

ON THE ISOMERIZATION OF ALLENE TO PROPYNE OVER A-TYPE
ZEOLITES

By

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The allene to propyne isomerization was investigated over different cationic exchanged forms of A-type zeolite. All of the investigated catalyst samples proved to be active to various extents, but the isomerization was accompanied by side-reactions in most cases. Purified Na₁₂A zeolite (A=Al₁₂Si₁₂O₄₈) offered the conversion and selectivity required for investigations of the kinetics of the isomerization.

Introduction

In heterogeneous catalytic reactions, the interconversion of the reactants takes place in the adsorbed layer on the surface of the catalysts. As concerns the overall process, the reaction $A \rightleftharpoons B$ is one of the most simple types, even though it passes through at least three distinct steps:



where the first step is the adsorption of reactant A on the active site X of the catalyst, the second one is the surface interconversion, and product B desorbs into the gas phase in the last step.

The overwhelming majority of heterogeneous catalytic reactions are much more complex than the hypothetical one characterized by the above reaction steps. In theoretical investigations, it is sometimes advisable to search for a particular reaction that proceeds exclusively through the three steps mentioned.

The allene to propyne isomerization is a reversible reaction. It is of first order in both directions, and thus it can be regarded as an ideal reaction for kinetic studies in the sense outlined. It can be observed merely in the gas phase, above 900 K, without catalysts [1-4]. Its kinetics has already been investigated with the use of homogeneous catalysts such as iodine vapour [5], or even different metal oxides as catalysts [6-8].

Zeolites are frequently used as catalysts in a wide range of reactions of different hydrocarbons, because of their well-defined crystalline structures and ion-exchange properties. Different cationic forms of type-A zeolites were chosen as potential catalysts of the allene isomerization on the basis of experience gained earlier in studies of the cyclopropane to propene transformation over this type of catalyst [9].

In this work we attempted to find a catalyst that accelerates the allene to propyne reaction without resulting in unwanted by-products. We also aimed to establish precise conditions leading to the acquisition of data suitable for later quantitative evaluation.

Method and materials

The compositions of the catalysts can be seen in Table I. They were prepared by ion-exchange of LINDE 4A zeolite. The Co^{2+} content of CoNaA was determined by polarography; other catalysts were analysed by neutron activation.

Table I

Zeolite	Unit cell composition of catalyst used
NaA	Na_{12}A ($\text{A}=\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$)
ZnNaA	$\text{Zn}_{5.4}\text{Na}_{1.2}\text{A}$
LiNaA	$\text{Li}_{9.6}\text{Na}_{2.4}\text{A}$
CaA	Ca_6A
CoNaA	$\text{Co}_5\text{Na}_2\text{A}$

From the powders, pellets were prepared by applying pressures of the order of 10^8 Pa. The pellets were crushed, and the 0.16-0.2 mm sieve-fraction was selected and stored over saturated ammonium chloride solution until use.

The allene was a MATHESON product of 99.3 % purity, which was used without further purification.

The experiments were carried out in a recirculatory batch reactor. A 100 mg sample of catalyst was put into the reactor and was heated to 678 K at a pressure of 1 Pa for 4 hours. It was then cooled down to the reaction temperature, which varied between 395 K and 460 K. The reaction temperature was continuously recorded via a Na-CrNi thermo-

couple reaching the middle of the catalyst bed. A large amount of nitrogen was used as diluting gas (up to 99 %) to maintain isothermicity in spite of the heat of sorption of allene.

Gas samples were taken from the reactor with a Carlo-Erba sampling valve and were analysed by means of GC with a column filled with 30 % DMS on CHROMOSORB-P; the carrier gas was nitrogen.

Experimental results

The kinetic curves obtained over CoNaA zeolite demonstrate that the isomerization of allene was accompanied by side-reactions, as shown in Fig. 1. At 395.5 K, the amounts of allene and propyne as functions of time are characterized by monotonously decreasing and increasing curves, respectively. Since no other products but allene and propyne can be detected in the gas phase, the sum of their concentrations (i.e. partial pressures) should not change after sorption equilibrium is reached. Actually, the shape of the overall mass balance curve c unambiguously shows that the amount of the gas phase steadily decreases. At 460 K, the monotonously decreasing nature of balance curve f can also be ascertained; further the propyne production curve e displays a peak. The effects of side-reactions are even more marked when ZnNaA catalysts are used (Fig. 2).

The isomerization can also be performed over CaA and LiNaA zeolites, but the activities of these catalysts are much lower than that of CoNaA.

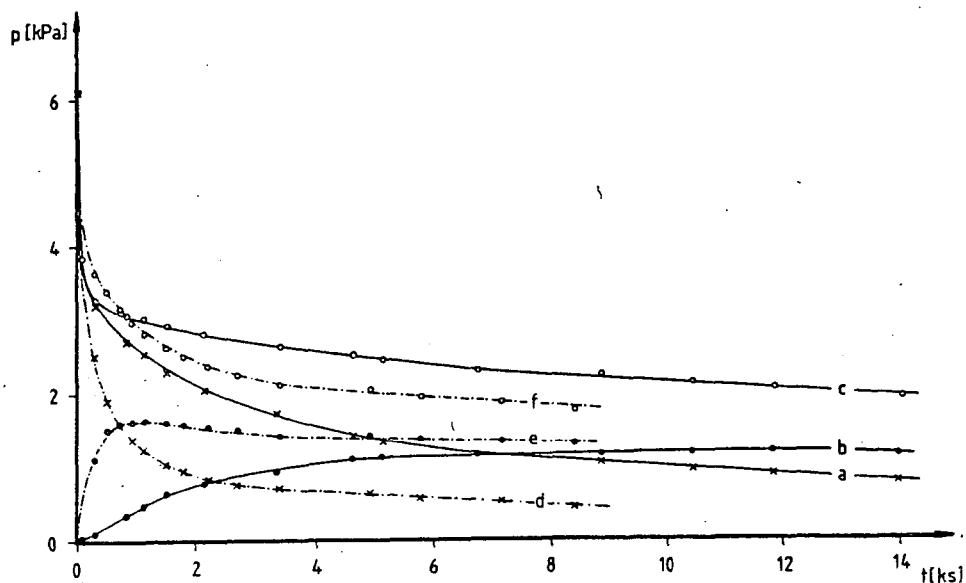


Figure 1.: Kinetic curves of isomerization of allene to propyne over CoNaA catalyst at 395.5 K (—) and at 460 K (---), showing partial pressures of allene (a, d), propyne (b, e) and their sum (c, f)

During examinations of the catalytic activity of the NaA base zeolite (LINDE 4A) that had been used to prepare the other catalyst samples, the curves of Fig. 3 were obtained. These show that this zeolite is also an active catalyst of the allene to propyne isomerization. The total pressure \underline{c} passes through a minimum after the quick decrease caused by the sorption step, and then reaches a constant value.

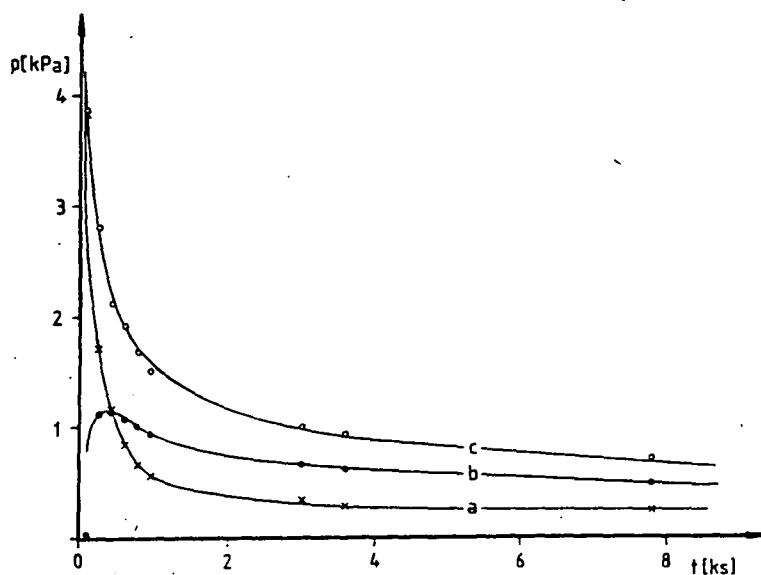


Figure 2.: Kinetic curves of allene isomerization over ZnNaA catalyst at 395.5 K, showing partial pressures of allene (a), propyne (b) and their sum (c)

Since the commercial Na-form zeolites generally contain Ca^{2+} and/or H^+ ions in traces, which may originate from the washing water during preparation or can be ascribed to partial hydrolysis, respectively, it seemed meaningful to prepare a "clean" sample of NaA. This was obtained by repeated ion-exchanges of the original NaA using NaCl solution. Figure 4 depicts kinetic curves ob-

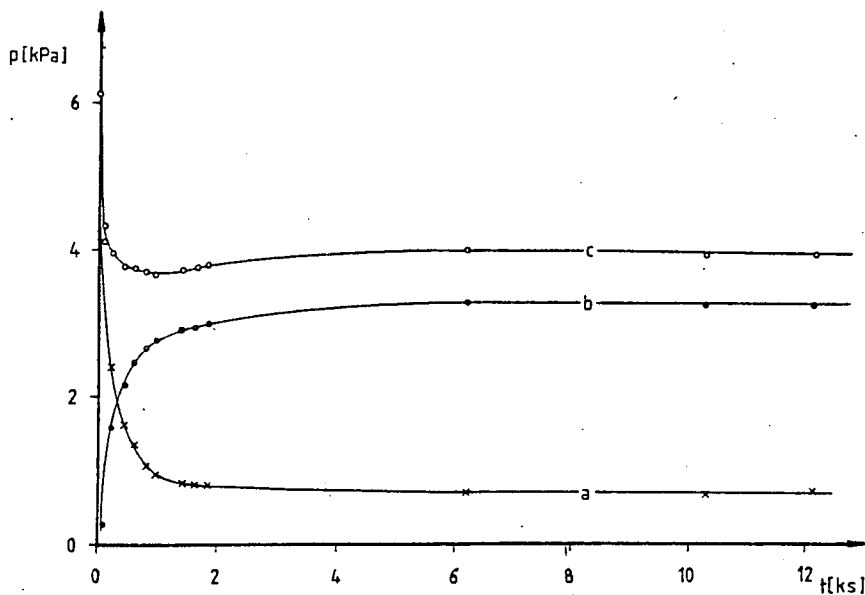


Figure 3.: Kinetic curves of transformation of allene to propyne over LINDE 4A zeolite at 395.5 K

tained from reactions carried out over NaA zeolite prepared in this way. It is obvious that curve c, representing the total pressure, has no minimum, i.e. the total amount of the gas phase does not alter during the whole experiment, apart from the fast initial decrease. Furthermore, the shapes of curves a and b, representing the diminishing of allene and the production of propyne, respectively, do not contradict the qualitative picture of apparent first-order kinetics.

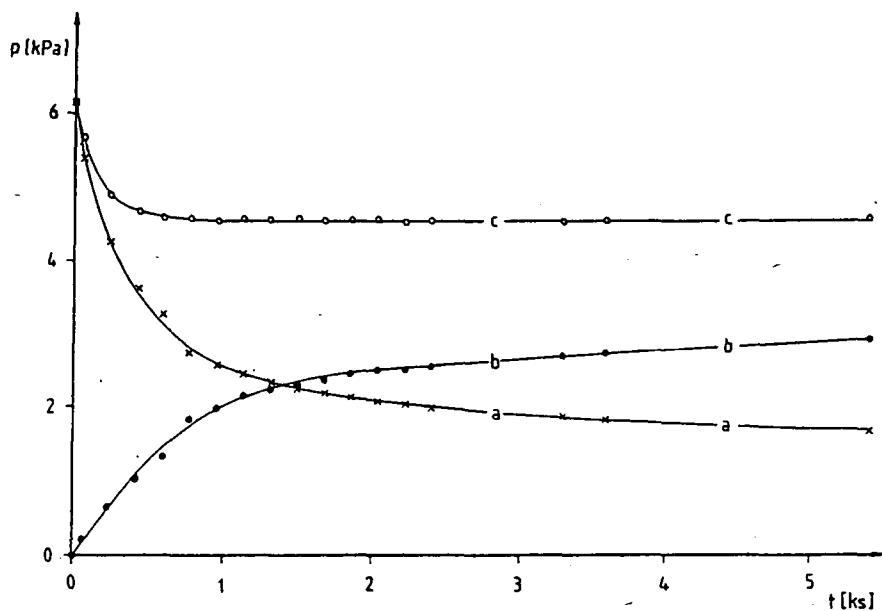


Figure 4.: Kinetic curves of allene to propyne isomerization over Na-exchanged NaA Zeolite catalyst

Discussion

Under the conditions used in this study, allene undergoes a comparatively fast isomerization over CoNaA and ZnNaA catalysts, accompanied by other reaction steps. These can be

polymerization steps producing condensed substances, and/or oligomerization reactions the products of which remain irreversibly sorbed on the surface of the catalyst, so that they cannot be detected in the gas phase. These products gradually reduce the activity of the catalyst by occupying some of the active sites, and they also cause a deficiency in the mass balance, which makes evaluation of the kinetic measurements practically impossible. Therefore, these catalysts are not suitable in an experimental model of the ideal $A \rightleftharpoons B$ type heterogeneous catalytic reaction.

Since Li^+ ions are smaller and more compact than Na^+ ions, the LiNaA catalyst was expected to be very active in the isomerization. Its peculiar behaviour, i.e. its weak activity, was in accordance with the results found by the investigation of the isomerization of cyclopropane to propene [10].

Over the original NaA catalyst, the initial decrease in the total pressure is related to the adsorption of allene. The succeeding increase (Fig. 3) can be explained by the difference between the sorption capabilities of the reactants.

The shapes of the kinetic curves obtained over Na^+ -exchanged NaA catalyst are in accordance with the kinetics of a homogeneous reversible reaction of apparent first order in both directions, except for the initial part referring to the adsorption step.

Thus, we found that all of the investigated A-type zeolites were active to various extents in the isomerization, but only the NaA samples offered the conversion and selectivity required for investigations of the kinetics of the allene to propyne isomerization.

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ИЗОМЕРИЗАЦИЯ АЛЛЕНА В ПРОПИН
НА ЦЕОЛИТАХ ТИПА А.

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Изучена алленето-пропиновая изомеризация на различных катион-замещенных цеолитах типа А. Все изученные образцы катализаторов оказались более или менее активными, однако, в большинстве случаев изомеризация сопровождалась побочными реакциями. Очищенный цеолит Na_{12}A оказал конверсию и селективность, необходимые для изучения настоящей кинетики изомеризации.