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The oxidation of alkenes in the presence of some transition metal elements exchanged with zeolites

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Abstract

The oxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP) in the presence of exchanged zeolite NaY (NaA and HS in some cases) with transition metal elements Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) in refluxing dichloromethane has been investigated. The results showed that the Mn–Na–Zeolite had the highest reactivity and selectivity with the formation of di(2-cyclohexenyl) ether as the main product. The optimum conditions were applied to cyclopentene and 1,1-diphenylethylene which afforded di(2-cyclopentenyl) ether and benzophenone, respectively. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The processes of catalytic oxidations have been intensively investigated over the past three decades. The reasons for this are many but specifically because of the technological importance of the conversion of raw materials and petrochemicals like alkanes, alkenes and aromatics into a variety of bulk industrial chemicals [1–6]. In this way, chemists have used different kinds of metal salts and oxides in the form of homogeneous catalysts [7–11], or supported metals [12], supported metal ions [13–15] and supported oxo metal catalysts [16,17] as heterogeneous systems. Supported metal ions include zeolites which are significantly important due to their ion exchange properties, crystallinity, thermal stability and cage structure which change the reactivities and especially selectivities towards a desirable product [18–24]. Transition metal elements can be introduced in different states and coordinations [25–29]. These materials catalyze the decomposition of organic oxidants like *t*-butylhydroperoxide. When this decomposition is performed in the presence of olefins, oxidation of double bond or allylic position occurs [30–34]. Since our main endeavors have been in both zeolite synthesis and its application in organic chemistry [35–37], we have

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found that zeolites NaY, NaA and HS [38–40] exchanged with transition metal elements of Cr, Mn, Fe, Co, Ni and Cu catalyze the oxidation of olefins.

2. Experimental

2.1. Preparation of zeolite catalyst; general procedure

100 ml of 0.1 M solution of metal salt ($CrCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 4H_2O$, $FeCl_2 \cdot H_2O$, $CuCl_2 \cdot 2H_2O$, $MnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$) was added to 1 g of zeolite in a 250 ml flask. The mixture was stirred for 24 h and then filtered. The solid was washed with enough water until the filtrate became colorless, and then dried at room temperature.

2.2. Oxidation of alkenes: general procedure

Zeolite catalysts were first vacuum dried at 120°C and then kept under the stream of dry nitrogen for one hour. A mixture of 2.65 mmol alkene, 3.71 mmol oxidant (80% in di-*tert*-butyl peroxide) and 0.6 g catalyst in 25 ml of solvent was refluxed for 8 h. After filtration and washing with solvent, the filtrate was concentrated on a rotary evaporator and then subjected to GC and GC-MS analysis using a Philips PU-4400 chromatograph (1.5 m 3% OV-17 column), Varian 3400 chromatograph (25 m DB-5 column) coupled with a QP Finnigan mass INCOF 50, 70 eV and Shimadzu chromatograph 14A–15A (2.5 m 3% OV-17 column) coupled with a QP-1000 Shimadzu mass, 70 eV.

3. Results

3.1. M–NaY catalytic oxidation of cyclohexene and cyclopentene

The oxidation of cyclohexene with TBHP and M–NaY in refluxing dichloromethane for 8

Table 1
Oxidation of cyclohexene with TBHP catalyzed by M–NaY zeolites

Catalyst	Conversion (%)	Yield (%)			
		Epoxide	Peroxide[a]	Ketone[b]	Ether[c]
NaY	27.7	10.09	8.81	29.0	52.72
Cr–NaY	36.36	12.66	7.03	44.95	28.27
Mn–NaY	57.76	1.37	—	—	98.30
Fe(III)–NaY	28.93	5.47	5.81	37.78	50.34
Co–NaY	41.67	17.08	2.22	41.74	36.11
Ni–NaY	32.46	1.17	2.27	16.28	78.81
Cu–NaY	45.70	0.72	5.31	23.34	71.20

[a] 1-(tert-butylperoxy)-2-cyclohexene. [b] 2-cyclohexenone. [c] di-(2-cyclohexenyl)ether.

h resulted in the formation of several products as shown in Table 1. When the oxidation of cyclopentene was carried out under the effect of Mn–NaY, 31% of olefin was converted with the selectivity of 98% towards the formation of di(2-cyclopentenyl) ether.

3.2. M–NaA and M–HS catalytic oxidation of cyclohexene with TBHP

The results of the oxidation of cyclohexene under these conditions are summarized in Table 2. In all cases, the reaction has been run in refluxing dichloromethane for 8 h.

3.3. The effect of changes in time and the amount of a catalyst

3.3.1. The effect of time
The effect of time on cyclohexene oxidation with TBHP under the influence of Cr–NaY is shown in Table 3. The selection of Cr–NaY

Table 2
Oxidation of cyclohexene with TBHP catalyzed by M–NaA and M–HS

Catalyst	Conversion (%)	Yield (%)			
		Epoxide	Peroxide	Ketone	Ether
NaA	28.30	12.97	10.17	2.63	74.23
Mn–NaA	33.45	1.38	20.00	2.29	76.34
HS	22.90	16.77	13.12	17.16	53.25
Mn–HS	55.90	1.79	—	5.71	92.50

Table 3
Effect of time on the oxidation of cyclohexene with TBHP in the presence of Cr–NaY

Catalyst	Time (h)	Conversion (%)	Yield (%)			
			Epoxide	Peroxide	Ketone	Ether
Cr–NaY	4	13.34	8.60	9.92	58.88	22.60
Cr–NaY	8	36.36	12.66	7.03	45.00	28.77
Cr–NaY	12	48.74	10.55	6.49	29.25	47.07

Table 4
Effect of Catalyst amount on the oxidation of cyclohexe with TBHP in the presence of NaY and Cr–NaY

Catalyst	Catalyst weight (g)	Conversion (%)	Yield (%)			
			epoxide	peroxide	ketone	ether
NaY	0.5	27.70	10.09	8.81	29.00	52.72
NaY	1	32.96	2.33	4.53	32.88	60.26
Cr–NaY	0.5	36.36	12.66	7.03	44.95	28.77
Cr–NaY	1	40.95	1.89	3.41	6.93	87.77

catalyst for this study has been based on the fact that the least selectivity was observed with this catalyst and the effect of reaction time on product distribution might prove interesting.

3.3.2. The effect of the amount of the catalyst

The effect of the amount of the catalyst on the results of the oxidation of cyclohexene with TBHP under the catalytic effect of NaY and Cr–NaY is shown in Table 4.

3.4. M–NaY catalytic oxidation of 1,1-diphenyl-ethylene with TBHP

Oxidation of 1,1-diphenylethylene with TBHP in the presence of NaY, Cr–NaY and Mn–NaY resulted in the formation of benzo-

phenone as the main product as shown in Table 5. The solvent was dichloromethane and the reaction mixture was refluxed for 8 h.
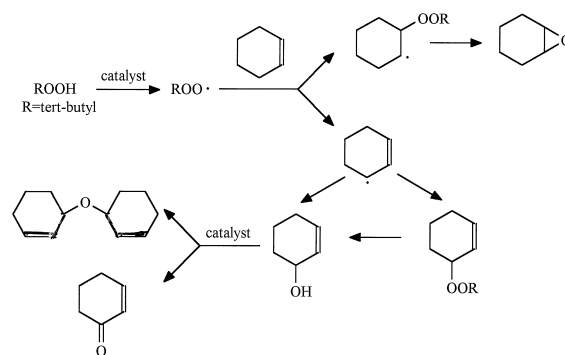
4. Discussion

The use of zeolite catalyst for oxygenation of organic substrates with molecular oxygen or peroxidic oxygen sources are of significant importance. These materials without any previous metal doping or exchanged with different kind of metals and transition metals can catalyze the oxygen transfer from an oxygenated source to olefins and oxidize these substances on double bond site or allylic position or both or bring about a destructive oxidation [41–44]. Since

Table 5
Oxidation of 1,1-diphenylethylene with TBHP catalyzed by M–NaY zeolites

Catalyst	Conversion (%)	Yield (%)	
		benzophenone	2,2-diphenylacetaldehyde
NaY	18.00	96.42	2.83
Cr–NaY	41.00	90.10	9.09
Mn–NaY	60.00	98.86	1.14

exchanging the sodium ion with transition metal cations certainly changes the acidic properties and electronic interactions of metal doped zeolite with substrate and alkyl peroxide oxidant, it was not surprising to observe different results on either reactivity of oxidation of cyclohexene and selectivities towards the distribution of different products. From the results indicated in Table 1, it is evident that the transition metals exchanged with zeolite Y have a significant effect on reactivity especially with Mn(II) which enhances the conversion percentage from 27.7 to 57.36%. As shown in Fig. 1, this catalyst has also the most selectivity on the formation of ether product. In all cases, the percentage yields of epoxide and peroxide products are not significant while the main products are ketone and ether. It is also clear that with the exception of Ni–NaY, the sum of ketone and ether yields is approximately constant and decreasing the former would cause increasing the latter. Therefore, one can deduce that these two products have arisen from a common intermediate. We believe that 2-cyclohexe-1-ol has been responsible for the formation of the ketone and ether and allow to suggest the following mechanism (Scheme 1).

Scheme 1.

Fig. 1. Effect of M–NaY catalyst on the percentage yield of ether.

The first step has often been proposed to be an interaction between the metal and TBHP already present in the mixture [17]. This interaction will lead to homolysis of peroxide reagent to produce *tert*-butylperoxy radical. This species could then promote a reaction leading to the oxidation of olefin. Such a reaction pathway could be responsible, at least in part, for the production of epoxide since another plausible route to this product might arise from the concerted electrophilic addition of alkene to TBHP. The formation of epoxide through this mechanism seems likely since such route has gained several experimental supports [45,46].

The main path of the reaction is oxidation of the allylic position. The reason is clear and can be attributed to the increased acidity of zeolite due to the hydrolysis of hydrated ion, an effect which has been observed by us [37] and others. Leibovich et al. have reported that the exchange of some monovalent ions of silver in zeolite NaX with divalent calcium ions decreases the oxidation yield of cyclohexene to the corresponding epoxide and facilitate the allylic site oxidation [30]. These authors have pointed out that increasing acidity of zeolite has been responsible for this change. As mentioned elsewhere, ketone and ether products should have arisen from the oxidation and etherification of 2-cyclohexene-1-ol. While Mn–NaY catalyst shows no tendency to further oxidation of alcohol and ether is formed under the reaction conditions, Cr–NaY oxidize the alcohol mostly to
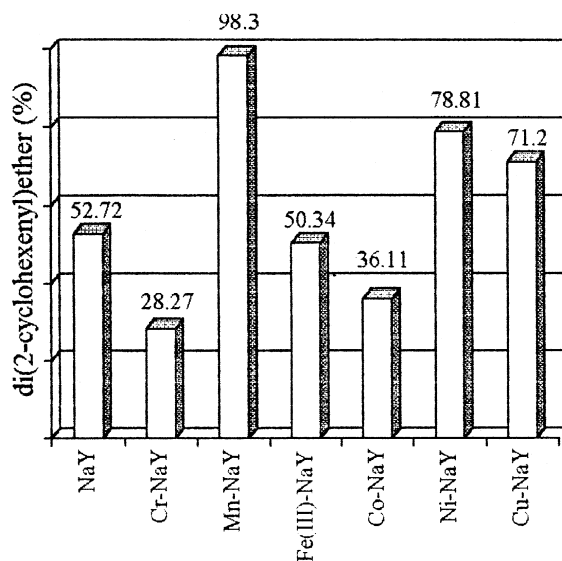
the corresponding ketone. Such behavior has been observed in the case of Mn (salen) complex encapsulated in zeolite Y cavities as an oxidation catalyst. When the oxidation has been performed on cyclohexene using iodosylbenzene, cyclohexene oxide and 2-cyclohexene-1-ol were identified as the main products. The authors believe that part of the products in zeolite system could arise from the Mn–NaY formed by degradation of Mn(salen) complexes since uncomplexed Mn–NaY also catalyzes the oxidation of cyclohexene, forming mainly 2-cyclohexene-1-ol [28]. On the other hand, there are many different reports on the oxidation of allylic and benzylic alcohols to the corresponding ketones in the presence of chromium (III) complexes [3].

The formation of ether as the main product under the effect of most catalysts has certainly arisen from the etherification of 2-cyclohexen-1-ol. Similar observations have been reported recently on the synthesis of several ethers including the di-(2-cyclohexenyl) ether via zinc chloride mediated etherification of 2-cyclohexene-1-ol [47]. Since the exchanged transition metal ions increase the acidity strength of zeolite, the formation of ether product is not surprising under these conditions.

The two catalysts Fe–NaY and Co–NaY are also effective on the further oxidation of 2-cyclohexene-1-ol to cyclohexenone. Oxidation of allylic methylene groups under Fe(III)-TBHP and Fe(III)-TBHP-PA(picolonic acid) have been reported by Barton and Wang [48]. Moreover, oxidation of cyclohexene with oxygen in the presence of a Co-zeolite has produced a mixture of epoxy and cyclohexenyl hydroperoxide [49]. Although the epoxy is not the major product under the effect of Co–NaY in our study (17.08%), the oxidation of allylic position to 2-cyclohexenone seems interesting.

As can be seen from Table 2, the exchange of Mn(II) with NaA and HS has increased the oxidation reactivity especially in the latter case. The similar pattern of product distribution with the enhancement of allylic position oxidation is

also observed in these two systems. The more conversion percentage observed in the case of Mn–HS catalyst is not surprising and arises from the fact that HS zeolite is a stronger Bronsted and Lewis acid than NaA due to its lower Si/Al ratio [50].

Table 3 gives the effect of time on product distribution. By increasing time, while conversion percentage and ether yield increases, the yield of ketone decreases. Although the ether increase is more than compensated by the decrease of ketone, the difference is not serious and the aforementioned intermediacy of 2-cyclohexene-1-ol is more justified.

The effect of the amount of catalyst listed in Table 4 affords an interesting result. Although the amount of catalyst Cr–NaY does not impose a dramatic change on conversion percentage of epoxide and peroxide yields, the percentage yields of ketone and ether decreases and increases respectively. The effect is paramount and shows the determining influence of the more abundance of acid sites although the acidic strength hs not been changed.

The catalytic properties of NaY, Cr–NaY and Mn–NaY on oxidation of 1,1-diphenyl-ethylene with TBHP are shown in Table 5.
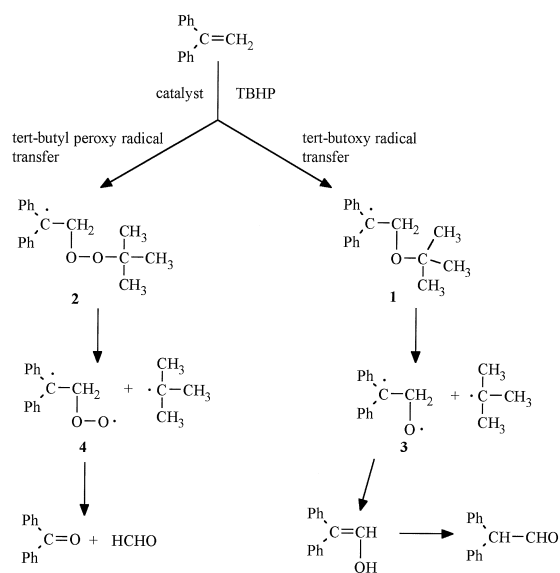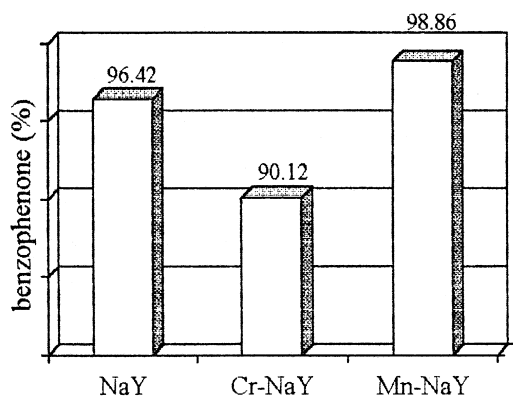

Scheme 2.

Fig. 2. Effect of M–NaY catalyst on the percentage yield of benzophenone.

Since this molecule does not have allylic hydrogens, oxidation occurs on double bond. We believe that the formation of the observed products might have arisen by the following mechanism (Scheme 2). Both radicals 1 and 2 are stable due to their double benzylic character. Therefore, fragmentation to radicals 3 and 4 and formation of stable *tert*-butyl radical can compete predominately with the other parallel reactions. The formation of diphenyl acetaldehyde and benzophenone (main product, Fig. 2) will then derived from these two radicals as shown in Scheme 2.

5. Conclusion

The oxidation of cyclohexene with TBHP using NaY as catalyst afforded a mixture of epoxide, peroxide, ketone and ether. On the other hand, inclusion of some transition metal elements inside the zeolite changed the product distribution. With Mn–NaY, ether was selectively formed as the result of exclusive oxidation of the allylic site.

In contrast, the oxidation of 1,1-diphenylethylene catalyzed by Mn–NaY yielded benzophenone as the main product. Destructive oxidation seems to be predominant in alkenes with no allylic hydrogens available for oxidation, al-

though more data should be collected to establish such deduction.

Acknowledgements

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