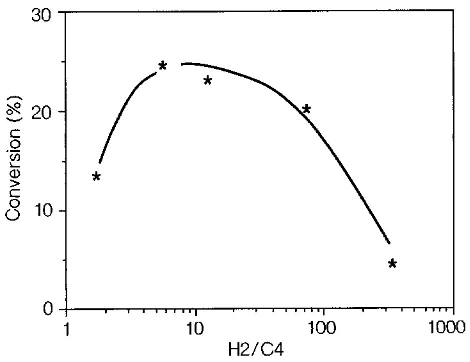


FIG. 4. Influence of the hydrogen/hydrocarbon ratio (P_{H_2} = 492–758 Torr; P_{C_4}: 2–268 Torr; catalyst ZrO_2/SO_4^{2-}: 200 mg; total gas feed rate = 0.25 ml/s).

an optimum in the H_2/C_4 ratio. Considering that the catalyst keeps its activity at both ends of the curve it appears that hydrogen has both a promoting and an inhibiting effect. Hydrogen must be present to hinder the deactivation but when the hydrogen coverage is too high the conversion drops. Presumably a high hydrogen pressure inhibits the reaction by inhibiting the dehydrogenation step; an alternative reason could be that the reaction becomes slower as hydrogen occupies a fraction of the active sites. Similar results have been observed on metal catalysts by Paál and co-workers (*14*). These results can be compared with those obtained in the disproportionation studies of toluene on H-mordenite. (*15*).

As this ambiguous behavior of hydrogen on the butane conversion reaction with the superacid catalyst can help to clarify the reaction mechanism, we intend to study this reaction with the help of kinetics combined with ^{13}C labeling of the starting hydrocarbon.

ACKNOWLEDGMENTS

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