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Selective isomerization of *n*-butenes into isobutene over aged H-ferrierite catalyst: nature of the active species

M. Guisnet [a,*], P. Andy [a], Y. Boucheffa [a], N.S. Gnep [a], C. Travers [b] and E. Benazzi [b]

[a] *Laboratoire de Catalyse en Chimie Organique, UMR CNRS 6503, Université de Poitiers,*
40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France
[b] *Institut Français du Pétrole, BP 311, 92506 Rueil-Malmaison, France*

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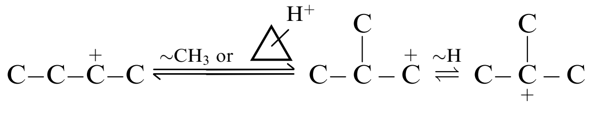
The nature of the active species responsible for butene isomerization over aged HFER samples is reexamined in the light of the change in the product yields at very short time-on-stream and of the reversible and irreversible increases in weight of the zeolite during the reaction. At very short time-on-stream, the selectivity of butene isomerization is that expected from a dimerization–cracking process, in particular simultaneous formation of isobutene, propene and pentenes. A rapid decrease of all the yields is observed with time-on-stream; however, for isobutene but not for the other products, the initial decrease is followed (after 10 minutes-on-stream) by an increase. The decrease in the yield can be related to the formation of carbonaceous compounds ("coke") which block the access to the pores, while the increase in isobutene yield can be explained by the development of a new isomerization mode which is very selective to isobutene. This new mode could be catalyzed by carbonaceous compounds and/or by reaction products which are shown to be retained inside the pores during the reaction. It is proposed that at short time-on-stream the increase in isobutene yield is due to an autocatalytic reaction, *n*-butene isomerization occurring on *t*-butyl carbenium ions formed by adsorption of isobutene molecules (which are slowly desorbed from the pores) on the protonic sites of the zeolite. At long time-on-stream, the active species would be benzylic carbocations formed from carbonaceous compounds trapped in the pores near the outer surface of the crystallites.

Keywords: *n*-butene isomerization, HFER, mechanisms, active species

1. Introduction

It has been recently claimed that ferrierite (FER) was an excellent catalyst for butene isomerization, capable of operating in the absence of water at a relatively low temperature (623 K) with a high selectivity to isobutene and a high stability [1,2]. This discovery has initiated a great deal of research in order to specify the characteristics of this zeolite (pore system, acidity) which are responsible for its high selectivity and also in order to understand the mechanism of butene isomerization. An important point which deserves to be emphasized is the large increase in selectivity to isobutene observed with time-on-stream.

On the fresh HFER sample, butene isomerization is accompanied by a significant formation of propene, pentenes and of various other products (in lower amounts): ethylene, hexenes, heptenes, octenes, propane, *n*-butane. As propene and pentenes appear, like, isobutene as primary products it has been concluded that butene isomerization occurred through a bimolecular (dimerization–isomerization–cracking) mechanism [3] (figure 1). This mode of reaction was not unexpected as monomolecular isomerization of *n*-butene formally involves the formation of an unstable primary carbenium ion [4]:



Furthermore, the extensive scrambling which occurs during the isomerization of ^{13}C *n*-butene confirms that over the fresh HFER samples, butene isomerization occurs through the bimolecular mechanism [5,6].

The increase in selectivity to isobutene with time-on-stream was obviously explained by a change in the reaction mechanism from a bimolecular mechanism to a monomolecular one, this change being attributed to the deposition of carbonaceous compounds (coke) [2,5,6–14]. In agreement with this change in isomerization mechanism, ^{13}C scrambling is no longer observed over an aged FER sample [5,6]. While this change in mechanism with time-on-stream is generally admitted, the effect of carbonaceous deposits on the selectivity (hence on the reaction mechanism) is a much debated question. According to various authors, the increase in selectivity to isobutene could be due to the poisoning of the non-selective acid sites located on the outer surface of the crystallites [8,12] and/or of the strongest acid sites which would be very selective to dimerization–cracking reactions [7,11]. The shape selectivity of FER for skeletal isomerization of *n*-butene may also be increased owing to a

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* To whom correspondence should be addressed.

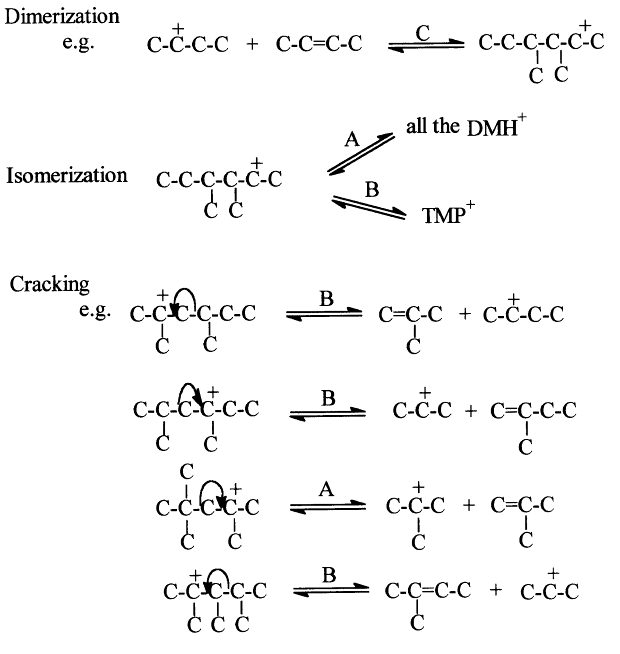

Figure 1. *n*-butene transformation through a bimolecular mechanism. Alkylation and cracking steps: A involves two tertiary carbenium ions, B one tertiary and one secondary carbenium ion and C two secondary carbenium ions. Isomerization steps: A occurs through alkyl shift, B through protonated cyclopropane intermediates.

restriction of channel dimensions by carbonaceous deposits [7,10,11].

However, all these proposals do not seem to be very convincing. Indeed the number of acid sites located on the outer surface of the crystallite is very limited as is shown by the very low activity of FER samples for iso-octane cracking at 773 K [13]. Furthermore, there is no preferential deposition of carbonaceous deposits on the outer surface of the FER crystallite [2,6,13]. As is generally the case with zeolite catalysts [15,16] the formation of coke (which requires not only reaction steps but also the retention of coke molecules) begins inside the FER pores. The preferential elimination of the strongest acid sites by coke deposits is most likely. However, it seems abnormal, at least at the relatively low reaction temperature, that the facile bimolecular isomerization (it only involves secondary and tertiary carbenium ion intermediates (figure 1)) is favoured on the strongest acid sites over the energetically unfavoured monomolecular isomerization (the reverse seems most likely). It can furthermore be remarked that because of the difficulty to form the unstable primary isobutylcarbenium ion, the mechanism of *n*-butane isomerization is generally considered to be intermolecular [17] as confirmed by experiments with ^{13}C labelled butane. Finally the hypothesis of a restriction of channel dimensions by carbonaceous deposits is only valid if coke is deposited on the outer surface of the crytallites (which we have rejected above). Indeed, carbonaceous compounds located inside the micropores could not limit but would completely block the access of the reactant to the pores hence to the acid sites.

Another explanation was advanced by our team [9,13], based on the observation that over two ferrierite samples (Si/Al = 8.9 and Si/Al = 13.8) at low *n*-butene conversion (< 15%) there was with time-on-stream not only an increase in the selectivity to isobutene but also an increase in the isobutene yield. At this low conversion, this increase in yield could not be explained by the suppression of rapid secondary transformation of isobutene into propene and pentenes [11]. Indeed over the ferrierite samples, isobutene isomerization is more selective than *n*-butene isomerization: 91.5% instead of 57% at time-on-stream equal to 5 min. The formation of propene + pentenes is 7 times faster from *n*-butene than from isobutene [3]. It should be emphasized that at high conversion, when thermodynamic equilibrium between *n*-butenes and isobutene is practically established, part of the increase in isobutene yield can be due to the suppression of secondary transformation of the *n*-butene–isobutene mixture into propene and pentenes. This increase in yield found at low conversion (hence in the rate of isobutene formation) was explained by the substitution of the non-selective bimolecular mechanism (catalyzed by the acid sites located in the zeolite pores of the fresh FER sample) with a new reaction mechanism involving as active sites carbenium ions resulting from the adsorption on the protonic sites of carbonaceous deposits blocked inside the zeolite pores [6,9,13]. In a first paper [9], tertiary carbenium ions were proposed as the active sites. However, the carbonaceous deposits were found to be composed of alkyl aromatics, hence benzylic carbocations were afterwards advanced as the active sites [13]. Whatever the type of carbocations proposed as active sites, the mechanism allows explanation of the rapid and selective transformation of one molecule of *n*-butene into one molecule of isobutene (this is a pseudomonomolecular mechanism).

In this paper the investigation at very short time-on-stream of *n*-butene transformation allows confirmation of the development of a selective isomerization mode. The nature of the species active in this selective isomerization will be discussed in the light of butene "adsorption–desorption" experiments carried out in a microbalance at the reaction temperature (623 K).

2. Experimental

The preparation of the HFER sample (Si/Al = 13.8, Na, K < 50 ppm) has been previously described [3,9,13]. The transformation of 1-butene was carried out in a flow reactor in the presence of nitrogen (N_2/1-butene molar ratio = 9) at 623 K under atmospheric pressure. The analysis of the effluents was carried out for time-on-stream long enough (> 80 s for the chosen weight of reactant introduced per hour and per weight of catalyst

(WHSV): 20 h^{-1}) to have a constant value of the GC peak area, hence a constant value of the reactant pressure in the reactor. Analysis of reaction products was performed on line by FID gas chromatography with a 50 m Chrompack PLOT Al_2O_3/Na_2SO_4 capillary column and a multiposition valco valve (ten positions).

The retention of products inside the pores of HFER was investigated at 623 K in a Sartorius 4433 electrobalance. After pretreatment of the HFER sample in vacuum (10^{-3} Pa) at 693 K for 3 h, *n*-butene was introduced at 16 kPa from a 5 ℓ vessel. With this large volume the decrease in the butene pressure was negligible. Desorption of the compounds which were reversibly retained was carried out at various times by treatment in vacuum (10^{-3} Pa) for 15 min.

3. Results and discussion

3.1. *Influence of time-on-stream (TOS) on n-butene transformation*

n-butene transformation was carried out at a WHSV value of 20 h^{-1}. At the shortest TOS value (such as the partial pressure of *n*-butene can be considered as constant in the reactor) the conversion is equal to 35% and the selectivity to isobutene equal to only 45%. The by-products are, in the order of significance (wt%): propene, pentenes, *n*-butane, octenes, heptenes, hexenes, propane, ethylene, isobutane. As previously discussed [3] the simultaneous direct formation of propene, pentenes and isobutene can be explained by a bimolecular mode of transformation of *n*-butene. The formation of all the other products except ethylene also involves bimolecular reactions: *n*-butane, propane and isobutane result from hydrogen transfer from coke precursors to the corresponding alkenes, octenes from dimerization of butenes, hexenes from dimerization of propene, heptenes from butene–propene reaction. Furthermore, ethylene most likely results from *n*-butene cracking.

A curious change in *n*-butene conversion as a function of TOS can be observed (figure 2): very rapid initial decrease followed by a quasi plateau then by a decrease. Moreover, the change in the yields with TOS depends very much on the product. For isobutene and for octenes there is a very rapid initial decrease followed by a slight increase then by a decrease (figures 3a and 3b) while for all the other products a continuous decrease in the yields is observed (figures 3c–3h).

The continuous decrease found for all the products except for isobutene and octenes is due to the formation of carbonaceous deposits. The carbonaceous deposits which are located inside the zeolite pores block progressively their access [13]. This decrease confirms that on the fresh samples all these reactions occur inside the zeolite pores. This is also the case for the formation of isobutene and for a large part of the octenes since there is a very rapid initial decrease. However, the blockage of the pores by carbonaceous deposits cannot explain the increase in the yield of isobutene and of octenes. As indicated in the introduction this increase in yield can no longer be explained by the suppression of rapid secondary transformations of isobutene in particular into the main by-products propene and pentenes. Indeed on the fresh FER sample these by-products are formed more slowly from isobutene than from *n*-butene [3]. Therefore the only possible explanation is that no desorbed or slowly desorbed products are active in the selective transformation of *n*-butene into isobutene.

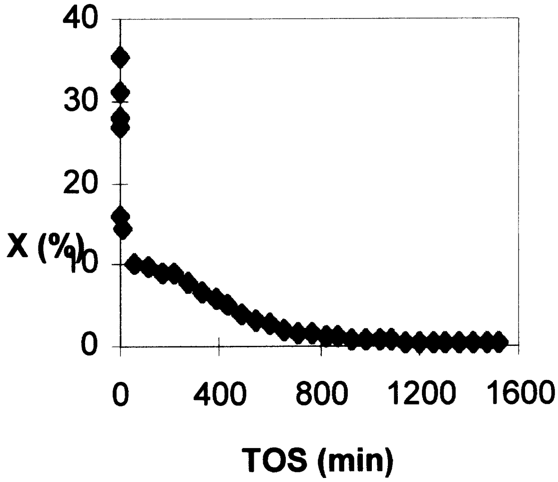

Figure 2. *n*-butene transformation over HFER at 623 K, WHSV = 20 h^{-1}. *n*-butene conversion (X (%)) versus time-on-stream (TOS (min)).

These products could be carbonaceous compounds which were found to be alkylaromatics [1–3]. However, in this case catalysis should occur only at the pore mouth. Indeed the transition state of butene isomerization catalyzed by benzylic carbocations is too bulky to be accommodated in the zeolite pores. The possibility of pore mouth catalysis seems however very limited at short time-on-stream as a large part of coke molecules are located inside pores which are not close to the outer surface of the crystallites. Indeed, from the comparison of the pore volume and of the volume occupied by coke molecules (calculated by supposing a density of carbonaceous compounds close to 1 g/cm^3) it can be estimated that 50% of the pore volume can be occupied by coke molecules. Moreover, at short time-on-stream the volume occupied by coke is close to the volume made inaccessible to nitrogen [13], which suggests a quasi homogeneous distribution of coke molecules in the crystallite pores. Hence, the mechanism involving benzylic carbocations as active sites seems unlikely at short time-on-stream values.

Non aromatic products, although not found during coke analysis can also be present in the zeolite pores during the reaction. Indeed it should be emphasized that the coked ferrierite samples undergo a treatment of 15 min

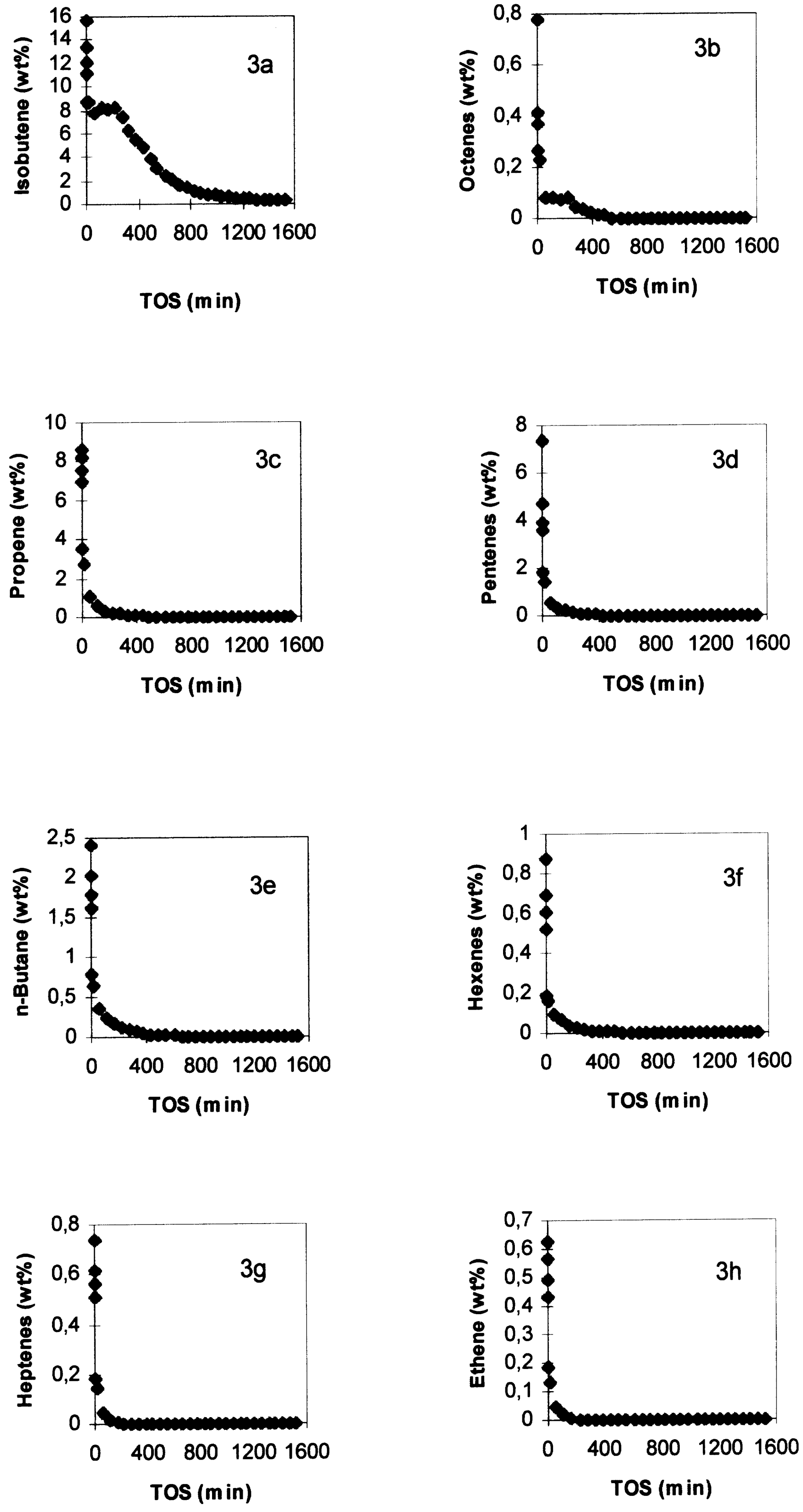

Figure 3. *n*-butene transformation over HFER at 623 K, WHSV = 20 h^{-1}. Yields in the main products (wt%) versus time-on-stream (TOS (min)).

under nitrogen flow before being removed from the reactor for coke analysis.

Therefore, the products which desorb slowly from the zeolite such as branched alkenes: isobutene [18], isopentenes or the products such as dimers which are blocked at the channel intersections [2] but can decompose into desorbable products are eliminated from the zeolite as a result of this nitrogen treatment.

3.2. Adsorption–desorption of n-butene

The adsorption of *n*-butene was carried out in a microbalance in order to determine the reversible and irreversible retention of products which occur during butene isomerization at 623 K. Figure 4 shows that there is a large increase in the weight of the HFER sample in the presence of *n*-butene, approximately 8 wt% after 8.5 h for a *n*-butene pressure of 16 kPa, whereas in the presence of the same pressure of *n*-butane the increase in weight is very small (< 0.3 wt%). Therefore this large increase is not due to the adsorption of *n*-butene but to the retention inside the pores of reaction products which desorb slowly (isobutene, isopentenes) or which decompose (dimers) into desorbable products or which cannot desorb (carbonaceous deposits). This retention is very rapid: 1.9 wt% after 1 min.

Whatever the contact time, hence the amount of products retained inside the zeolite pores, the treatment of the samples in vacuum (10^{-3} Pa) for 15 min causes a decrease in weight (figure 4) indicating the presence of dimers and of slowly desorbed isobutene and isopentene in the pores. Therefore the increase in isobutene yield observed at short time-on-stream values may be due to a catalytic role of these products which can easily be transformed into tertiary carbenium ions. The most probable active sites are *t*-butyl carbenium ions formed from isobutene more so than trimethylpentyl carbenium ions formed from dimers. Indeed the transition state of *n*-butene isomerization over trimethylpentyl carbenium ions is too bulky (its size is close to that of trimers) to be accommodated in the zeolite pores, which is not the case for the transition state of *n*-butene iomerization over *t*-butyl carbenium ions whose size is close to that of dimers. Figure 5 shows that the pseudomonomolecular isomerization of *n*-butene over *t*-butyl carbenium ions involves facile steps (B alkylation, A isomerization and A cracking). This isomerization is faster than the bimolecular isomerization of *n*-butene which involves more difficult steps (in particular C alkylation and B isomerization). This isomerization is very selective as the formation of propene and pentenes involves one supplementary A isomerization step and B cracking instead of a A cracking step for isobutene formation (figure 5).

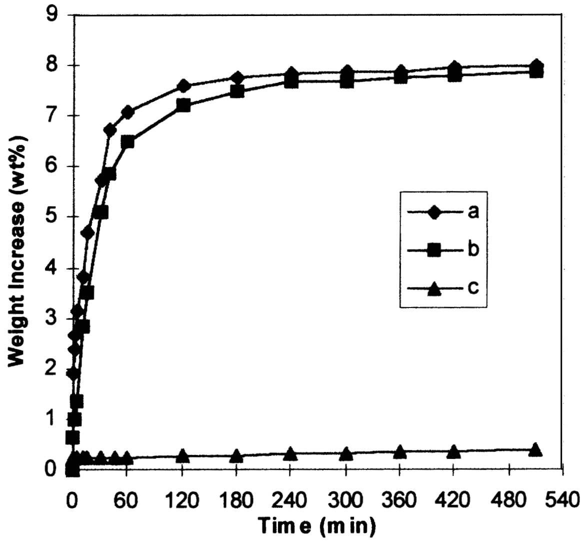

Figure 4. Total (a) and irreversible (b) increase in weight of a HFER sample at 623 K, $p_{n\text{-butene}} = 16$ kPa and total increase (c) for $p_{n\text{-butane}} = 16$ kPa versus time (t (min)).

4. Conclusions

Experiments at very short time-on-stream show that while, as expected from deactivation through coke deposits there is a rapid and continuous decrease in the yields in most of the products (including propene and pentenes), the change in isobutene yield is quite unexpected: rapid initial decrease followed by an increase then by a slow decrease. This confirms the development of a new isomerization mode much more selective than the dimerization–isomerization–cracking mechanism which is responsible for the simultaneous formation of isobutene, propene and pentenes over the fresh HFER sample. Reaction products retained in the zeolite pores and adsorbed on the protonic sites are the active species for this selective isomerization. At short time-on-stream

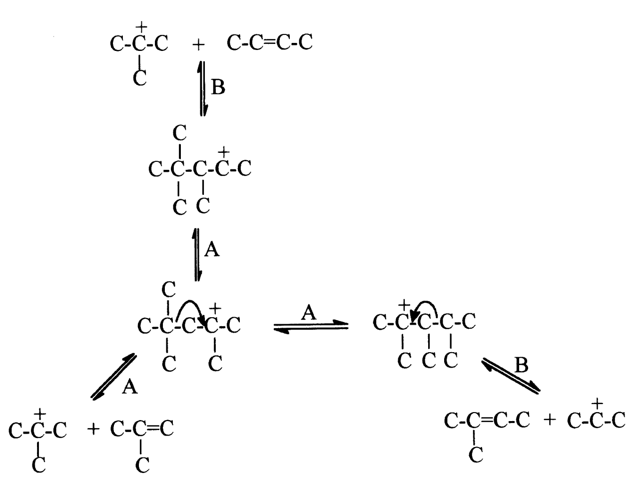

Figure 5. Mechanism of butene transformation over aged HFER samples. Alkylation and cracking steps: A involves two tertiary carbenium ions, B one tertiary and one secondary carbenium ion. Isomerization step A involves an alkyl shift.

(after 10 min reaction), *t*-butyl carbenium ions formed from isobutene are most likely the active species (autocatalytic reaction) while at long time-on-stream these may be benzylic carbocations sterically blocked near the outer surface of the crystallites (pore mouth catalysis) [13].

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