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Influence of the Atmosphere on Dodecen-1 Isomerization

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Abstract: In industrial adsorption processes carried out in liquid phase, charges are not always degassed before being injected and so they may contain dissolved oxygen that could induce undesired reactions responsible for premature adsorbent aging. To check this, we compared the reactivity of dodecen-1 in liquid phase at 150°C under air and under argon on two differently active solids, NaY and NaHY-6.7%. It shows that the oxidant atmosphere has a significant influence on the dodecen-1 reactivity. Oxygenated compounds are formed and irreversibly adsorbed on zeolite, leading to the filling of the porosity. This effect is more marked on the less active solid.

Keywords: Acidity, dodecen-1 isomerization, NaY, surface modifications, test reaction

INTRODUCTION

In adsorption or separation processes, the main objective is either to adsorb an impurity or to extract a valuable constituent from a mixture. So, in both cases but more particularly in the second one, the valuable molecules have to be adsorbed and desorbed easily and without any chemical transformation. Otherwise, process yield would decrease and

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the adsorbent would potentially undergo a premature aging. Indeed, reaction products could either irreversibly adsorb themselves on the adsorbent surface and/or be coke precursors and consequently be responsible for adsorbent deactivation through pore blockage and/or filling. Therefore, in such processes, adsorbents are selected regarding to their activity: they have to be as less reactive as possible like cationic zeolites (1–9). However, even this kind of solids is not completely inert depending on operating conditions. Especially, if feeds are not degassed, they will be in contact with oxygen of air that could favor parasite reactions (10,11). To try to evaluate the consequence of using such feeds, we have tested the reactivity of a highly active olefin, dodecen-1, at 150°C on two faujasite Y (NaY and NaHY-6.7% corresponding to NaY exchanged at 6.7% by protons) under argon and under air. In this last case, the solution will be exposed to oxygen as a non-degassed feed. In our previous study (12), it was shown that NaY zeolite possesses residual protonic sites mainly located at its external surface and/or in cavities directly connected to its surface on which dodecen-1 can be slowly isomerized under inert atmosphere (argon) at 150°C. These results will be reminded and compared in this paper, to the ones observed for the same system but submitted to an oxygenated atmosphere. It will be shown that in this last case, a large quantity of oxygenated molecules is formed and adsorbed irreversibly in the zeolite (phenomena highlighted by the analysis of adsorbents recovered after the test reaction). These compounds will induce a deactivation of the zeolite and this phenomenon will be as more visible as the zeolites are less active.

EXPERIMENTAL SECTION

Materials

The commercial NaY from *Zeolyst International* (*CBV100*) is used as received and after an ion exchange treatment. The bulk Si/Al ratio is close to 2.50 (determined by ^{29}Si NMR i.e. corresponding to a bulk elemental analysis), the BET surface area is equal to 838 m^2/g and the microporous volume to 0.349 cm^3/g calculated using the Dubinin-Radushkevich equation from nitrogen adsorption.

Ion exchange used to prepare NaHY zeolite consists of suspending 50 g of saturated NaY zeolite (water content: 25 wt.%) in 250 ml of a 3 g/l NH_4Cl solution (*VWR International- Prolabo*) in a flask on which a water cooler is adapted to prevent the liquid evaporation. The system is heated at 90°C through a heating jacket and stirred during approximately 4 h. Subsequently, the mixture is filtrated on a Büchner and washed with 1 l of distilled water at 90°C. The filtration cake is dried at 100°C in a muffle furnace during 12 h. The recovered solid is calcinated in a tubular oven under air to remove water but above all the NH_3 and thus to create of H^+: first, the solid is heated at 80°C during 1 h and then the temperature is increased up to 550°C and maintained at this temperature during 4 h in a flow of compressed air (30 l/h). The resulting sample is referenced NaHY-6.7%, 6.7% corresponding to the exchange level determined by ICP-AES (Induced Coupled Plasma – Absorption Emission Spectroscopy).

Test Reaction

3 g of previously activated Y faujasite (heating at 450°C for 2 h under N_2 flow (30 l/h)) are suspended in 75 g of dodecen-1 (purity: 95%, *Sigma Aldrich*) in a round-bottom flask, 3-neck angled (500 ml). On the top of the flask, a cooler (refrigeration fluid: water at 20°C) and a 2 ml syringe equipped with a needle are adapted. Depending on the selected atmosphere for dodecen-1 isomerization, the reaction mixture is either degassed boiling argon during few minutes and after then maintained under inert atmosphere or simply let in contact with air. The round-bottom flask is heated in a silicon bath kept at 150°C and the system is magnetically stirred at 500 rd/min (Heating and stirring plate – *Ret Control-Visc IKA Werke*) during around 24 h. 0.05 ml samples are removed at regular intervals of time and are analyzed by gas phase chromatography (Chromatograph: *Agilent 6890 Series GC System 7683 Series Injector*; Column: *PONA*, diameter: 200 µm, film thickness: 0.5 µm, length: 50 m).

The optimal conditions of the test reaction were determined and presented in a previous work (12). A blank test (test without zeolite) was made to confirm that no reaction occurs when the dodecen-1 is heated at 150°C, either under air or under argon.

Extraction of Carbonaceous Compounds after Test

After the test reaction, the filtered solids are submitted to a coke extraction procedure developed in *LACCO (UMR CNRS 6503)* laboratory in Poitiers-France (13). First, the solid is washed with dichloromethane (CH_2Cl_2) with a soxhlet in order to extract the weakly adsorbed carbonaceous compounds supposed to be mainly located at the external surface. After then, the recovered solid is completely dissolved in a concentrated hydrofluoric acid (HF) solution in order to extract the compounds irreversibly adsorbed on the zeolite. Carbon content is analyzed in both cases, i.e. before and after CH_2Cl_2 extraction, by total burning at

1020 °C under helium and oxygen with *Thermoquest NA2100* analyzer. Solutions of extractions are also analyzed by gas phase chromatography (Chromatograph: *GC Varian 3800 – injector 1079*, Column: *Factor Four VF5ms*, diameter: 0.25 µm, film thickness: 0.25 µm, length: 30 m) coupled to mass spectroscopy (*Analyzer triple quadruple Varian 1200 L* with an electric impact source of 70 eV) in order to identify the carbonaceous compounds.

RESULTS AND DISCUSSION

Study of NaY

To isomerize itself, dodecen-1 needs Brönsted acid sites as it has been demonstrated in a previous work (12). In their presence and under inert atmosphere, dodecen-1 is totally converted into successively all its double bond position isomers (dodecen-2 (cis and trans), dodecen-3 (cis and trans), dodecen-4 (cis and trans), dodecen-5 (cis and trans), and dodecen-6 (cis and trans)). These olefins (mainly the ones with the double bond in middle of the chain) can also react together (reaction catalyzed by acid sites) and form C_{24} dimers and C_{36} trimers. Depending on the number and strength of acid sites of the considered zeolite, the isomerization is initially more or less fast and the total conversion is reached after more or less time. From the tangent slope of the initial part of the dodecen-1 conversion curve, the initial reaction's rate, supposed to be directly related to the dodecen-1 reactivity towards the adsorbent, is estimated. It allows to evaluate the adsorbent activity. By choosing an arbitrary time of reaction, the conversion and the nature of the products formed also give information on the activity of the solid.

Figure 1 compares the conversion of dodecen-1 as a function of time obtained over NaY when reactions were carried out under either air or

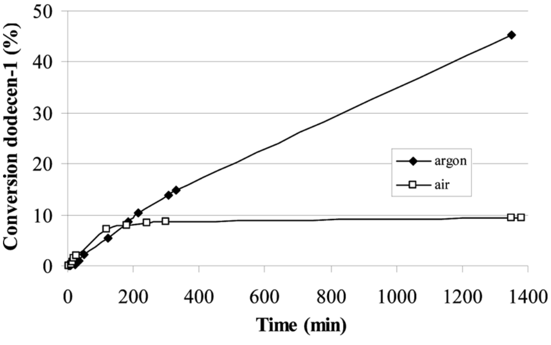


Figure 1. Reaction curves of dodecen-1 contacting NaY, under argon and air.

Table 1. Initial transformation rate and conversion of dodecen-1 under NaY and NaHY-6.7%

		NaY	NaHY-6.7%
Initial transformation rate $\times 10^{-5}$ (mol/min/g_{zeo})	Argon	7.2	590
	Air	6.8	433
Conversion (24 h) (%)	Argon	47	100
	Air	8	77
Maximal conversion (%)	Argon	100 (after 7 days)	100 (after 180 min)
	Air	8 (after 200 min)	77 (after180 min)

argon. The initial activity of dodecene-1, the conversion obtained after 24 h reaction and the maximal conversion are reported in Table 1. From both curves and calculations, it appears that depending on the atmosphere, the dodecen-1 behavior changes. Its initial reactivity seems to remain almost the same: there is only a small slowing down around 6% from the test under argon to the one under air; this is not really surprising as the reaction is conducted on the same solid that is to say in the presence of the same number of acid sites with the same strength. But rapidly (from nearly 100 min) the two curves diverge (Fig. 1). Instead of reaching, as under argon, the 100% maximal conversion value predicted by thermodynamical calculations, the conversion of dodecen-1 obtained when tested under air reaches a steady state at around 8%. Moreover, dodecen-1 isomerizes itself under air only into dodecen-2 (cis and trans) and dodecene-3 (cis and trans). Other potential isomers that appeared successively during the reaction under argon are never formed. In other words, the extent of the dodecen-1 isomerization is limited. The active sites seem to be progressively deactivated. This phenomenon could be explained by an irreversible adsorption of molecules. However, as it is not observed when the reaction occurs under inert atmosphere, we have to suppose that under air, dodecen-1 and/or its isomers undergo chemical transformations leading to products possessing a great affinity to the zeolite surface and more specifically to its acid sites.

To better understand the differences of the dodecen-1 behavior, solids recovered after reaction under air and under argon were treated successively by CH_2Cl_2 and HF in order to extract carbonaceous compounds adsorbed respectively reversibly and irreversibly on zeolite (Table 2). Carbon content analyses of NaY after test show that NaY zeolite contacted to dodecen-1 under air adsorbs less carbonaceous compounds (almost two times less: 14% vs. 30%) compared to zeolite

Table 2. Carbon content of zeolites after dodecen-1 test reaction

Zeolite	Atm.	$\%C_{Total}$ in the zeolite after test	$\%C_{Total}$ dissolved with CH_2Cl_2	$\%C_{Total}$ not dissolved with CH_2Cl_2
NaY	Argon	30	28.5	1.5
	Air	14	3	11
NaHY-6.7%	Argon	43	27	16
	Air	33	20	13

contacted to dodecen-1 under argon. However, in the case of reaction under air, the main part (about 80 against 5% under argon) of adsorbed carbonaceous compounds is strongly adsorbed in the zeolite pores and a HF treatment is necessary to recover them. If we suppose that these compounds are adsorbed on active sites, this explains the observed limited conversion of dodecen-1: strongly adsorbed molecules permanently block the active sites used by dodecen-1 to isomerize itself. Thanks to the analysis by gas phase chromatography coupled with mass spectrometry of the HF and CH_2Cl_2 extraction solutions, such a difference in compounds adsorption strength on NaY depending on the atmosphere of the dodecen-1 isomerization can be explained: the carbonaceous compounds are chemically different (Fig. 2). On chromatograms of extraction solutions for NaY maintained under argon (Fig. 2-I-a and II-a), detected peaks are principally those of dodecen-1, its isomers, and C_{24} dimers. Traces of oxygenated molecules are also present: a small amount of air is probably introduced at the time of the addition of zeolite in the flask. On the contrary, for NaY tested under air (Fig. 2-I-b and II-b), peaks correspond predominantly to C_{12} oxygenated forms of dodecen-1 (ketones, alcohols, aldehydes, carboxylic acids, esters, etc.) and to oxygenated and nonoxygenated dodecen-1 C_{24} dimers (C_{24} compounds). Oxygen atoms of these oxygenated molecules probably establish a specific interaction with either the compensating cations (acting as a Lewis acid site) or the protons (acting as Brönsted acid site) and their hydrogen in β-position is likely to be adsorbed on the next basic framework oxygen (Scheme 1-a (14) and Scheme 1-b (15,16)). This second interaction will be particularly strong in the case of the carbonyl compound because of the known acidity of the hydrogen in β-position. And for all kinds of oxygenated molecules, the strength of adsorption will increase with the basicity of the framework oxygen (oxygen more basic in cationic zeolites than in protonic one). This type of irreversible adsorption of oxygenated molecules would explain their higher difficulty to be desorbed compared to the purely carbonaceous dodecen-1 and dodecen-1 isomers and thus the observed deactivation.

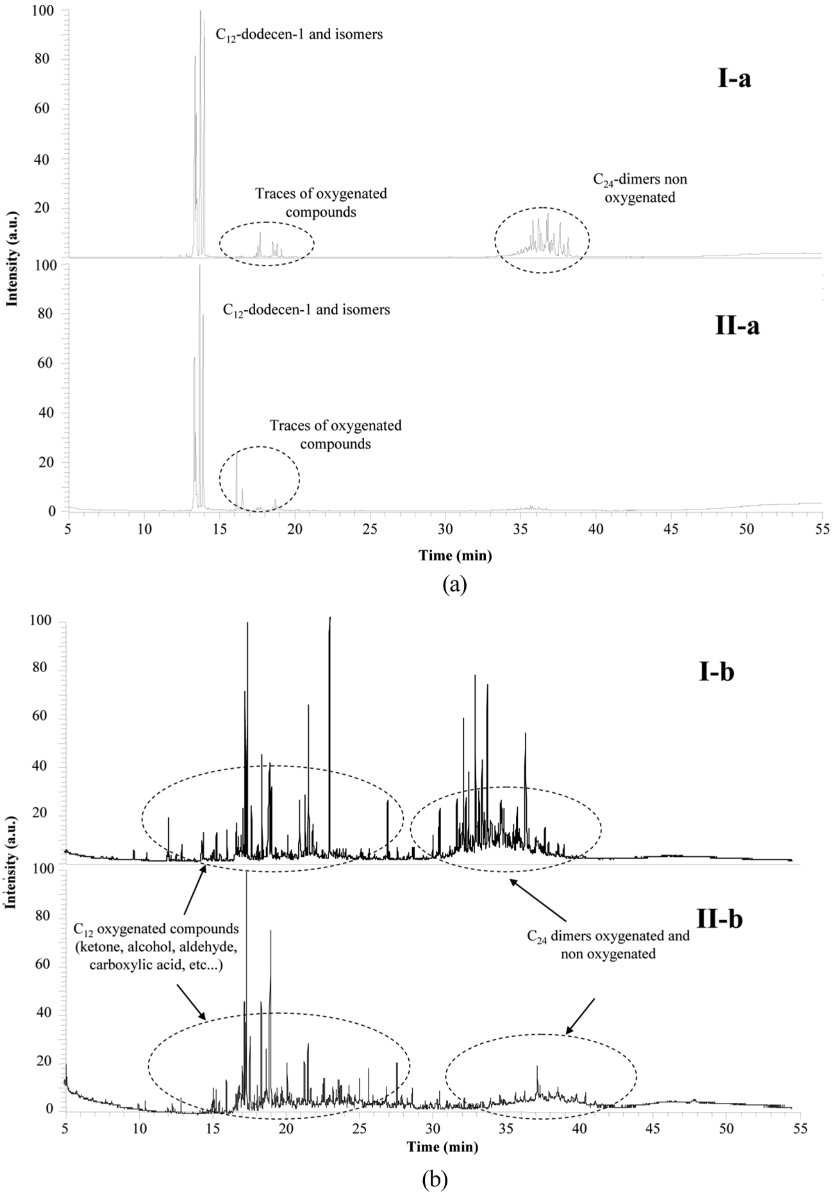
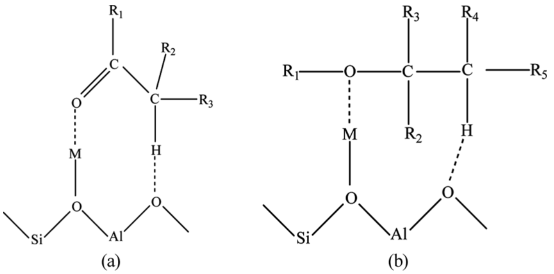


Figure 2. Chromatographic analysis of the carbonaceous compounds extracted by CH_2Cl_2 (I) and HF(II) from NaY after 24 h dodecen-1 isomerization under argon a) and under air b).



Scheme 1. Adsorption of oxygenated compounds with a) a carbonyl group and b) a hydroxyl group, over a cationic or acid site M.

The formation of oxygenated molecules is necessarily a consequence of the simultaneous presence of olefins (in the present case dodecen-1, isomers and dimers) NaY and oxygen from air at 150°C. In the literature, some authors propose that cationic zeolites can act as basic catalysts for oxidation reactions (14–17) by allowing the formation of a free-radical-oxygen species that will react with the double bond of an alkene. The resulting peroxide intermediate can then evolve into either an epoxide by reacting with a second alkene or into aldehyde by simple decomposition. The aldehydes can then transform themselves in other oxygenated compounds as for example carboxylic acids. We suppose that these kinds of transformations could occur in our case, the activation of the oxygen from air being assumed by Na^+ cation. As cations are mainly located in the zeolite pores and not at its external surface, we suppose that oxidation reactions begin in the porosity of NaY. Indeed, there, the oxygen has a more pronounced basic character so peroxide intermediates will be more stabilized. The resulting oxygenated compounds would probably adsorb themselves on Na^+ cations and the porosity of the zeolite will be progressively filled in. But as NaY zeolite does not have Brönsted active sites in its porosity, this will not have a consequence on the residual activity of the NaY towards dodecen-1 isomerization as it is confirmed by experimental results that show quite similar initial reaction rate and behavior during the first 100 min whatever the atmosphere. When all the inside Na^+ sites are deactivated, some more oxidation reactions will occur at the external surface ever on Na^+ cations. But the so produced oxygenated molecules can be adsorbed either on Na^+ cations or on Bronstëd sites. This last phenomenon will lead to the deactivation of the NaY towards dodecen-1 isomerization that is observed after around 100 min of reaction. Such a deactivation would be an advantage if it was not accompanied by a filling of the zeolite porosity that makes the zeolite ineffective adsorbent.

Study of NaHY

In order to evaluate the influence of the atmosphere on the potential degradation of feeds and/or adsorbent depending on the activity of the solid, we tested a NaY partially exchanged by protons, NaHY-6.7%.

Conversion curves of dodecen-1 obtained on this zeolite under air and under argon have the same profile (Fig. 3). As reported in Table 1, from the reaction carried out under argon to that carried out under air, the initial reaction rate slows down by nearly 27%: under air some active sites are rapidly deactivated. This deactivation is confirmed by the limitation of the conversion at nearly 77%. So, deactivation seems to take place for NaHY-6.7% as for NaY but in a lower extent.

Extractions with successively CH_2Cl_2 and HF indicate that the quantity of carbonaceous compounds adsorbed on the zeolite is lower after dodecen-1 reaction under air than under argon, as in the case of NaY (Table 2). However, the proportion of reversibly and irreversibly adsorbed molecules seems to remain quite the same whatever the atmosphere under where the reaction is carried out. But, analysis of extraction solutions shows that under air and under argon, the nature of these molecules is different (Fig. 4). After reaction under argon, dodecen-1 and its C_{12} isomers, a large amount of C_{24} dimers and some C_{36} trimers were detected (Fig. 4-I-a and II-a). Traces of oxygenated compounds are also present. Under air, dodecen-1 seems to be transformed almost exclusively in C_{24} dimers (Fig. 4-I-b and II-b). Dodecen-1, C_{12} isomers, and oxygenated compounds are only detected as traces. This confirms that depending on the initial activity of the adsorbent (quantity of protonic sites) the sensitivity towards the atmosphere is not the same. This absence of formation of oxygenated compounds on NaY partially exchanged by

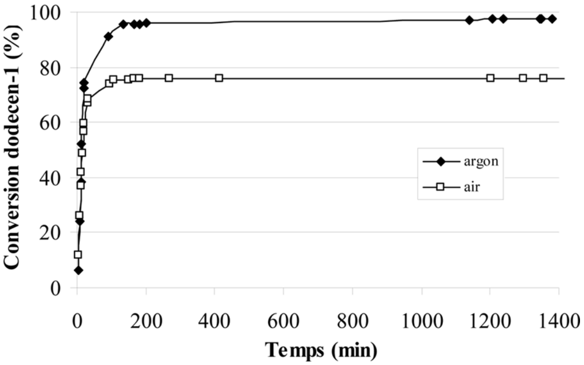
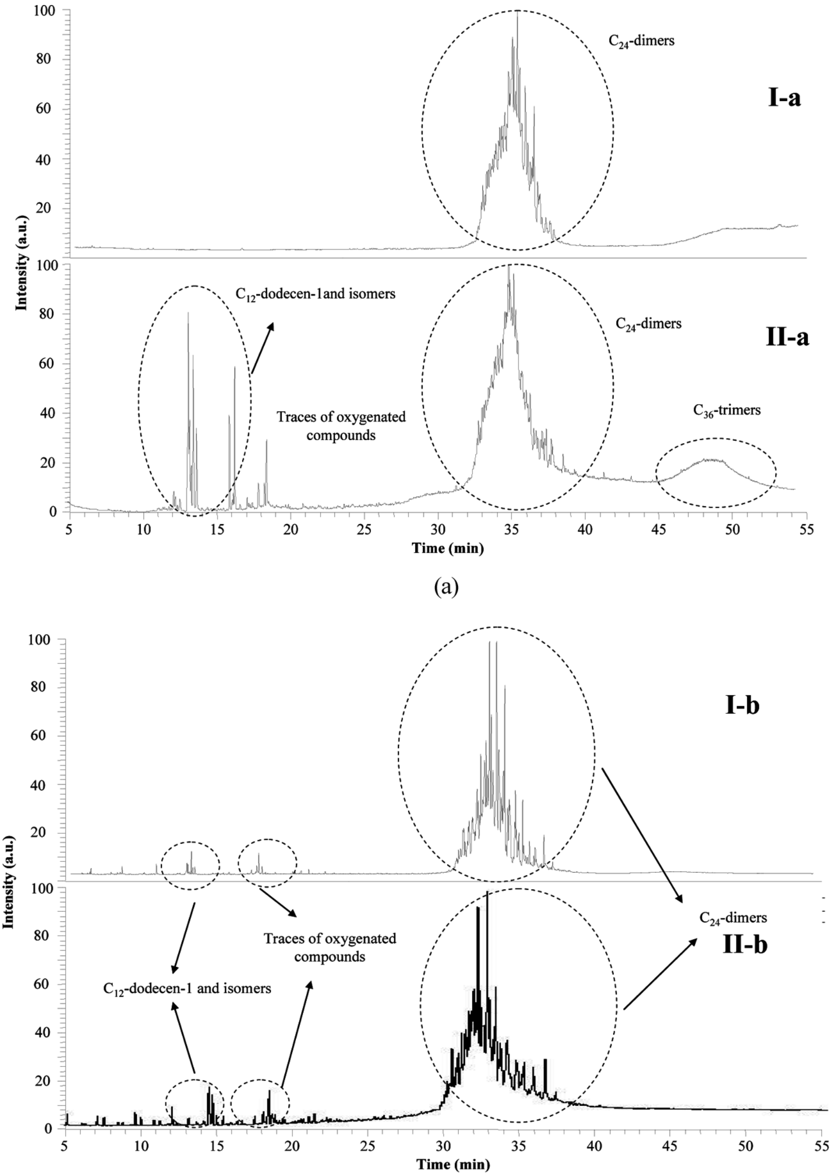


Figure 3. Reaction curves dodecen-1 contacting NaHY-6.7%, under argon and air.



(a)

(b)

Figure 4. Chromatographic analysis of the carbonaceous compounds extracted by CH_2Cl_2 (I) and HF(II) from NaHY-6.7% after 24 h dodecen-1 isomerization under argon a) and under air b).

protons submitted to air could be explained either by a too low basicity of the framework oxygen to activate oxygen of air (17) or by a too fast isomerization and/or dimerization of dodecen-1 so that oxidation do not have the time to occur. This second hypothesis seems to us more probable because of the observed weak decrease of the NaHY-6.7% activity towards dodecen-1 isomerization. Some oxidation of dodecen-1 or of its isomers occurs in a small extent in the porosity and the resulting oxygenated compounds adsorb probably themselves on some sites leading to the observed permanently decrease of NaHY-6.7% activity. The blocked sites are probably the strongest protonic ones as no more trimers are formed when isomerization of dodecen-1 proceeds under air.

CONCLUSION

This study shows that in the presence of oxygen (free oxygen or dissolved in the feed), the stability of the solution containing reactive molecules as it could be the case in some industrial feeds can not be guaranteed anymore. Indeed, molecules as long chain olefins may be oxidized perhaps thanks to the presence of Na^+ that would activate oxygen from air and to the basicity of the oxygen of zeolite framework that would stabilize peroxide intermediates. Indeed after contact with NaY at 150°C, we found oxygenated compounds irreversibly adsorbed on NaY that was not the case when the test was carried out under argon. In their new state, oxygenated olefins strongly interact with cationic and/or acid sites that is reflected by a slowing down of the initial reaction rate, a lowering of the conversion (the 100% of conversion predicted by thermodynamic is no more reached whatever the time of reaction) and a decrease of the products number (only dodecen-2 and dodecen-3 are detected). This transformation of the reactant has to be avoided because even if the deactivation of active sites is quite favorable, the second consequence of an irreversible adsorption of molecules at the adsorbent's surface induce a disastrous blockage and/or a filling of the useful porosity of the solid compromising its performance.

The comparison of the behaviors of NaY and NaHY-6.7% indicates that for more active solids, operating conditions have less influence. Indeed, even if some sites are immediately deactivated under air, a high conversion of dodecen-1 is still reached: the reaction rates of dodecen-1 isomerization and dimerization should be higher than the rate of oxidation. But if the process concerns adsorption, both rates of oxidation and adsorption will probably be very close to each other and consequently reactant transformation will be harmful.

Thus in any case, it would be preferable to avoid the presence of oxygen in industrial adsorption processes above all in presence of cationic adsorbents. Therefore a preconditioning of the feed like a degassing is strongly recommended.

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