React. Kinet. Catal. Lett., Vol. 15, No. 2, 279–284 (1980)

DOUBLE BOND MIGRATION AND SKELETAL ISOMERIZATION OF OLEFINS ON FLUORINATED ALUMINAS

M. Otremba and M. Taniewski

Silesian Politechnical University, 44-101 Gliwice, Poland

Received June 27, 1980
Accepted August 7, 1980

Studying the effect of fluorination of alumina on its activity in double bond migration and skeletal isomerization of butenes and pentenes, it was suggested that fluorination not only affects the distribution of acidic sites but also their character.

В резултате исследований эффекта фторирования окиси алюминия на ее активносиь в миграции двойной связи и в скелетной изомеризации бутенов и пентенов выражен взгляд, что фторирование влияет не только на распеделение активных центров но также на их характер.

INTRODUCTION

It is well known that isomerizations of olefins readily proceed in the presence of acidic catalysts /1,2/. There is some evidence for the existence of a correlation between the acidity of a catalyst surface and its isomerization activity. Isomerization of butene-1 to butene-2 is sometimes even used as a model reaction for testing catalyst acidity. Although it was established long ago that double bond shift proceeds much faster than skeletal isomerization of olefins, virtually no attempts were reported to determine the relative activities of the same catalyst in different isomerizations of a given olefin or in the same mode of isomerization for series of olefins.

Fluorinated aluminas are among the most effective catalysts for the isomerization of olefins /3-5/. There is evidence that fluorination of alumina affects mainly the distribution of the sites with different acid strengths rather than the overall acidity of the surface /6-9/.

The object of this work was to examine the relative catalytic activity of a series of fluorinated aluminas with different fluorine contents in the isomerization of butene-1 to cis- and trans-butenes-2 (B1 to B2), of n-butenes to isobutene (nB to iB) and of n-pentenes to isopentenes (nP to iP).

EXPERIMENTAL

Catalysts were prepared by impregnation of γ-Al_2O_3 (specific surface area 250-270 $m^2\ g^{-1}$) with aqueous solutions of NH_4HF_2 and subsequent calcination at 770 K /5/. For impregnation, (catalyst 1, containing 6.3% F), 2.5% (cat. 2, 3.2% F), 0.8% (cat. 3, 1.1% F) and 0.27% (cat. 4, 0.4% F) NH_4HF_2 solutions were used. Pure alumina was also used.

The experiments were carried out with 50 mg of a catalyst by a conventional flow method. A feed mixture containing olefin (99 mol % butene-1 or pentene-1, both Fluka AG products) and argon (5% of olefin) was passed over the catalyst at a flow rate of 0.33 $cm^3\ sec^{-1}$. The measurements of catalytic activity were conducted by a nonisothermal method applying a linear increase of reaction temperature (0.02 K sec^{-1} in the case of reactions B1 to B2 and nP to iP or 0.04 K sec^{-1} in the case of nB to iB). For studying B1 to B2 and nP to iP, each time fresh samples of the catalyst were used. Reaction nB to iB was studied as a continuation of the runs B1 to B2 at higher temperatures. The reaction products were analyzed by gas chromatography.

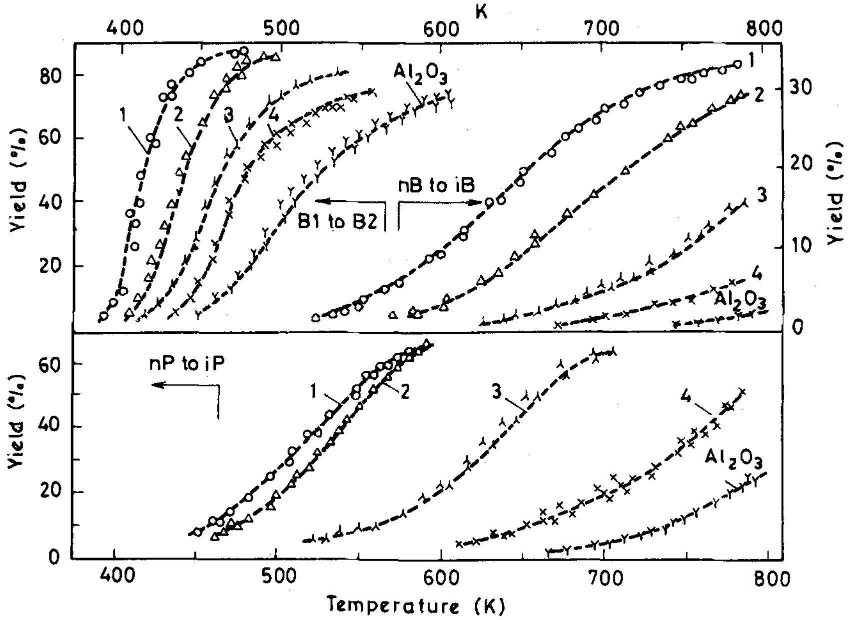

Fig. 1. Yields of isomerization products as a function of temperature (1-4 - numbers of the catalyst)

RESULTS AND DISCUSSION

The yields of the iromerization products formed in each of the three reactions studied in the presence of the five catalysts applied are presented in Fig. 1 as a function of temperature. The measurements were repeated 2-3 times and all experimental points are included in Fig. 1.

It is evident from Fig. 1 that the catalysts activity in each reaction markedly rises with the increase of the concentration of fluorine. In each case the rate of isomerization decreases in the sequence:

B1 to B2 > nP to iP > nB to iB

It has been clearly demonstrated that skeletal isomerization of both olefins was preceeded by complete equilibration between isomeric normal olefins.

Figure 1 reveals enormously wide variations in the catalyst activity, which leads to serious difficulties in establishing a quantitative basis for comparison. Even in the case of a single reaction (B1 to B2) the differences in activity, depending on the fluorine content, are so large that it becomes almost impossible to find a common temperature which may serve as a basis for comparison of the activities of a set of catalysts. Fortunately, in this case there exists a possibility to compare the activities by determining the temperatures at which the same yield of the product is obtained. Such a procedure may be applied also for comparing all the reactions studied, but only in the case of the same catalysts, e.g. cat. 1 at 30% yield (403 K for B1 to B2, 723 K for nB to iB, 508 K for nP to iP). In this way the data characterize the relative activities, but they are, obviously, functions of the yield chosen arbitrarly for the purpose of comparison. Even so, the wide application of this approach to all catalysts used becomes impossible because of the increasing distance between the regions of activity with decrease of the fluorine concentration.

Our results clearly indicate that the activating role of fluorination is much more pronounced in the case of skeletal isomerization of both olefins than in the case of double bond migration in n-butenes.

As follows from our experimental studies, the isomerization of olefins is accompanied by the formation of side products, viz. dimers, C_{n-1} olefins, C_{n+1} olefins (n-number of carbon atoms in the initial olefin) and small amounts of lower hydrocarbons. The yield of dimers, initially very low, increases with rising temperature, reaches a maximum (530-580 K) and then falls down. The products of dismutation and decomposition are formed only at higher temperatures and their yield increases with the rise of temperature. In Fig. 2 are shown the overall yields of all side products, demonstrating the dependence of the selectivity of isomerizations on the catalyst and temperature. Pure alumina and catalysts 3 and 4 produce only negligible or very low yields of side products. The increase of fluorine concentration leads to a marked rise in the yield of side products.

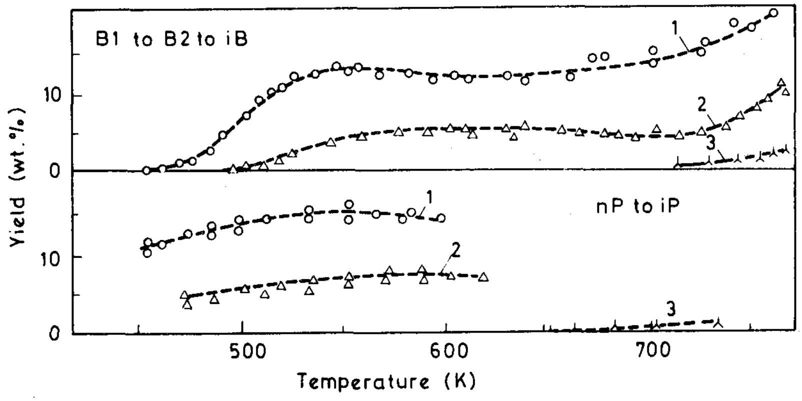

Fig. 2. Overall yields of side products as a function of temperature (1-4 – numbers of the catalyst)

It should be noted that the remarkably high variations observed in catalyst activities for double bond shift, skeletal isomerization and side product formation as a function of fluorine content do not support the view about the existence of a simple quantitative relationship between the overall acidity or the acidity of the sites with certain acid strengths on the one hand and the catalytic activity on the other. Our results rather suggest that the fluorination of alumina not only affects the distribution of acidic sites, but probably also the very character (i.e. the energy state) of the active sites.

REFERENCES

1. Ya.T. Eidus, R. Izmailov: Usp. Khim., 26, 212 (1957).
2. Ya.T. Eidus, B.K. Nefedov: Usp. Khim., 32, 1025 (1963).
3. V.S. Choudhary: Ind. Eng. Chem. Prod. Res. Dev., 16, 12 (1977).
4. M. Otremba, W. Zajdel, M. Taniewski: Neftekhimiya (In press).
5. M. Otremba, W. Zajdel, M. Taniewski: Przem. Chem. (In press).

6. A.N. Webb: Ind. Eng. Chem., 49, 261 (1957).
7. V.A. Chernov, T.V. Antipina: Kinet. Katal., 7, 739 (1966).
8. R. Covini, V. Fattore, N. Giordano: J. Catal., 9, 315 (1967).
9. H. Reitsma, C. Boelhouwer: J. Catal., 333, 39 (1974).