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# Study on catalytic synthesis of 1,3-benzodioxoles by HY zeolite

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**Abstract** The acetalization and ketalization of various aldehydes and ketones with catechol by using HY zeolite as catalyst were studied. Effect of the reaction time, mole ratio of reactants, and amount of catalyst on the yield of benzodioxoles were investigated. Results show that HY is an efficient catalyst for the acetalization and ketalization with high conversion and selectivity in mild conditions. The best reaction conditions: molar ratio of catechol to aldehydes or ketones is 1:1.4, catalyst amount is 3.5 g/1 mol catechol, reaction time is 5 h. Under these conditions, the conversion and selectivity were over 50% and 97%, respectively.

**Keywords** benzodioxoles, HY zeolite, condensation, catalyze, synthesis

## 1 Introduction

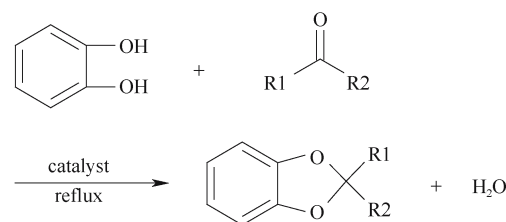
The 1,3-benzodioxole ring system is an integral part of many natural products, such as sesamol and piperine [1]. Recently, 1,3-benzodioxoles with various substituents at the 2 position have received more and more attention, which are inhibitors of mono-oxygenases, and have been widely used in pesticides or pesticide intermediates, herbicides, antioxidants, antimicrobials, and medicines [2–8]. The synthesis of 1,3-benzodioxole derivatives is also useful for the protection of catechol or carbonyl compounds in organic synthesis and thus the synthesis assumes great importance in both biological chemistry and organic synthesis [9–10].

In general, 1, 3-benzodioxoles are prepared by proton or Lewis acid catalyzed condensation of carbonyl compounds with catechol. Many acid catalysts, such as phosphorus pentoxide [11], toluene-*p*-sulfonic acid [12], trimethylsilyl

chloride (TMSCl) [13], phosphorus trichloride [14], super acid [15], montmorillonite KSF or K-10 [16], have been used to catalyze this reaction. But they still have some problems. Take phosphorus pentoxide for example, a large amount of phosphorus pentoxide is used as both acid catalyst and dehydrating agent and the work-up is tedious and inconvenient. The disadvantage of using toluene-*p*-sulfonic acid as catalyst is long reaction time (8–120 h) and unsatisfactory yield. As to chloride (TMSCl) and phosphorus trichloride, the catalysts are either venomous or expensive. The zeolites appear to be promising catalysts with obvious advantages of easy separation, controlled acidity, shape selectivity, and reusability. In this paper, we report HY zeolite as catalyst for the synthesis of 1,3-benzodioxoles from catechol and carbonyl compounds. The effects of the mole ratio, amount of catalyst, reaction time, and the reuse of the catalyst on the yields were investigated. The results showed that HY zeolite has high activity for the reaction without the drawbacks mentioned above.

## 2 Experimental

### 2.1 Reaction equation



R1, R2 alkyl or hydrogen

### 2.2 Reagents and equipments

All organic reagents were commercial products with purity of >98% and used without further purification. Cyclohexanone, acetone, butanone, propionaldehyde, *n*-butyraldehyde, iso-valeraldehyde, diphenyl ketone, and benzaldehyde were

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purchased from Shanghai Chemicals Co. *n*-Valeraldehyde, *n*-hexanone, and *n*-octylaldehyde were obtained from Fluck.

The crystalline nature of the zeolites was established by X-ray diffraction studies performed using a Bruker D8 Advance X-ray diffractometer from Germany. BET surface area and pore volume measurements were performed using a Quancachrome 02108-KR-1 surface area analyzer from American. GC measurements were taken on a SHIMADZU (GC-14B) gas chromatograph. GC-MS measurements were performed on an American Agilent 6890/5973N.

### 2.3 Synthesis of HY zeolite

NaY zeolite was synthesized in our laboratory according to the methods given in Ref. [17]. The product was submitted to 1 mol/L  $\text{NH}_4\text{NO}_3$  with stirring at 343 K for 4 h. Then the mixture was filtrated and washed till free of  $\text{Na}^+$  using de-ionized water, and dried at 383 K over night in an air-oven and calcined at 773 K in a muffle furnace for 3 h. The procedures were repeated three times. We obtained HY zeolite with  $n(\text{SiO}_2) : n(\text{Al}_2\text{O}_3) = 7$ .

### 2.4 Preparation of 2-substituted and 2,2-disubstituted 1,3-benzodioxoles

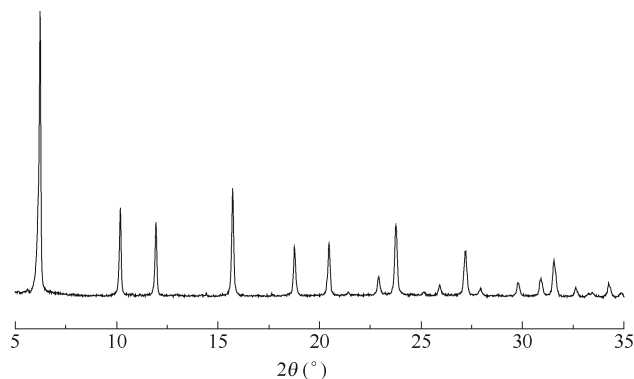
A mixture of carbonyl compounds (about 0.1 mol), 10 mL cyclohexane, catechol, and catalyst were mixed together in a three-necked round-bottom flask equipped with magnetic stirrer, thermometer, and a Dean-Stark apparatus used to remove the water continuously from the reaction mixture. The mixture was refluxed for the specified periods. The process of the reaction was monitored by GC analysis of the small aliquots withdraw at half an hour intervals. On competition, the catalyst was recycled by filtering off and washing with acetone, then dried in oven at 453 K for about 1 h. The qualitative analysis of the liquid reaction mixture was carried out on a GC-MS with HP-5 column using helium as carrier gas. The column temperature was raised from 40 to 260°C at a heating rate of 10°C  $\text{min}^{-1}$ . The quantitative analysis of the reaction mixture was carried out on a temperature-programmed SHIMADZU (GC-14B) gas chromatograph. The concentration of the reactant and product was directly given by the system of GC chemstation according to the area of each chromatograph peak.

## 3 Results and discussion

### 3.1 Characterization of the catalyst

The crystalline nature of the HY zeolite was established by the X-ray diffraction (XRD) studies performed using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The result showed in Fig. 1.

The XRD pattern of the catalyst matched well with that of the reference reported, which indicated that the catalyst we obtained was pure.



**Fig. 1** The XRD pattern of HY zeolite

### 3.2 Catalytic synthesis of 2-substituted and 2,2-disubstituted 1,3-benzodioxoles

In order to figure out the optimum reaction conditions, the effects of the mole ratio, amount of catalyst, reaction time and the reuse of the catalyst on the ketalization of catechol and cyclohexanone were investigated carefully.

#### 3.2.1 The effect of the mole ratio of catechol to cyclohexanone in the reaction

The effect of the mole ratio of catechol to cyclohexanone on the yield was investigated. The results were summarized in Table 1.

**Table 1** Effect of mole ratio of catechol to cyclohexanone in the reaction

$n(\text{catechol})/n(\text{cyclohexanone})$	conversion/%	selectivity/%
1:1.0	80.7	99.7
1:1.2	81.3	99.5
1:1.4	83.2	99.3
1:1.6	83.5	99.2
1:2.0	82.9	99.5

Reaction conditions: cyclohexane 10 mL, HY 0.25 g, catechol 0.1 mol, reaction time 4 h, at reflux temperature.

The results from Table 1 showed that both of the conversion and selectivity increased with the addition of cyclohexanone. The odds of the collision between the reactants increased when the amount of cyclohexanone increased, which accounted for the increase of the yield. The conversion reached the peak value when the mole ratio was 1:1.4. If we continued to increase the amount of cyclohexanone, the conversion changed a little, moreover, there was a decreased trend instead. On one side, the self-condensation of cyclohexanone occurred instead of the reaction we needed, which was proved on the GC-MS. On the other hand, the small molecule of cyclohexanone entered the channels of the catalyst and that made the catechol more difficult to enter the channels to react with cyclohexanone. So the proper mole ratio of catechol to cyclohexanone is 1:1.4.

### 3.2.2 The effect of reaction time

The effect of the reaction time on the yield was investigated. The results were summarized in Table 2.

**Table 2** Effect of reaction time

Time/h	1	2	3	4	5	6
Conversion/%	28.6	53.9	78.9	80.7	81.4	81.3
Selectivity/%	100	99.8	99.7	99.7	99.6	99.5

Reaction conditions: cyclohexane 10 mL, HY 0.25 g, catechol 0.1 mol, cyclohexanone 0.1 mol, at reflux temperature.

It could be seen from Table 2 that the conversion increased with the time. The conversion increased very quickly at beginning and it changed little 5 h later. The reaction was controlled by kinetics at first. The reactants decreased while the product increased with the time, and the reaction was controlled by thermodynamics gradually. It reached the equilibrium 5 h later. If the reaction time prolonged continually, the byproducts were produced. So the proper reaction time was 5 h.

### 3.2.3 The effect of the amount of catalyst in the reaction

The effect of the amount of catalyst on the yield was investigated. The results were summarized in Table 3.

**Table 3** Effect of catalyst amount in the reaction

Amount of catalyst/g	0.05	0.10	0.25	0.35	0.45
Conversion/%	76.6	78.9	80.7	82.2	82.0
Selectivity/%	99.9	99.8	99.7	99.5	99.7

Reaction conditions: cyclohexane 10 mL, catechol 0.1 mol, cyclohexanone 0.1 mol, reaction time 4 h, at reflux temperature.

The results showed in Table 3 indicated that the conversion increased with the amount of catalyst. The active catalytic sites increased when the amount of catalyst increased. At first, the conversion increased quickly, because the active catalytic sites increased, which could activate more reactant during the certain time. However, the conversion changed a little when the amount of catalyst was 0.35 g. It was a course that the catalyst activated the reactants, and sufficient time and energy were needed during the course. So even the active catalytic sites increased, the conversion increased little. So the proper amount of catalyst was 0.35 g.

### 3.2.4 The effect of reuse of recovered catalyst in the reaction

The effect of reuse of recovered catalyst on the yield was investigated. The results were summarized in Table 4.

The results from Table 4 showed that the catalytic activities reduced quickly after recovery. The catechol molecules entered the pore of the catalyst to fix strongly with the active

**Table 4** Effect of recycled times of catalyst used in reaction

Recycled times	1	2	3	4
Conversion/%	80.7	57.7	33.8	13.9
Selectivity/%	99.7	99.9	99.8	100

Reaction conditions: cyclohexane 10 mL, HY 0.25 g, catechol 0.1 mol, cyclohexanone 0.1 mol, reaction time 4 h, at reflux temperature.

sites. Meanwhile, the molecules of catechol are bigger, which could jam the catalyst channels. The high C/H ratio is another reason. When the catalyst was reused, the molecules of reactants can not enter the pores of the catalyst, which account for the decrease of the activities. The activities of the catalyst refreshed after calcining at 550°C (conversion 80%, selectivity 99%).

### 3.2.5 The results of different aldehydes and ketones

To study the scope of this protocol, the condensation of catechol with various carbonyl compounds were performed. The results were summarized in Table 5.

**Table 5** Reaction results of different aldehydes and ketones

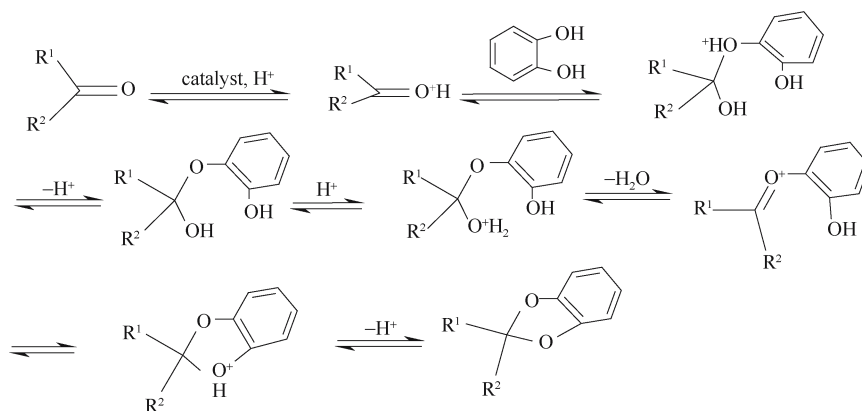
Aldehydes (ketones)	Conversion/%	Selectivity/%
Cyclohexanone	80.7	99.7
Butanone	57.5	99.3
Propionaldehyde	35.4	99.9
<i>n</i> -Butyraldehyde	61.4	99.8
<i>n</i> -Valeraldehyde	72.4	99.6
<i>iso</i> -Valeraldehyde	67.3	98.2
<i>n</i> -Hexylaldehyde	65.4	98.3
Diphenyl ketone	72.7	99.4
<i>n</i> -Octylaldehyde	65.8	98.4
Acetone	32.1	99.8
Benzaldehyde	58.3	97.9

Reaction conditions: cyclohexane 10 mL, HY 0.25 g, catechol 0.1 mol, carbonyl compounds 0.1 mol, reaction time 4 h, at reflux temperature.

It could be deduced from Table 5 that the catalyst has high activity for various carbonyl compounds. Because there are many protonic and Lewis acid sites on the surface and the channels of the zeolite, which could catalyze the reaction efficiently. Meanwhile, its 12 MR provide not only three-dimensional open channel with the diameter of 0.74 nm but also super cavities with the diameter of 1.3 nm which benefits the reaction greatly. The catalyst has very high activity for cyclohexanone because its carbonyl is fixed outside of the cyclohexanone ring, which makes it easily to be contacted with the catalyst and activated. As to acetone, the conversion was especially low because the low reaction temperature. On the other hand, acetone can be mixed with water easily, which made it difficult to remove water from the reaction system. So only the low conversion was obtained.

### 3.2.6 The probable mechanism of the reaction

The reaction was the acid catalyzed course and the probable mechanism is showed below.



It can be concluded from the mechanism that the determining factor for the reaction is the acidity, while HY zeolite suffices that. Meanwhile, the reaction is reversible, so simultaneously removing the water from the reaction system could improve the yield significantly.

## 4 Conclusions

HY zeolite has high activities for the condensation of catechol and carbonyl compounds with the conversion over 50% and the selectivity over 97%. The optimum reaction conditions: catalyst 3.5 g/mol catechol, the mole ratio of catechol to cyclohexanone 1:1.4, reaction time 5 h.

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