

## A Green Synthesis of 2-Ethylantraquinone by Dehydration of 2-(4'-ethylbenzoyl) benzoic Acid over Solid Acid Catalysts

Ren Shu XU, Xin Wen GUO\*, Gui Ru WANG, Zhu Xia ZHANG

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012

**Abstract:** The dehydration of 2-(4'-ethylbenzoyl) benzoic acid (BE acid) to 2-ethylantraquinone (2-EAQ) was investigated over solid acid catalysts. The results showed that H-beta zeolite catalyst modified by dilute HNO<sub>3</sub> solution exhibited an excellent performance. In our study, the conversion of BE acid can reach 96.7%, and the selectivity to 2-EAQ is up to 99.6%.

**Keywords:** 2-Ethylantraquinone, 2-(4'-ethylbenzoyl) benzoic acid, H-beta, dehydration.

2-EAQ is an important intermediate for the synthesis of hydrogen peroxide, pharmaceuticals, pesticides, and dyes. With the increasing demand for hydrogen peroxide, it needs to enhance the yields of 2-EAQ. However, in the conventional process, concentrated H<sub>2</sub>SO<sub>4</sub><sup>1-2</sup> is employed as the catalyst in the dehydration of BE acid for the synthesis of 2-EAQ, which produces a series of environmental impacts and safety concerns. For these reasons, a substitute process, which has little or no hazards to environments, should be pursued. Recently, due to the special pore structure<sup>3-4</sup> and relatively high density of acid sites<sup>5</sup>, H-beta zeolite has attracted much attention in the synthesis of anthraquinone<sup>6-7</sup>. However, in the dehydration of BE acid into 2-EAQ, some undesired by-products, such as methylantraquinone and anthraquinone, may be formed over H-beta zeolite catalyst, which leads to a lower selectivity to 2-EAQ. In this paper, we first reported the dehydration of BE acid for the synthesis of 2-EAQ over H-beta zeolite catalyst and a high selectivity to 2-EAQ was achieved through adjusting the acidity of the H-beta zeolite catalyst and the reaction conditions.

### Experimental

The H-Y catalyst was prepared by calcining NH<sub>4</sub>-Y (obtained from the Chinese Danyang Group) at 823 K for 4 h. The H-ZSM-5 zeolite and the H-Beta zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 22) were acquired by treating the sodium form zeolites (offered by the Institute of Industrial Catalysis, Dalian University of Technology). The obtained catalyst was calcined at 823 K for 4 h.

---

\* E-mail: guoxw@dlut.edu.cn

The H-beta zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 22$ ) was dealuminated by dilute  $\text{HNO}_3$  solution with different acid concentration, and then we got the H-beta zeolites ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 107$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 162$ ). The obtained catalysts were calcined at 823 K for 4 h. From XRD (Rigaku D/max-2400) pattern, we observed that the crystal structure was not destroyed, when H-beta zeolite (22) was dealuminated by  $\text{HNO}_3$  solution. The bulk  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the H-beta zeolite was determined by XRF (SRS-3400 X).

The reaction of BE acid dehydration was carried out in a batch reactor. In a typical experiment, the solid BE acid was first heated to the reaction temperature in the reactor, and then the catalyst was put into the reactor with continuous magnetic stirring. After a period of reaction, the reaction system was cooled, and the reaction mixture was treated with 1,4-diethylene dioxide, dissolving both product and reactant, followed by a separation in a centrifuge. The products were analyzed by liquid-chromatogram (Agilent 1100), using ZORBAX SB-C18 (250×4.6 mm) column at room temperature.

## Results and Discussion

**Table 1** shows the results obtained in the dehydration of BE acid on various zeolite catalysts under the studied reaction conditions, and H-beta exhibited an excellent performance. While both HY zeolite and H-ZSM-5 zeolite exhibited the low conversion of BE acid and low selectivity to 2-EAQ. It can be seen that over HY and H-ZSM-5 catalysts, most of BE acid was converted into MAQ. **Table 1** also shows the effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of H-beta zeolite on the reaction properties. The H-beta (107) exhibited the most excellent performance in the dehydration of BE acid, the conversion of BE acid reaches 85.9% and the selectivity to 2-EAQ is 95.9%.  $\text{NH}_3$ -TPD (CHEMBET-3000) and FTIR spectra of adsorbed pyridine (EXUINOX 55) revealed the changes of the acidity of H-beta with the changes of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. It can be concluded that the suitable acid nature and the suitable distribution of acid sites favored the dehydration of BE acid for the synthesis of 2-EAQ.

From **Table 2**, it can be seen that reaction temperature has a great effect on the conversion of BE acid and a slight effect on the selectivity to 2-EAQ. With the increasing of the reaction temperature, the conversion of BE acid increases dramatically, while the selectivity to 2-EAQ increases slowly. The conversion of BE acid reaches 96.7%, and the selectivity to 2-EAQ is up to 99.6% at 550 K.

**Table 1** The dehydration of BE acid over different catalysts

Catalyst	conversion(%)	Production distribution (%)			Yield of 2-EAQ (%)
		AQ	MAQ	2-EAQ	
HY	3.5	1.9	73.6	18.4	0.6
H-ZSM-5	16.1	5.7	76.3	5.6	0.9
H-beta (22)	62.8	0.4	5.4	93.1	58.5
H-beta (107)	85.9	0.5	2.5	95.9	82.4
H-beta (162)	77.4	0.8	3.9	93.8	72.6

Notes: BE acid/catalyst = 3.5 (g/g), Reaction temperature = 523 K, Reaction time = 1.5 h, AQ = anthraquinone, MAQ = 2-methylantraquinone and 1-methylantraquinone, 2-EAQ = 2-ethylantraquinone

**Table 2** Effect of temperature on the dehydration of BE acid over H-beta (22)

Temperature (K)	conversion(%)	Production distribution (%)			Yield of 2-EAQ (%)
		AQ	MAQ	2-EAQ	
523	62.8	0.4	5.4	93.1	58.5
540	92.0	0.1	2.4	97.4	89.6
550	96.7	0.4	0.0	99.6	96.3

Notes: BE acid/catalyst =3.5 (g/g)

Reaction time= 1.5 h

### Conclusion

H-beta zeolite catalyst is an efficient catalyst for the substitute of concentrate H<sub>2</sub>SO<sub>4</sub> catalyst in the dehydration of BE acid for the synthesis of 2-EAQ. High selectivity to 2-EAQ can be achieved by adjusting the acidity of the H-beta zeolite catalyst and the reaction temperature.

### References

1. Ito, Kenji, S. Hiroyuki, I. Yasuhisa, Japanese Patent 7118198, **1995**.
2. Devic, Michel, WO Patent 96/28410, **1996**.
3. Merger, US Patent 4 045 456, **1976**.
4. K. Yoo, E. C. Burckle, P. G. Smirniotis, *Catal. Lett.*, **2001**, 74, 85.
5. J. Weitkamp, Y. Traa, *Catal. Today*, **1999**, 49, 198.
6. O. V. Kikhtyanin, K. G. Ione, G. P. Snytnikova, *et al.*, *Stud. Surf. Sci. Catal.*, **1994**, 84, 1905.
7. E Santacesaris, A. Scaglione, B. Apicella, *et al.*, *Catalysis Today*, **2001**, 66, 166.

Received 4 April, 2005