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HYDRATION REACTION OF ALKYNES CATALYZED BY ZEOLITES

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The catalytic hydration reaction of alkynes over modified Y-faujasite zeolites is reported. Protonic, Ce^{3+}, and Ca^{2+} exchanged Y zeolites are shown to be efficient catalysts for this reaction; the case of the Hg^{2+} exchanged zeolite is also discussed.

1. Introduction

The use of zeolites as selective catalysts in organic syntheses is a field of growing importance. Zeolites are salts of solid silicoaluminic acids characterized by a strictly regular structure of their crystalline lattice [1], and by their high acidity and shape selectivity [2]. Attention to the broad potential of zeolites in organic reactions was first drawn in the sixties by Venuto [3,4], and various applications of their catalytic properties have been recently reviewed [5].

In recent papers, we have reported results concerning the acylation of aromatic compounds by carboxylic acids over Y-type zeolites [6,7]. It was especially found that a Y-faujasite zeolite exchanged with Ce^{3+} cation was a very efficient and selective catalyst for this reaction.

Our current interest in the development of heterogeneous catalysis led us to consider the use of such zeolites as catalysts in the hydration reaction of alkynes. This reaction is generally carried out in diluted acidic conditions with mercuric ion salts (often the sulfate) as catalysts [8,9]. Nevertheless, the loss of the catalyst during the reaction and environmental problems due to the use of mercury make this reaction a not so convenient method as it should be for the preparation of carbonyl compounds.

The present note is concerned with the catalytic hydration of some alkynes over Y-faujasite type zeolites, protonic and Ce, Cd and Hg-exchanged ones respectively.

2. Experimental

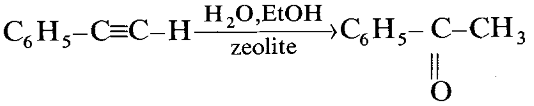
The reactions were carried out in a 0.1 litre stirred autoclave operating in a batch mode and equipped with a system for sampling of liquid during the reaction. The autoclave was charged with the freshly calcined zeolite (calcination overnight at 500 ° C in air, prior to use) (500 mg) and the alkyne (1 g) together with 50 ml ethanol and 1 ml distilled water, and then heated to 200 ° C. As soon as the temperature of 200 ° C is reached, a first sample is made, which is considered sample $t = 0$.

The cation-exchanged zeolites were prepared by conventional ion exchange as already reported in [6]. The level of ion exchange was 70% for Ce^{3+} and Cd^{2+}, and 85% for HY which derived from thermal decomposition of NH_4Y.

3. Results and discussion

The hydration reactions of phenylacetylene, 1-phenyl-propyne, 1-hexyne and 2-hexyne were respectively studied over proton, Ce, Cd and Hg exchanged Y zeolites.

For example:



$$C_6H_5{-}C{\equiv}C{-}H \xrightarrow[\text{zeolite}]{H_2O,EtOH} C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

a. Table 1 gives the percent of ketones obtained after one hour reaction using the first three zeolites (H, Ce, Cd) as catalysts.

The first conclusion which can be drawn from these results is that zeolites are able to catalyse hydration reactions of alkynes, confirming their acidic properties.

Protonic Y zeolite, derived from thermal deamination of NH_4Y, is the most efficient in this respect.

The observed sequence of activity for hydration of alkynes at 200 ° C is the following: **HY > CeY > CdY**.

Table 1
Hydration of alkynes over Y-zeolites

zeolite	ketones		
	$C_6H_5{-}CO{-}CH_3$ from $C_6H_5{-}C{\equiv}C{-}H$	$C_6H_5{-}CO{-}CH_2{-}CH_3$ from $C_6H_5{-}C{\equiv}C{-}CH_3$	$CH_3{-}(CH_2)_3{-}CO{-}CH_3$ from $CH_3{-}(CH_2)_3{-}C{\equiv}C{-}H$
HY	97	68	10
CeY	97	52	6
CdY	90	29	2

Table 2
Hydration of alkynes over a Hg-Y zeolite

after	% ketone		
from	$C_6H_5-C{\equiv}CH$	1-hexyne	2-hexyne
$t = 0$	77	60	30
$t = 1$ h	99	70	30
$t = 2$ h	99	70	30

Acetophene is, easily and quantitatively produced from the hydration of phenylacetylene over these catalysts. This result is in agreement with the special high reactivity of phenylacetylene towards hydration already found in homogeneous catalysis. [10–12].

In the case of 1-phenyl-propyne, these zeolites lead to a good selectivity: only propiophenone is produced; no traces of methyl (benzyl) ketone are detected after total conversion of the alkyne.

The catalytic activity of these zeolites is lower towards hydration of aliphatic alkynes. For example, we observed only 10% of 2-hexanone from 1-hexyne over HY after one hour reaction, and no detectable amount of ketonic compound in the same conditions from 2-hexyne.

b. The behaviour of the Y zeolite exchanged with Hg^{2+} cation is somewhat different (table 2).

Hydration reaction is faster over such a zeolite: for example, acetophenone is already obtained in a substantial amount (77%) at $t = 0$. Same results are observed concerning aliphatic alkynes. 1-hexyne leads to the formation of 60% of 2-hexanone at $t = 0$ and 70% after 1 hour reaction, but this percentage remains constant with time. With 2-hexyne, a conversion of 30% of the alkyne is observed at $t = 0$, giving a mixture of 2- and 3-hexanones, but this percentage does not increase with time. Such results can be explained by a loss of activity of the zeolite.

Microanalysis of samples of the Hg-exchanged zeolite before and after the reaction shows that mercury is totally driven out of the zeolite after the reaction, which is not the case for the preceding zeolites (table 3).

The high amount of ketone obtained in the case of Hg-exchanged zeolite compared to the others implies that mercuric ions are largely involved in the

Table 3
M content in samples of M-exchanged Y zeolites used in hydration reactions

Hydration reaction of	Hg%		Ce%		Cd%	
	before	after	before	after	before	after
$C_6H_5-C{\equiv}C-H$	30.0	0.2	9.6	9.5	13.0	12.8
$CH_3(CH_2)_3-C{\equiv}C-H$	30.0	0.5	9.6	9.4	13.0	11.5

reaction, as it was shown in homogeneous catalysis [10,11]. The formation of a complex (mercurinium ion) with the π-electrons of the unsaturated system is assumed to explain the role of mercury [13]. Nevertheless, a very fast loss of activity of the catalyst is then observed, which is explained by the removal of mercury from the zeolite. Such a behaviour of Hg-exchanged zeolites was already reported; it has effectively been found that reducible metals could be easily removed from zeolites by hydrogen treatment [14].

The initial increasing of the activity of a Y zeolite exchanged with Hg^{2+} cation is thus lowered by the fast loss of mercury from the zeolite, so that it cannot be considered as a catalyst for hydration of alkynes.

4. Conclusion

Due to their acidic properties, protonic, Ce^{3+} and Cd^{2+} exchanged Y zeolite constitute efficient catalysts in the hydration reactions of alkynes. It is thus possible to substitute such solid catalysts for mercuric salts, so that environmental problems due to the pollution by mercury are excluded.

Studies are actually in progress in order to explain the catalytic activity of the zeolites in the hydration reaction of alkynes, depending on their structure, acidity and nature of exchanged cations.

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