Cobalt-Tetraamide-Phthalocyanine Immobilized on Fe₃O₄/Chitosan Microspheres as an Efficient Catalyst for Baeyer–Villiger Oxidation

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ABSTRACT: Cobalt-Tetraamide-Phthalocyanine (CoTaPc) immobilized onto magnetic Fe₃O₄ chitosan microspheres (Fe₃O₄/CTO) was synthesized via a simple immersion method, which is an efficient catalyst for the oxidation of cyclic ketones to lactones with O₂/benzaldehyde as the oxidant. The CoTaPc-Fe₃O₄/CTO catalyst was applied for the first time in the Baeyer–Villiger (B–V) oxidation reaction. Characterization results obtained from X-ray diffraction, UV–vis, Fourier transform infrared, and scanning electron microscopy showed that the combination of CoTaPc and magnetic Fe₃O₄/CTO microspheres was achieved. The catalyst could be easily separated from the reaction system with an external magnet and reused several times without the remarkable loss of activity. In addition, a possible radical mechanism for the B–V oxidation in this catalytic system is proposed and verified by controlled experiments.

INTRODUCTION

Baeyer–Villiger (B–V) oxidation is a significant organic reaction for converting ketones to the corresponding lactones or esters, which are indispensable intermediates for the synthesis of antibiotics, steroids, pheromones, and other fine chemicals in laboratory and industrial chemistry. In the traditional stage of B–V oxidation, the mainly used oxidants are peracids, such as persulfuric acid, perbenzoic acid, m-chloroperbenzoic acid (m-CPBA), and peroxide (H₂O₂). However, peracids are usually expensive, dangerous, and difficult to transport and store. High concentration of hydrogen peroxide has a good oxidation effect on the B–V reaction, but the water produced by the reaction is prone to hydrolyze lactones, and high concentration has a higher risk in industrial production. Based on the above-mentioned factors, the harmfulness and high economic cost of peroxide limit its practical application. Another strategy uses aldehydes and molecular oxygen as green oxidants, known as the Mukaiyama method. Many research studies have been focused on the aldehyde/O₂ oxidation system because the use of O₂ fulfills the considerations of environment, economy, and safety.

O₂/benzaldehyde as an environmentally friendly system employs various catalysts, such as metal complexes, hydroctalite, transition metal ions or metal oxides, and metal supported on various supports, in B–V oxidation. In a previous report, where copper tetrasulfophthalocyanine-intercalated hydroctalite was used as a catalyst for the B–V reaction, good results have been achieved in the O₂/benzaldehyde system.

As a typical biomimetic catalyst, metal phthalocyanine has attracted widespread attention as it has excellent catalytic oxidation performance for many substrates in oxygen. However, there are two problems affecting the catalytic efficiency of phthalocyanine. First, phthalocyanine is not soluble in common solvents. In addition, phthalocyanine molecules tend to aggregate because of π–π stacking. To overcome the first problem, our group modified the metal phthalocyanine to water-soluble metal tetracarboxyl phthalocyanine for the cyclohexene epoxidation reaction and the catalytic degradation of printing and dyeing wastewater. However, the process of hydrolyzing metal tetaamide phthalocyanine to metal tetracarboxyl phthalocyanine is environmentally unfriendly and the yield is low, so we tried to use the easily synthesized metal tetaamide phthalocyanine as a catalyst for the B–V reaction. In order to solve the problem that phthalocyanines are easy to stack, our team prepared a CoPc/Al₂O₃ catalyst by the “ship-in-a-bottle” method. It catalyzed the B–V reaction in the O₂/benzaldehyde system and obtained good catalytic performance. However, in the reaction system, the phthalocyanine molecules on Al₂O₃ easily fall off, resulting in inconvenient recovery of the catalyst.
and affecting the catalytic efficiency. Therefore, from the perspective of industrialization, it is our goal to develop a kind of immobilized phthalocyanine catalyst with simple preparation, high catalytic efficiency, convenient recovery, and reusability.

In recent years, magnetic microspheres have shown great application potential in many research fields because of their unique strong magnetic responsiveness and excellent chemical stability and recoverability, such as biological separation and enrichment, enzyme immobilization adsorption, and catalysis. Immobilized magnetic phthalocyanine can be easily recovered and reused in further reactions. In addition, immobilizing phthalocyanine on magnetic microspheres can also transform phthalocyanine into a heterogeneous catalyst and increase its durability in the reaction because the deactivation of the active center always results from the oxidative decomposition and aggregation of metal complexes caused by the π−π interaction in the homogeneous system.

Considering the above-mentioned aspects, we prepared simple cobalt tetraamide Phthalocyanine (CoTaPc) supported on magnetic microspheres as an efficient, durable, and recyclable catalyst for the B−V reaction in the O2/benzaldehyde system.

In this work, CoTaPc immobilized on Fe3O4/CTO was prepared as the catalyst for B−V oxidation with a green and efficient catalytic approach in the O2/benzaldehyde oxidative system for the first time. The catalytic activity and reuse of the catalyst CoTaPc-Fe3O4/CTO were evaluated systematically. On this basis, the oxidation mechanism of cyclohexanone was proposed and verified by Raman spectroscopy and controlled experiments.

■ RESULTS AND DISCUSSION

Characterization of the Catalyst. Figure 1 shows the FT-IR spectra of CoTaPc, chitosan, Fe3O4/CTO, and CoTaPc-Fe3O4/CTO. Figure 1a shows a characteristic amide group at 1680−1630 cm−1 (−C=O) and 3500−3060 cm−1 (−NH). Adsorption bands at 1094, 1154, 1327, and 944−768 cm−1 were attributed to the phthalocyanine ring skeleton. From the spectrum of chitosan (Figure 1b), bands at 3450 cm−1 (−OH), 2870 cm−1 (−C−H), 1630 cm−1 (−C=O), 1380 cm−1 (−C−N), and 1090 cm−1 (−C−O) can be observed. The spectrum of Fe3O4/CTO is shown in Figure 1c, and the peak at 580 cm−1 corresponded to the Fe−O−Fe stretching. The characteristic peak of chitosan shifted from 1640 to 1630 cm−1, indicating that the chitosan was coated with Fe3O4 particles. As shown in Figure 1d, the spectrum of CoTaPc-Fe3O4/CTO showed primary and secondary bands at 1640 cm−1 (C=O) and 1570 cm−1 (−NH), respectively, which corresponded to the amide bond of electrostatic adsorption interaction.

The UV−vis spectra of different materials are shown in Figure 2, and the compounds are dissolved in dimethylformamide (DMF) before analysis. These two substances have strong absorption in the B band of the near-ultraviolet region (250−400 nm) and Q band of the visible light region (600−700 nm), which proves that the structure of phthalocyanine exists. The peaks at 667 and 607 nm are mainly attributed to the transition of the macrocyclic phthalocyanine from highest occupied molecular orbital to lowest unoccupied molecular orbital monomers. It can be seen from the figure that the position of the characteristic peak of the UV−vis spectrum has not changed before and after the loading, which indicates that CoTaPc has been successfully loaded to the surface of Fe3O4/CTO.

The prepared samples were analyzed by XRD, as shown in Figure 3. Nine characteristic peaks of Fe3O4 were observed in sample a and sample c and their indices were (111), (220), (311), (222), (400), (422), (511), (440), and (533). These peaks are consistent with the databases in the ICDD/JCPDS.
file (PDF no. 26–1136). It was also explained that the coating of CTO and loaded CoTaPc did not lead to the phase transition of Fe₃O₄. Figure 3b shows that the peak at 26.5° belongs to the crystal plane of CoTaPc. In Figure 3c also, a peak at 26.5° can be observed, indicating that CoTaPc successfully loaded on the surface of Fe₃O₄/CTO.

As represented in Figure 4, the surface morphologies of Fe₃O₄/CTO were investigated through SEM micrographs. The morphologies of the Fe₃O₄/CTO particles show nearly spherical shapes with an average diameter of 5 μm, which suggests the good monodispersion.

**Catalytic Activity of CoTaPc-Fe₃O₄/CTO in B–V Oxidation.** To explore the effects of the solvent, temperature, molar ratio, catalyst amount, solvent amount, and time on the B–V oxidation catalyzed by CoTaPc-Fe₃O₄/CTO, Tables 1 and S1–S3 summarize the results of these factors affecting the conversion of cyclohexanone to caprolactone.

Table 1 (entry 1–5) evaluates the effect of temperature on the reaction. It can be observed that the conversion of cyclohexanone can reach 40.4% at 0 °C; as the temperature increases to 15 °C, the conversion of cyclohexanone increases rapidly to 94.5%. However, with the reaction temperature continuing to increase, the conversion of cyclohexanone declines slowly. Significantly, we obtained very high conversion at 15 °C, which can reduce the risk of industrial production. The catalyst amount was optimized by maintaining the reaction temperature at 12 h, and the effects of the catalyst amount are shown in Table 1 (entry 6–9). The conversion of cyclohexanone increased with the increasing amount of the catalyst, peaked at 5%, and then gradually declined, which shows that the excessive amount of the catalyst hinders the progress of the reaction. The main reason is that the reaction is heterogeneous and when stirred, the catalyst can be uniformly dispersed in the reaction mixture and if the amount of the catalyst continues to increase, it will exceed the amount of the solid-phase catalyst that the reaction mixture can bear. Therefore, considering the efficiency and economic cost of the catalyst, the optimum dosage of the catalyst is 5% of the mass of the substrate. The effect of time on the conversion of cyclohexanone was explored (Table 1, entry 10–15). With the increase of the reaction time, the conversion of cyclohexanone increased rapidly within 10 h of reaction, but when the reaction time continued to prolong, the trend of conversion of cyclohexanone slowed down. Finally, the conversion was maintained at about 94% between 12 and 14 h and did not continue to increase. In order to select a suitable solvent, the effect of different solvents on B–V oxidation is investigated and shown in Table S1. With DCE as the solvent, the conversion of cyclohexanone reached a maximum. Under optimized conditions, the conversion of cyclohexanone was 84.2 and 83.5%, which indicates that EtOAc and MeCN have great potential as solvents in B–V oxidation. Subsequently, Table S2 shows that 25 mL of DCE was the optimal condition. When the amount of benzaldehyde increased to 2 equiv, the performance of B–V oxidation is excellent (Table S3). In summary, the optimal conditions for B–V reactions catalyzed by CoTaPc-Fe₃O₄/CTO are 15 °C, 2 equiv benzaldehyde, 25 mL of DCE, catalyst amount: 5% mass of substrate and time: 12 h.

Under the optimized reaction conditions, various ketones using 1,2-dichloroethane as the solvent in B–V oxidation are explored and listed in Table 2. It is gratifying that all kinds of cyclic ketones can be successfully transferred to the corresponding lactones with excellent selectivity and conversion under mild conditions except cycloheptanone (Table 2, entry 1–4, 7). CoTaPc-Fe₃O₄/CTO shows little catalytic activity to cycloheptanone, which was mainly due to the stability of cycloheptanone and the nucleophilic reaction of perbenzoic acid was not easy to occur. Experiments have shown that CoTaPc-Fe₃O₄/CTO has an excellent catalytic performance on oxidation of 2-adamantanone. Although the rate of the reaction depends on the structure of ketones, it can be inferred that various ketones can be oxidized to corresponding lactones with CoTaPc-Fe₃O₄/CTO under such mild reaction conditions.

Some data of other catalytic systems based on O₂/ benzaldehyde in the B–V oxidation of cyclohexanone are collected in Table 3. It can be seen that most of the catalysts had high catalytic efficiency under high temperature, which leads to some potential risks and limits their prospects in industrial applications. The catalytic efficiency of other reported catalysts is lower than that of item 1, and the synthesis of these catalysts is cumbersome. Therefore,
CoTaPc-Fe₃O₄/CTO, which is economical, synthesized simply, and easy to recover, shows excellent potentials in the B–V reaction.

The reuse of the catalyst was investigated. When the reaction is over, CoTaPc-Fe₃O₄/CTO can be easily separated by magnetic separation. The used catalyst is washed with ethanol several times and dried in an oven at 60 °C. Figure 5 shows the performance of the catalyst in the reused cycles of cyclohexanone oxidation. In five runs, the catalyst did not show a significant decrease in activity and the selectivity was more than 99%, indicating the catalyst CoTaPc-Fe₃O₄/CTO showed considerable stability and reusability.

Possible Mechanism of Catalytic Oxidation of Cyclohexanone. In order to clarify the role of the catalyst and verify the mechanism of B–V oxidation catalyzed by CoTaPc, a series of controlled experiments were carried out. A large number of reports have proposed that the mechanism of B–V oxidation involves different types of free radicals. Therefore, 2,2,6,6-tetramethylpiperidine-1-yloxy (Tempo) was introduced into the reaction system as a free radical scavenger. When the catalytic amount of Tempo was added to the reaction, the

Table 2. B–V Oxidation Reaction of Various Ketones

| Entry | Ketones | Product | Time, h | Con. (%) | Sel. (%) |
|-------|---------|---------|---------|----------|----------|
| 1     |         |         | 12      | 94.5     | >99      |
| 2     |         |         | 12      | 90.0     | >99      |
| 3     |         |         | 14      | 95.9     | >99      |
| 4     |         |         | 12      | 90.2     | >99      |
| 5     |         |         | 12      | 61.6     | >99      |
| 6     |         |         | 12      | 22.3     | >99      |
| 7     |         |         | 12      | 88.5     | >99      |
| 8     |         |         | 12      | 0        | 0        |

“Reaction conditions: ketone 0.025 mol, benzaldehyde 0.05 mol, DCE 25 mL, CoTaPc-Fe₃O₄/CTO 0.12 g, O₂ 24 mL/min, and 15 °C. "The conversion and selectivity were determined by GC on the basis of the internal standard method (chlorobenzene).

Table 3. Comparison of Various Catalysts in the B–V Oxidation of Cyclohexanone Based on O₂/Benzaldehyde

| Entry | Catalyst | Con. (%) | Sel. (%) | Recycle of catalyst | Ref | T (°C) |
|-------|----------|----------|----------|---------------------|-----|--------|
| 1     | CoTaPc-Fe₃O₄/CTO | 94.5     | >99      | practicable         | this work | 15     |
| 2     | Ketjen Black | 65       | >99      | practicable         | 29  | 50     |
| 3     | 15Sn–TiO₂ | 91.4     | 93.2     | practicable         | 30  | 70     |
| 4     | Fe–Sn–O mixed oxides | 93.5   | 97.3     | practicable         | 31  | 25     |
| 5     | Mg–Sn–O mixed oxides | 87.6   | 97.3     | practicable         | 31  | 25     |
| 6     | Co–Sn, Cu–Sn and Ni–Sn | 78.5–83.1 | 85–89 | practicable         | 32  | 50     |
| 7     | [H₄TPP][HPW₁₂O₄₀] | 56.1     | 43.1     | practicable         | 33  | 40     |
| 8     | MnAlPO | 78       | 98       | practicable         | 34  | 25     |
| 9     | SnTPP/4A-MS | 83       | 99       | practicable         | 35  | 60     |

CoTaPc-Fe₃O₄/CTO, which is economical, synthesized simply, and easy to recover, shows excellent potentials in the B–V reaction. The reuse of the catalyst was investigated. When the reaction is over, CoTaPc-Fe₃O₄/CTO can be easily separated by magnetic separation. The used catalyst is washed with ethanol several times and dried in an oven at 60 °C. Figure 5 shows the performance of the catalyst in the reused cycles of cyclohexanone oxidation. In five runs, the catalyst did not show a significant decrease in activity and the selectivity was more than 99%, indicating the catalyst CoTaPc-Fe₃O₄/CTO showed considerable stability and reusability.
desired product was not detected. It is clear that the reaction involves a free radical pathway.

In general, the O2/aldehyde oxidation system of B−V oxidation has two reaction steps: (step 1) aldehyde and O2 produce peracid and (step 2) the reactant is oxidized by peracid. It is valuable to find out if the catalyst promotes the first or second stage of the reaction. It can be observed from Figure S1 that the oxidation of benzaldehyde to perbenzoic acid occurs through self-oxidation and CoTaPc-Fe3O4/CTO can promote the B−V oxidation. In order to clarify whether CoTaPc-Fe3O4/CTO accelerated the production of peracid, m-chlorobenzaldehyde was used for the reaction. The reaction of m-chlorobenzaldehyde with O2 was carried out with and without CoTaPc-Fe3O4/CTO. After the reaction, the catalyst and catalyst-free reaction system were evaporated to remove the solvent. The obtained samples were analyzed using a Raman spectrum analyzer, and the Raman spectra are shown in the Figure 6.

The characteristic peak distributions of m-CPBA can be observed with the O−O stretch from the Figure 6. According to previous reports,36 the O−O stretching appeared near 882 cm−1. By comparing sample a and sample b, it is found that there is an obvious characteristic peak of O−O in sample b. The experimental phenomenon indicates the presence of m-CPBA in sample b. However, no characteristic peak of O−O was found in sample a, so the experiment confirms that CoTaPc-Fe3O4/CTO is beneficial to the conversion of benzaldehyde to peracid. On the other hand, CoTaPc-Fe3O4/CTO is also introduced in the second step of using m-CPBA as the oxidant, and blank experiments are carried out under the same conditions as a comparison. The similar results for abovementioned two reactions shown in Figure S2 demonstrate that CoTaPc-Fe3O4/CTO gives little catalytic contribution to the cyclohexanone oxidation by m-CPBA.

Based on the above-mentioned study, the possible mechanism of O2/benzaldehyde oxidation of cyclohexanone is proposed in Scheme 1. First of all, benzaldehyde interacts with the active sites in CoTaPc-Fe3O4/CTO to form acyl radicals. Then, oxygen is quickly captured by acyl radicals to form peroxy radicals. At the same time, the generated free radicals were adsorbed on the surface of CoTaPc-Fe3O4/CTO, which improved the reaction efficiency. After that, the peroxy group acts as a carrier and reacts with another benzaldehyde molecule to form perbenzoic acid. Then, perbenzoic acid attacks the cyclohexanone carbonyl carbon nucleophilic addition reaction to form the Criegee intermediate. Then, the Criegee intermediate is decomposed into ε-caprolactone and benzoic acid by the intramolecular rearrangement reaction.

### CONCLUSIONS

In a word, a simple and easily recoverable magnetic heterogeneous catalyst (CoTaPc-Fe3O4/CTO) has been successfully prepared and used for the first time to catalyze B−V oxidation under O2. Various characterizations of the sample show that CoTaPc has been successfully loaded on the surface of Fe3O4/CTO, which makes it possible to separate the catalyst from the reaction system with permanent magnets. CoTaPc-Fe3O4/CTO is a green, effective, and economical B−V reaction catalyst which exhibits excellent catalytic activity. The catalyst can be reused several times without obvious activity loss. In addition, a reasonable mechanism was proposed and verified by the introduction of a free radical scavenger (Tempo) and Raman spectroscopy. Using green CoTaPc-Fe3O4/CTO as the catalyst and oxygen as the oxidant, the condition is mild, which is a promising process and has great potential for industrial application.

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**Figure 5.** Reusability of CoTaPc-Fe3O4/CTO for B−V oxidation. Reaction conditions: cyclohexanone 0.025 mol, benzaldehyde 0.05 mol, CoTaPc-Fe3O4/CTO 0.12 g, reaction time 12 h, 15 °C, and O2 24 mL/min.

**Figure 6.** Raman spectra of m-CPBA, sample a: m-chlorobenzaldehyde reacted with O2 without the catalyst and sample b: m-chlorobenzaldehyde reacted with O2 over CoTaPc-Fe3O4/CTO. Reaction conditions: m-chlorobenzaldehyde 0.025 mol, CoTaPc-Fe3O4/CTO 0.12 g, 1,2-dichloroethane 25 mL, pumping O2, 15 °C, and 1 h.

**Scheme 1.** Plausible Mechanism of Oxidation of Cyclohexanone
Scheme 2. Synthesis of Cobalt-Tetraamide-Phthalocyanine

Figure 7. Photographs of CoTaPc-Fe₃O₄/CTO in water: (a) without external magnetic field and (b) with external magnetic field.

**EXPERIMENTAL SECTION**

Materials. The information for the related materials is found in the Supporting Information.

Preparation of the Catalyst. **Preparation of CoTaPc.** Scheme 2 shows the synthesis way of CoTaPc. To obtain a pure product and high yield, we performed the reaction at high temperature and all the reactants were melted (Scheme 2). First, 8.3 g (34.9 mmol) of cobalt(II) chloride hexahydrate was pulverized with 27.5 g (143 mmol) of 1,2,4-benzenetricarboxylic anhydride, 50 g (0.833 mol) of urea, 0.42 g (2.14 mmol) of ammonium molybdate tetrahydrate, and 3.75 g (70 mmol) of ammonium chloride in a mortar (180 mm in diameter) until homogeneous and until the color changed from white to dark purple. The mixture was placed in a three-necked flask with mechanical stirring and refluxing and then heated for 1 h at 130 °C. Subsequently, the temperature was increased to 230 °C and maintained for 4 h. The precipitate gradually changed from purple to bluish black. The obtained solid was washed repeatedly with boiling water until the filtrate was colorless. Further, it was washed three times with acetone and methanol and dried in a vacuum oven at 80 °C and 0.09 Mpa for 5 h to obtain a blue-black solid which is CoTaPc.²

**Preparation of Fe₃O₄/CTO Microspheres.** Synthesis of Fe₃O₄/CTO was based on previous study with some modifications. Fe₃O₄ particles were prepared by the coprecipitation method.³,⁴ FeCl₃·6H₂O (12.43 g, 0.046 mol) and FeSO₄·7H₂O (6.4 g, 0.023 mol) were added into 150 mL of deionized water in a 250 mL three-necked flask under mechanical stirring (700 rpm). After 30 min, the solution was added with 20 mL of ammonium hydroxide (25%) and heated up to 70 °C for an hour under a nitrogen atmosphere. When the solution is cooled to room temperature, the Fe₃O₄ particles are collected with a magnet and washed with deionized water and ethanol three times. Then, Fe₃O₄ particles are collected and dried in a vacuum oven at 50 °C for 5 h. CTO (0.5 g) was added into 20 mL of 2% acetic acid solution; Fe₃O₄ particles (0.5 g) are dispersed in a mixture of 70 mL of paraffin and 1.25 mL of span80. Then, the above-mentioned mixtures were blended together and degassed through ultrasonic concussion until well-mixed. The suspension was transferred to a three-necked flask equipped with a mechanical stirrer and 3 mL of 25% glutaraldehyde solution was added. The speed of mechanical agitation is set to 600 rpm. After 4 h, the chitosan magnetite composite particles were recovered from the reaction mixture with a magnet. The separated magnetic particles were washed three times with water and ethanol and finally dried in a vacuum oven at 50 °C.⁵

**CoTaPc Immobilized on Magnetic Microspheres.** 0.5 g of CoTaPc was dissolved in DMF (50 mL) and the solution was stirred for 30 min until the phthalocyanine was completely dissolved and then 0.5 g of Fe₃O₄/CTO microspheres was added. The mixture was stirred continuously at room temperature for 72 h, and then the solvent was removed using a rotating evaporator. The catalyst was washed with deionized water three times. Then, the catalyst can be quickly collected through external magnets (Figure 7) and dried in a vacuum oven at 70 °C. Finally, the catalyst CoTaPc-Fe₃O₄/CTO was achieved.

Characterization Methods of the Catalyst. Characterization methods of the CoTaPc-Fe₃O₄/CTO catalysts are listed in the Supporting Information.

**Catalytic Performance of B–V Oxidation.** Cyclic ketone compound (0.025 mol), benzaldehyde (0.05 mol), CoTaPc-Fe₃O₄/CTO (0.12 g), 1,2-dichloroethane (25 mL), and 0.03 mol chlorobenzene (the inert internal standard) were separately added to a 100 mL jacketed bottle. Subsequently, the jacketed bottle was attached to a mechanical stirrer and connected to a serpentine condenser and the mechanical agitation was set to 500 rpm for 12 h. O₂ was bubbled into the solution (24 mL/min). The conversion and selectivity were analyzed by gas chromatography on the basis of the internal standard method (chlorobenzene). The reaction mixture was washed and suction filtered and the filtrate was adjusted to pH 7–8 with a saturated NaHCO₃ solution. Then, the organic phase was extracted with ethyl acetate, and after rotary evaporation, anhydrous sodium sulfate was added to remove water. Finally, the mixture was separated by column chromatography to the corresponding lactone.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00443.
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