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Catalysis Today 61 (2000) 117–122

CATALYSIS TODAY

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Generation of H_2O_2 from H_2 and O_2 over zeolite beta containing Pd and heterogenized organic compounds

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Abstract

The catalytic generation of H_2O_2 from H_2 and O_2 has been studied over zeolite beta-supported Pd and zeolite beta-adsorbed organic compounds such as 1,4-benzoquinone (BQ), hydroquinone (HQ), azobenzene (AB) and hydrazobenzene (HAB). According to catalytic results, zeolite beta-supported Pd catalysts display effective performance relative to those prepared from other types of zeolites reported and Pd-loaded zeolite beta-adsorbed HQ catalysts show enhanced activity compared to zeolite beta-supported Pd catalysts. In situ UV–Vis spectroscopic study indicates that HQ can readily be converted to BQ reversibly under H_2 and air inside zeolite beta only in the presence of Pd. The results suggest that HQ acts as a strong hydrogen transfer agent to promote the production of H_2O_2 from H_2 and O_2 in cooperation with a Pd catalyst. By contrast, adsorption of BQ, AB and HAB induces suppression of the catalytic properties of Pd/zeolite beta. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: H_2O_2; Zeolite beta; Pd; Hydroquinone-adsorbed Pd-zeolite; UV–Vis DRS

1. Introduction

The production of H_2O_2 from H_2 and O_2 has been attracting considerable interest in both chemical industry and academic study [1–5]. H_2O_2 is known to be not only an environment-friendly agent but also a highly selective oxidant in the manufacture of numerous organic and inorganic chemicals [1]. It has long been recognized that quinone compounds act as working compounds, which play a pronounced role in the commercial preparation of H_2O_2 from H_2 and O_2 while present in the organic phase. Besides the traditional anthraquinone autoxidation (AA) process that has been worldwide studied and developed, H_2O_2 can be prepared using supported group VIII metal catalysts, especially supported Pd catalysts owing to their high selectivity and simple handling [1]. The use of solid catalysts can overcome the disadvantage of organic solvent contamination toward aqueous peroxide solution during the separation process. The processes for producing H_2O_2 with Pd supported on inorganic materials such as SiO_2, Al_2O_3, zeolites and carbon have been studied over the last 20 years, but the available literature consists of almost exclusively patents [6–9] and only a few papers have appeared. Moreover the patented zeolites include only mordenite and ZSM-5 [8]. From these patents, it can be seen that all the supported Pd catalysts require high pressures of H_2 and O_2 to prepare useful concentrations of H_2O_2. Recently Meiers and Holderich [3] reported the generation of H_2O_2 from H_2 and O_2 at 10°C on a Ti silicalite loaded with Pd and Pt.

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PII: S0920-5861(00)00351-5

Zeolite beta is said to be a promising catalytic material, since like other high silica content zeolites it can possess high thermal and acid treatment stability, high strength acid sites and hydrophobicity [10]. In this paper, we present a new system prepared by loading of $Pd(NH_3)_4Cl_2$ into zeolite beta, which shows high catalytic activity for the production of H_2O_2 from H_2 and O_2 under mild conditions. While the heterogenization of organometallic catalysts on a large variety of inorganic supports has extensively been studied and applied in many reactions for two decades, little has been done regarding the study of supported quinone compounds for the production of H_2O_2 [11]. Therefore, we took up the study of zeolite-adsorbed catalysts with various organic compounds for the production of H_2O_2 from H_2 and O_2. We show the beneficial cooperative effect of heterogenized hydroquinone (HQ) on the catalysis of Pd/zeolite beta. We also give an interpretation of the reaction mechanism with adsorbed HQ and the chemical behaviors of different types of organic compounds inside zeolite beta in terms of spectroscopic study in correlation with the catalytic results.

2. Experimental

NH_4 type zeolite beta (Si/Al=12.5) was supplied by PQ corporation and was converted to H type zeolite beta by calcination at 550°C in air before use. The organic compounds 1,4-benzoquinone (BQ), HQ, azobenzene (AB) and hydrazobenzene (HAB) were purchased commercially (Aldrich).

Zeolite beta-encapsulated Pd catalysts were prepared according to the following procedure. In an Erlenmeyer flask, an aqueous suspension of $PdCl_2$ was converted to an aqueous solution of $Pd(NH_3)_4Cl_2$ by adding an excess amount of NH_4OH (25% NH_3) under stirring at room temperature. Then the aqueous solution was heated at 60°C for 0.5 h to remove unreacted NH_3. H type zeolite beta was added to this $Pd(NH_3)_4Cl_2$ solution and ion exchange was performed by stirring this slurry at 60°C for 10 h. Afterwards, the solid sample was washed with hot water and dried at 110°C overnight. Prior to catalytic testing, Pd^{2+} ion-exchanged sample was subjected to three different treatments, viz.: (1) calcination in air at 400°C; (2) calcination in air at 400°C and reduction under H_2 at 150°C; (3) calcination in air at 400°C and reduction under He at 300°C. For adsorbing an organic compound, zeolite beta or the above Pd-zeolite was added to 0.1 M benzene solution of organic compound, and the mixture was stirred under N_2 at 60°C for 20 h. Then the resulting solid sample was washed with benzene and acetone at room temperature in air followed by drying at room temperature in air. Thermogravimetric analysis indicates that there are 15, 18 and 20 wt.% of HQ, BQ and HAB, respectively, over Pd/zeolite.

The catalytic production of H_2O_2 was carried out at room temperature and atmospheric pressure. To a 500 ml glass flask, 0.1 g catalyst and 400 ml of 0.01 N HCl aqueous solution were charged. The solution was bubbled with an equimolar dilute gas mixture of H_2 and O_2 (40:40 ml min^{-1}) under vigorous stirring. Each gas is diluted with 50% helium. After 1 h of reaction, 5 ml of reaction mixture was withdrawn with syringe to be analyzed by titration with a standard $KMnO_4$ solution within ±5% experimental error.

UV–Vis DRS measurements were performed on a Shimadzu UV 2501 PC spectrophotometer. The solid samples were measured in a UV–Vis DRS sample holder connected to an atmosphere controlled cell.

3. Results and discussion

The comparative catalytic activities were examined for H_2O_2 production from H_2 and O_2 over zeolite beta and $Pd(NH_3)_4Cl_2$/zeolite beta with 0.3% Pd loading following different treatments. Zeolite beta alone gives rise to 1.2 mmol H_2O_2 after 1 h of reaction. This amount of H_2O_2 corresponds to a catalytic activity of 46 mol (unit cell)$^{-1}$ h^{-1}. This result clearly indicates that zeolite beta is fairly active for H_2O_2 production from H_2 and O_2, as quoted in the literature. For zeolite beta itself, we observed a small ESR signal at g=4.3 which might be due to Fe or Mn impurities. Although it is not clear, it seems the catalytic activity for the formation of H_2O_2 could be attributed to this. In the case of Pd/zeolite beta, it was observed that the amounts of H_2O_2 formed were about 3–4 times higher than that over zeolite beta alone. Among the three Pd/zeolite beta catalysts, the one reduced under He was the most active, resulting in 4.6 mmol H_2O_2 after 1 h of reaction that is equivalent to a turnover number (TON) of 1.6×10^3 mol (Pd mol)$^{-1}$ h^{-1}. H_2-reduced Pd/zeolite

Table 1
Catalytic properties of zeolite beta-supported Pd catalysts in the production of H_2O_2 from H_2 and O_2 at room temperature and atmospheric pressure[a]

Pd loading (%)	H_2O_2 (mmol)	TON (mol (Pd mol)$^{-1}$ h^{-1})	[H_2O_2] formed/[H_2] added (%)
0	1.2	–	2.4
0.3	4.6	1.6×10^3	9.0
0.6	6.4	1.2×10^3	13
0.9	6.0	1.1×10^3	12
1.2	5.1	4.8×10^2	10
2.0	4.6	2.4×10^2	9.0

[a] Pd/zeolite beta was treated in flowing He at 300°C for 3 h. Reaction conditions: 0.1 g catalyst, 400 ml of 0.01 N HCl, H_2:O_2=40:40 ml min^{-1} and 1 h of reaction.

beta was found to be only slightly less active than former. These data show that the presence of Pd inside zeolite beta can lead to the effective enhancement of catalytic activity for H_2O_2 production as compared to zeolite beta alone.

On the basis of the above comparative catalytic results, we determined the catalytic activities for the production of H_2O_2 from H_2 and O_2 as a function of Pd loading over He reduced Pd/zeolite beta. As shown in Table 1, the amount of produced H_2O_2 increased sensitively with higher Pd loading until 0.6% and subsequently decreased slightly as the Pd loading increased. The optimal amount of H_2O_2 produced (6.4 mmol) was clearly observed with 0.6% Pd loading. However, the TON actually decreased with increasing Pd loading in the range from 0.3 to 2.0%. The observed H_2O_2 production activities over zeolite beta-supported Pd catalysts are much higher than those over other types of zeolite-supported Pd catalysts reported in [8,12,13]. A comparison of catalytic activities over various zeolite-supported Pd catalysts is shown in Table 2. This difference in catalytic activity is undoubtedly due to different support effects. Zeolite beta can be regarded to play a promotional role in the catalysis of Pd. Besides anthraquinone and its derivatives which are widely used as working compounds in the AA process, HAB and BQ are known as alternative candidates to play a similar role in the hydrogen transfer and H_2O_2 production [14,15].

Therefore, we attempted to design zeolite-adsorbed catalysts with AB, HAB, BQ and HQ. Due to the larger molecule size, anthraquinone and its derivatives can access only the larger pore zeolites. This restricts their heterogenization via adsorption into some zeolites. Thus, we intended to search for effective working compounds of smaller molecular size. HQ can be regarded as the H-form of BQ. They can be assumed to be interconverted by oxidation and reduction in a cyclic process. Although the patented organic compounds for the manufacture of H_2O_2 include BQ, the role and performance of BQ have been little disclosed [15,16]. HQ has not been reported to be employed as a working compound to produce H_2O_2.

The catalytic activities for the production of H_2O_2 from H_2 and O_2 over zeolite beta and Pd/zeolite beta (1.2 wt.% Pd loading and reduced by H_2 at 150°C)

Table 2
Catalytic properties of various zeolite-supported Pd catalysts after 1 h reaction for producing H_2O_2 from H_2 and O_2

Zeolite	Si/Al	Pd (%)	T (°C)	P (atm)	TON (h^{-1})	Refs.
H-BEA	12.5	0.9	25	1	1.1×10^3	This work
H-BEA	12.5	1.2	25	1	4.8×10^2	This work
NaY		1.0	28	1	2.6×10^2	[12]
H-MOR	18.0	1.0	10	50	73	[8]
Na-MOR	18.0	1.0	10	50	9	[8]
H-ZSM-5	15.0	1.0	10	50	56	[8]
Na-ZSM-5	15.0	1.0	10	50	11	[8]

before and after adsorption of BQ and HQ are compared. The presence of BQ inside zeolite beta resulted in slightly increased catalytic activity over zeolite beta (from 1.2 to 1.5 mmol) and greatly decreased catalytic activity over Pd/zeolite beta (from 3.9 to 1.3 mmol). The diminution of catalytic activity by addition of BQ may be tentatively attributed to the blocking of BQ and zeolite beta active sites for hydrogen transfer by strong adsorption of BQ on the acid sites of zeolite beta, or BQ might be decomposed or polymerized over zeolite and Pd/zeolite. However, when HQ was adsorbed into zeolite beta and Pd/zeolite beta, the catalytic activity of zeolite beta was slightly decreased and that of Pd/zeolite beta was increased by a factor of 1.5. The significantly increased activity over Pd/zeolite beta shows that adsorbed HQ exerts a positive promotion on the catalysis of Pd/zeolite beta for the production of H_2O_2. On the other hand, adsorbed HQ is not capable of bringing about an increase of activity for zeolite beta in the absence of Pd. The different effects caused by HQ will be interpreted in terms of UV–Vis study.

Fig. 1 shows the comparative catalytic activities for the production of H_2O_2 from H_2 and O_2 over zeolite beta and Pd/zeolite beta before and after adsorption of AB and HAB. The presence of AB or HAB inside zeolite beta and Pd/zeolite beta, respectively, resulted in decreased catalytic activities. Since AB or HAB are much more bulkier than BQ or HQ, they may not enter into zeolite channel and may simply block the pore opening of zeolite, which is the main reason for the diminution of catalytic activity.

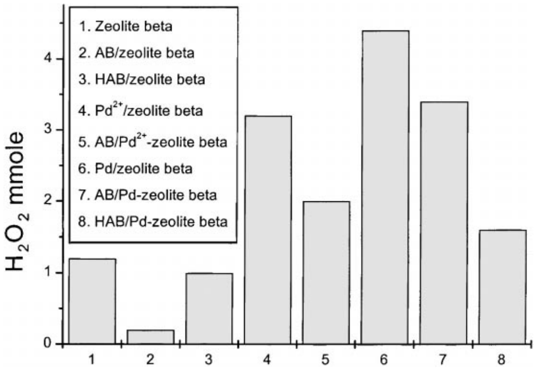


Fig. 1. Production of H_2O_2 from H_2 and O_2 after 1 h reaction over zeolite beta and Pd/zeolite beta (0.3 wt.% Pd loading) before and after adsorption of organic compounds.

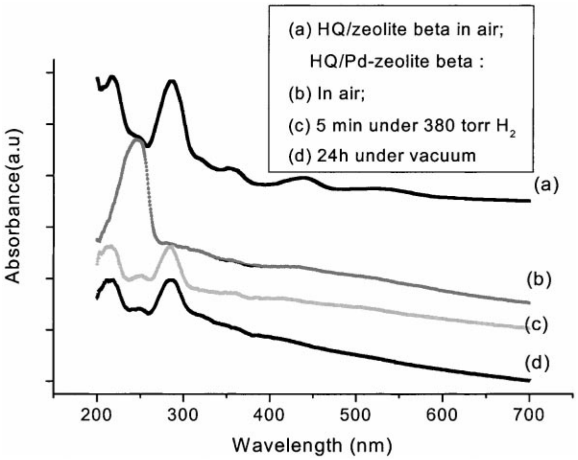
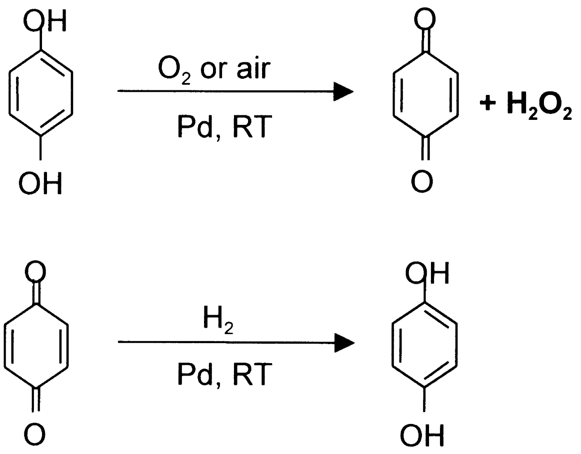


Fig. 2. UV–Vis DRS of adsorbed HQ inside zeolite beta.

The understanding of the behavior of organic compounds inside zeolites is important in the selection of working compounds and the mechanistic study of H_2O_2 production. Although many organic compounds have been demonstrated to be effective working compounds for the production of H_2O_2 in the AA process, the reaction mechanism has not been elucidated. In order to understand the effect of working compounds in the catalytic reaction, we studied the interaction of organic compounds with the inner surface of zeolite beta and the reactivity of adsorbed samples with H_2 and O_2 by UV–Vis spectroscopy.

Fig. 2 shows the UV–Vis spectral evolution of HQ on the inner surface of Pd-loaded zeolite beta under different atmospheres. In the absence of Pd, HQ/zeolite beta displayed a pair of peaks at 220 and 280 nm in air which are characteristic of physisorbed HQ as shown in Fig. 2(a). Accordingly, HQ is stable toward O_2 inside zeolite beta alone and is believed not to convert to BQ at room temperature without Pd. For this reason, adsorbed HQ has no promotional effect on the production of H_2O_2 over zeolite beta, as evidenced by catalytic study. In the presence of Pd, HQ behaved differently. The initial sample prepared from HQ and Pd/zeolite beta exhibited a single peak at 240 nm in air as shown in Fig. 2(b). This peak is identical in wavelength to that of BQ in ethanol and thus is assigned to BQ adsorbed inside zeolite beta. As soon as the sample was exposed to H_2 at room temperature, the peak at 240 nm depleted in favor of the appearance of two peaks at 220 and 280 nm (Fig. 2(c)). The latter two peaks are obviously attributed to HQ adsorbed inside zeolite beta, by comparison with those of HQ in ethanol. The spectral change indicates that BQ was promptly converted to HQ on Pd-loaded zeolite beta via hydrogenation at room temperature. The spectrum in Fig. 2(c) was maintained unchanged following 24 h of treatment under vacuum. After admission of atmospheric air onto the sample, the 240 nm peak intensity was progressively restored at the expense of the peak intensities at 220 and 280 nm. This shows that HQ cannot be dehydrogenated to form BQ on a Pd catalyst without intervention of O_2. The results demonstrate that adsorption of HQ into Pd-loaded zeolite beta under N_2 yields physisorbed HQ only and that BQ results rapidly from the oxidation of HQ on the Pd surface after exposure of HQ/Pd-zeolite beta to air. When the sample was exposed to a mixture of H_2 and air, the observed spectrum consisted of three peaks at 220, 240 and 280 nm, indicating that the co-presence of HQ and BQ on Pd-loaded zeolite beta. Based on the above UV–Vis spectroscopic results, we suggest the following reaction mechanism of H_2O_2 production from H_2 and O_2 with a zeolite-supported HQ catalyst.



The catalytic process shows that there is a cooperative effect between HQ and metallic Pd on the hydrogen transfer for producing H_2O_2. Actually, the cooperative catalysis of HQ and Pd suggested by UV study may be correlated to the increased catalytic activity by adsorption of HQ into Pd-loaded zeolite beta by catalytic test. In addition, a metallic catalyst is required to produce H_2O_2 in the oxidation step of HQ in the present catalytic process, in contrast to the AA process.

If BQ was used as a starting working compound, a complex and uninterpreted UV–Vis spectrum was obtained on both BQ/zeolite beta and BQ/Pd-zeolite beta. This spectrum composed of three broad peaks at 250, 360 and 520 nm, which deviates much from the original BQ UV–Vis spectrum in solution. The spectral shape was kept unchanged after exposure of BQ/Pd-zeolite beta to H_2, indicating that the new species derived from BQ is unable to accept hydrogen to form HQ. The inertness of the new species toward H_2 presumably results from the chemisorption of BQ on the acid sites of zeolite beta, or BQ might be decomposed or polymerized over zeolite and Pd/zeolite. The UV observations seem to explain the negative effect of BQ on the catalytic production of H_2O_2 from H_2 and O_2.

After HAB had been adsorbed into Pd-loaded zeolite beta, the observed spectral pattern in air plausibly resembles that of HAB in ethanol, that HAB cannot be converted to AB with O_2 in the presence of Pd at room temperature. This result implies that HAB cannot act as a hydrogen transfer agent in the catalytic cycle of H_2O_2 production from H_2 and O_2. In the case of AB, a complex UV spectrum was observed in air after adsorption, which exhibited a great change from that of AB in ethanol. This may be related to the interaction of AB with the acid sites of zeolite beta, as is the case of BQ. The new species derived from AB was found not to vary reversibly in the presence of H_2 and air. Heterogenized AB inside zeolite beta cannot play a catalytic role in the production of H_2O_2, in accordance with the catalytic test results.

4. Conclusions

In this paper, we have described a systematic study of a zeolite beta-supported Pd catalyst system and a study of zeolite beta-heterogenized catalysts with organic compounds for the production of H_2O_2 from H_2 and O_2 under mild conditions. To our knowledge, the present paper is the first report on the preparation of H_2O_2 with zeolite beta-supported catalysts. The zeolite beta-supported Pd catalysts exhibit considerably high catalytic activity as compared with other types of zeolite-supported Pd catalysts reported. Catalytic activity of zeolite beta itself might be due to the presence of Fe or Mn impurities. An effective cooperative action occurs between Pd and zeolite beta to enhance the formation of H_2O_2.

The present paper also reports the first example of successful application of HQ as a starting working compound in preparing zeolite-heterogenized catalysts for the production of H_2O_2 from H_2 and O_2. HQ is easily converted to BQ reversibly under H_2 and O_2 inside zeolite beta only in the presence of Pd, which shows a strong ability to transfer hydrogen in cooperation with Pd metallic particles. This is in agreement with the enhancement of catalytic activity of Pd/zeolite beta by adsorption of HQ. However, BQ cannot be recommended as a starting working compound to prepare zeolite-heterogenized catalysts, in contrast to the case with BQ dissolved in organic solvents. This is probably because BQ has strong tendency to chemisorb on the acid sites of zeolite, or BQ might be decomposed or polymerized over zeolite and Pd/zeolite, being incapable of transferring hydrogen to produce H_2O_2. The catalytic test results confirm that adsorption of BQ decreases the catalytic activities of both zeolite beta and Pd/zeolite beta. The comparison of different behaviors between HQ- and BQ-derived catalysts indicates that the design of zeolite-adsorbed organic catalysts is highly dependent on the starting organic compound used. Whether quinone and hydroquinone can be interconverted reversibly inside zeolites can be regarded as the criterion to select working compounds.

Attempt to achieve effective zeolite-adsorbed catalysts with AB and HAB is not successful. Heterogenized HAB is rather stable in air and unable to convert to AB on Pd. AB is assumed to chemisorb on the acid sites of zeolite and adsorbed AB is inactive for the hydrogen transfer. Hence neither adsorbed AB nor HAB are catalytically active for the production of H_2O_2 from H_2 and O_2. The catalytic test results prove that adsorption of both AB and HAB leads to the diminution of catalytic activities of zeolite beta and Pd/zeolite beta.

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