Effect of magnesium ferrite on highly selective phenol hydroxylation catalyst

Jing Zhao*

Material and Chemical Engineering, Zibo Vocational Institute, Zibo, China.

***Corresponding author:** zhjing7510@163.com

Abstract:

Due to the lack of phenol hydroxylation activity of common catalysts, the conversion rate is low, which cannot meet the application requirements. The effect of magnesium ferrite on the high selective phenol hydroxylation catalyst is proposed. Based on the analysis of the synthesis route of phenol, the related mechanism and influencing factors are obtained according to its properties, and the effect of magnesium ferrite on the highly selective phenol hydroxylation catalyst is studied. The experimental results show that during the hydroxylation activity experiment, the ferrite magnesium catalyst can increase the conversion rate of phenol to 56.5% and the yield of hydroquinone to 50.9% at the highest; During the conversion process, the product selectivity is most focused on catechol, accounting for over 50%. Hydroxyphenol has a certain selection percentage, accounting for about 30% to 40%. Benzoquinone has little selectivity and tends towards 0%. The results show that the application of magnesium ferrite in the preparation of highly selective phenol hydroxylation catalyst can effectively improve the conversion rate, under the same reaction conditions, the catalytic activity of magnesium ferrite catalyst is close to that of TS-1 catalyst, which is superior to La-Sr-Cu-O catalyst and tungstate phosphorus heteropoly compound catalyst, and make up for the preparation defects of traditional catalysts.

Keywords: Magnesium Ferrite; Phenol; Hydroxylation; Catalyst

1. Introduction

Hydroxylation refers to the reaction of introducing hydroxyl into organic compounds. Alcohols and phenols can be synthesized by hydroxylation [1]. These two kinds of substances have a wide range of uses in fine chemical industry, mainly used in the production of synthetic resin, various auxiliaries, dyes, pesticides, surfactants, spices and food additives. In addition, many important intermediates and products containing other functional groups, such as alkylphenol ether, diaryl ether, aryl primary amine and diaryl secondary amine, can also be prepared by the conversion of phenol hydroxyl groups. There are many ways to introduce hydroxyl into compound molecules, including reduction, addition, substitution, oxidation, hydrolysis, condensation and rearrangement. For example, the reduction of fatty acids and their esters or other oxygenated compounds (such as aldehydes or ketones) by reduction method, and the condensation of aromatics with ethylene oxide to alcohols in the pres-

ence of catalysts are important methods for the synthesis of alcohols in industrial production. Magnesium ferrite is produced by high temperature calcination and regrinding of magnesium compound and iron oxide. Because of its high price, it is mainly used in occasions requiring high heat resistance, non-toxic and inert, such as plastic, enamel, toys, etc..

In recent years, some spinel composite oxide catalysts have been widely concerned in the selective oxidation of hydrocarbons because of their low price, simple preparation process and good catalytic performance. The results are as follows: Some scholars used magnesium ferrite to catalyze the selective oxidative dehydrogenation of butene to butadiene, and related experiments were carried out. The results show that the proposed method has good catalytic performance in light alkylation of phenol, with high reaction speed and high product selectivity [2]. Ethylbenzene to styrene is an important industrial process. Some scholars
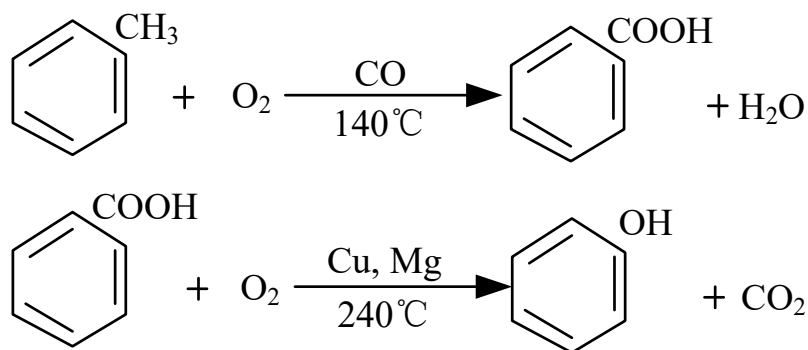
Figure 1. The synthesis process of phenol from toluene.

have found that ultrafine powder magnesium ferrite and zinc ferrite have good oxidative dehydrogenation properties of ethylbenzene, and magnesium ferrite is better than zinc ferrite, and related follow-up tests have been carried out in view of this discovery [3]. The results show that the first difference spectrum of magnesium ferrite is asymmetric, while the spectrum of other samples is basically symmetric, which indicates that the surface of magnesium ferrite samples has obvious irregularity, that is, there are many defects, so it is easier to capture more gaseous oxygen molecules, become chemisorptive oxygen molecules, and then converted into active oxygen species. Some scholars have studied the catalytic effect of ultrafine magnesium ferrite particles on the oxidative dehydrogenation of ethylbenzene and cyclohexane. The results show that magnesium ferrite series ultrafine particles have obvious catalytic effect [4]. In this context, the study attempts to analyze the interaction between highly selective phenol hydroxylation and Magnetium Ferrite from the aspects of hydroxylation characteristics, phenol properties, and catalyst types. In order to study the effect of magnetic flux on highly selective phenol hydrogenation catalyst and provide technical reference for phenol synthesis, accelerating the development of the phenol synthesis industry.

2. Study on the effect of magnesium ferrite on highly selective phenol hydroxylation catalyst

2.1 Characterization of hydroxylation of phenol and magnesium ferrite

When magnesium ferrite was used in the light alkylation of benzene, its catalytic activity and phenol selectivity were significantly improved compared with other catalysts. The reason for the increase of catalyst activity is that Fe_3O_4 is formed by reduction at the defect site of MWCNTs, which is more likely to lead to the formation of hydroxyl radicals; the increase of phenol selectivity is due to the consumption of excess hydroxyl radicals, which has been proved by characterization. Iron containing catalysts are still attracting researchers' interest due to their simple preparation, low price and good catalytic activity [5, 6]. At present, the research focus is mainly on the selection of catalyst support, the goal is to maximize the selectivity of phenol.

Theoretically, it is quite difficult to realize the route of phenol production from benzene by direct alkylation. This is because benzene molecules have high thermodynamic stability. Carbon atoms in benzene ring are shielded by common electrons, which is conducive to electrophilic reaction. The product phenol is more active than benzene. Once phenol is generated, it is easy to further react. In order

Table 1. The general physical properties of hydroquinone.

Nature	Pyrocatechol	p-dihydroxybenzene
Melting point (°C)	105	172-175
Boiling point (°C)	246	287
Flash point (°C)	127	165
Ignition point (°C)	510	515
Relative density	1.34	1.33
Relative vapor density	3.79	3.81
Vapor pressure (kPa)	1.33	0.133
Solubility	31.2	5.8

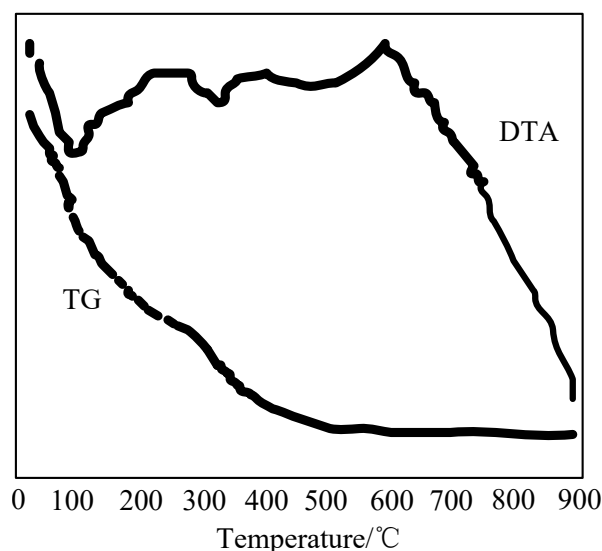**Figure 2.** TG-DTA map of the forebody MgFe$_2$O$_4$.

to solve these problems, the selection of oxidants and the application of catalysts play a significant role. Therefore, magnesium ferrite was applied to the reaction process, and magnesium ferrite was loaded on various carriers, including nanotubes, activated carbon and spherical carbon by equal volume impregnation. The catalyst was calcined at 400 °C for 3 hours. XRD and XPS patterns showed that the iron species in the calcined catalyst no longer existed in the form of Fe$_2$O$_3$. There are many industrial processes for phenol production, among which sulfonation, chlorobenzene hydrolysis, cycloheSxane oxidation, toluene benzoic acid, cyclohexene, RASI Hooke and cumene are the most common ones. Cumene is the most important and mature one in the world [7, 8], but it is still mature. However, the most appropriate synthesis route should be selected according to the actual situation. The synthesis process of phenol from toluene is as shown in Fig. 1. The raw materials used in this process are abundant and cheap. The one-time investment of this production process is low, which greatly reduces the production cost. In addition, the by-products of this production process are benzoic acid, benzaldehyde and benzyl alcohol. Investors can adjust the product structure according to the changes of market demand to realize the optimization of the process. Its disadvantages are: low atom utilization rate (60.2%); low conversion rate of catalytic oxidation of toluene with cobalt and selectivity of benzoic acid; low selectivity of product phenol, and easy deactivation of catalyst efficiency in this process [8, 9]. The selectivity of phenol is related to the selection of carrier and the content of vanadium species. The selectivity of phenol decreased with the increase of benzene conversion and vanadium species content, but increased with the increase of hydrogen peroxide conversion. The pore structure of the support will cause diffusion restriction on the reaction, so that the phenol generated in the pore cannot be diffused out and further oxidized to reduce the selectivity of phenol [10, 11].

2.2 Effect of phenol properties on the preparation of catalyst

Based on the characterization results of hydroxylation of phenol and magnesium ferrite, the influence of magnesium ferrite on highly selective phenol hydroxylation catalyst was analyzed. The physical and chemical properties of phenol may have an uncertain effect on the preparation of catalyst. Therefore, the specific analysis of phenol can ensure the smooth preparation of catalyst.

2.3 Oxidative decomposition

Catechol is a colorless or white crystal with the smell of phenol. When the solid or solution is exposed in the air or there is light, it will gradually oxidize to brown. Pyrocatechol is flammable, sublimable, soluble in water, ether, benzene, chloroform, soluble in alkaline aqueous solution and pyridine [12, 13]. It has certain toxicity. The poisoning symptoms are similar to those of phenol, such as respiratory tract irritation, blood pressure rise, temperature instability, etc.

Hydroquinone is a white crystal with the smell of phenol. The general physical properties of it are shown in Table 1. It exists in three crystal forms: α type, crystallized in water, in triangular needle shape or triangular shape, which is a stable crystal form; β type, crystallized in methanol or isopropanol which is not in contact with air, in triangular shape, which is an unstable crystal form; γ type, the monoclinic crystal form obtained by sublimation, which is an unstable crystal form. Hydroquinone is combustible in case of open fire and high heat, and it will be decomposed by high heat to release toxic gas. It is easy to dissolve in hot water, ethanol and ether, but hard to dissolve in benzene. It is toxic, if adults take 1 g by mistake, they will have headache, dizziness, tinnitus, pale complexion and other symptoms. The commercial hydroquinone is light gray and can sublime without decomposition when the temperature is slightly lower than its melting point [14].

2.4 Catalyst thermal analysis

The thermal analysis of catalyst $MgFe_2O_4$ precursor was carried out as shown in Fig. 2.

The TG curve shows that the weight loss is obvious before 500 °C. The reason of weightlessness is attributed to the decrease of water content and the decrease of a small amount of unwashed NO^{3-} in the forebody. The catalyst is stable when calcined above 500 °C. The downward heat absorption peaks of 100 °C and 300 °C in DTA curve are caused by the loss of different types of water. The upward exothermic peak at 600 °C is attributed to the heat generated by the decomposition of nitrate ions.

2.5 Hydroxylation reaction

(a) Weak acidity and complexation: hydroquinone is a weak acid with two dissociation constants, $K_1 = 7.5 \times 10-10$, $K_1 = 7.5 \times 10-10$ in water (30 °C). Hydroquinone can be mixed with alkali hydroxide or alkali carbonate to form monophenol salt or bisphenol salt in solution. Catechol or its derivatives can react with metal salts to form metal complexes because of two adjacent conjugated hydroxyl groups. These complexes are often used as various analytical reagents.

(b) Oxidation reaction: hydroquinone is easier to oxidize than phenol, and can be transformed into corresponding quinone by mild oxidation. In alkaline or acidic solution, hydroquinone or catechol can transfer one electron to form a semibenzoquinone radical, and then transfer another electron to form the corresponding benzoquinone. Hydroquinone is oxidized to p-benzoquinone, also known as 2,5-cyclohexadiene-1,1-dione. Catechol is oxidized to o-benzoquinone, also known as 3,5-cyclohexadiene-1,2-dione. After the oxidation of catechol or hydroquinone, the o-benzoquinone or p-benzoquinone can be further attacked by the nucleophilic attack of hydroxyl group, and a substitution reaction will take place to generate o-hydroxy-p-benzoquinone (2-hydroxy-2,5-cyclohexadiene-1,4-dione). The reducibility of catechol is stronger than that of hydroquinone. The basic solution of catechol absorbs oxygen after placing. The color will turn from colorless to green, then brown, and finally black, which is due to the formation of quinone and quinone polymer.

(c) Hydrogenation reaction: hydroquinone is hydrogenated to change benzene ring into alicyclic ring. For example, 1,4-cyclohexanediol can be obtained by hydrogenation of hydroquinone with nickel catalyst.

(d) Substitution reaction: hydroquinone can carry out the typical substitution reaction of phenol, such as halogenation, sulfonation, nitration, alkylation, coupling, etc. However, the reactivity of substitution reaction on O-ring and hydroquinone benzene ring is different, and the single substitution reaction of catechol generally takes place at 4 or 3 positions; the two hydroxyl groups on hydroquinone benzene ring are symmetrical, and the reactivity is the same when the single substitution reaction takes place at the other four positions. The difference in reactivity between o-dihydroxybenzene and hydroquinone is due to the difference in electron cloud density caused by the difference in hydroxyl position of the two benzene rings [15, 16].

(e) Cyclization reaction: pyrocatechol and o-phenylenediamine, o-phenylphenol, o-aminophenylthiophenol and ethylenediamine are cyclically formed into corresponding heterocyclic compounds such as dihydrophenazine, phenoxazine, phenothiazine and quinoxaline; 1,3-benzodioxolane can be formed with dichloromethane. 1,4-dihydroxynaphthalene can be formed by the reaction of hydroquinone with maleic anhydride. See Fig. 3 for details.

(f) Etherification reaction: it is easy to synthesize one or two ether compounds with hydroquinone by alkylation
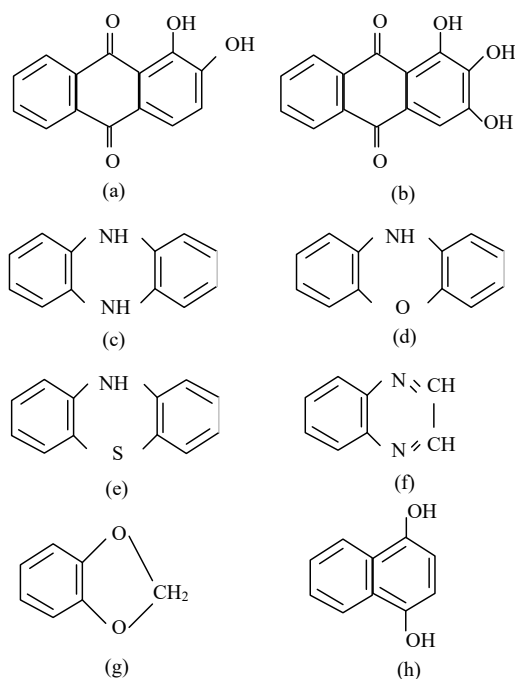

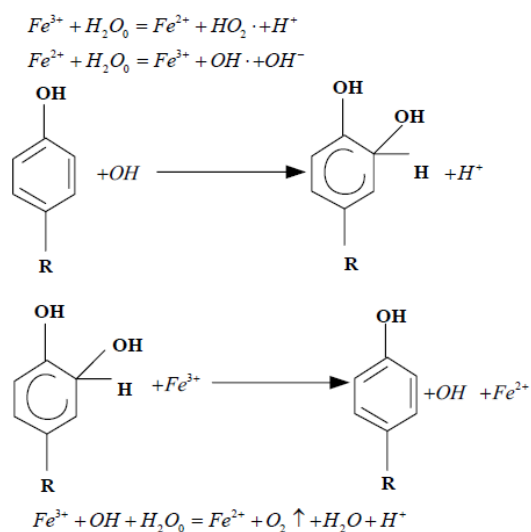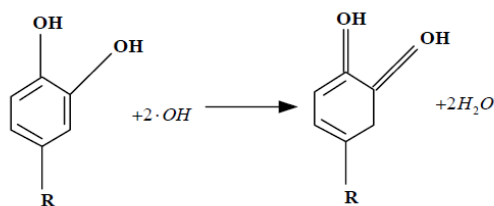**Figure 3.** The products of hydroquinone cyclization.

Figure 4. Mechanism of hydroxylation catalyzed by iron-based catalyst.

Figure 5. Deep oxidation of product molecules.

Figure 6. Comparison of characterization results.

reagent. Generally speaking, it is very difficult to control the reaction stage of monoether only, and the products are often mixtures.

(g) Reimer-Tiemann reaction: hydroquinone can undergo Reimer-Tiemann reaction to generate aldehydes. For example, the mixture of catechualdehyde (2,3-dihydroxybenzaldehyde) and Protocatechualdehyde (3,4-dihydroxybenzaldehyde) was obtained under the basic condition of catechol and chloroform.
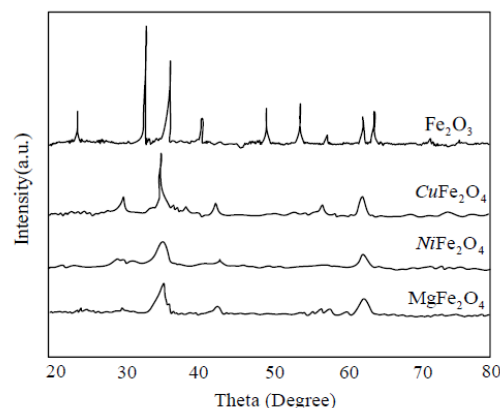
(h) Kolbe-Schmitt carboxylation reaction: hydroquinone can also undergo Kolbe-Schmitt carboxylation reaction, introducing CO2 into benzene ring to form carboxyl group. The reaction is usually carried out in the presence of alkali carbonate. Hydroquinone reacts with potassium carbonate at $130\,^{\circ}C$ in aqueous solution to form 2,5-dihydroxybenzoic acid.

(i) Polycondensation reaction: under acidic or alkaline conditions, hydroquinone can react with formaldehyde to obtain hydroxymethyl derivatives, which can polycondensate to obtain polymer compounds [17]. For example, catechol condenses with formaldehyde (or acetaldehyde) to form catechol methane, which can further condense.

According to its properties, the specific morphological transformation is analyzed as follows.
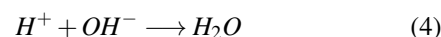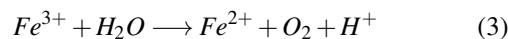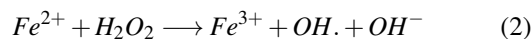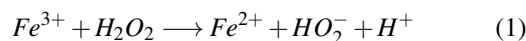
2.6 Catalytic speciation

The mechanism of hydroxylation of phenol and hydrogen peroxide was studied based on the characterization of hydroxylation of phenol and magnesium ferrite and the analysis of the influence of phenol performance on the preparation of catalyst.

The mechanism of phenol hydroxylation has not been determined. It is generally believed that the hydroxylation of phenol on solid acid and titanium silicalite is electrophilic substitution reaction mechanism, while the hydroxylation of phenol catalyzed by metal salts and metal oxides is free rad-
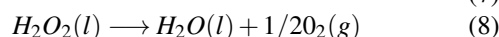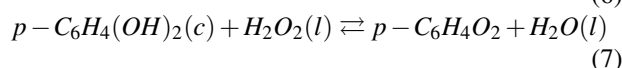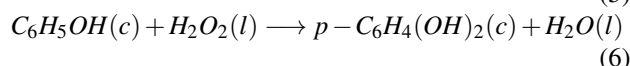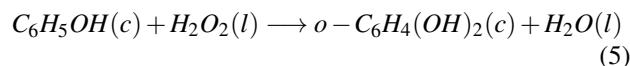
ical reaction mechanism. The mechanism of hydroxylation of phenol with hydrogen peroxide catalyzed by supported transition metal oxides is as follows:

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^- + H^+ \tag{1}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH\cdot + OH^- \tag{2}$$

$$Fe^{3+} + H_2O \longrightarrow Fe^{2+} + O_2 + H^+ \tag{3}$$

$$H^+ + OH^- \longrightarrow H_2O \tag{4}$$

According to the above reaction mechanism, the main reactions involved in phenol hydroxylation reaction system are as follows:

$$C_6H_5OH(c) + H_2O_2(l) \longrightarrow o - C_6H_4(OH)_2(c) + H_2O(l) \tag{5}$$

$$C_6H_5OH(c) + H_2O_2(l) \longrightarrow p - C_6H_4(OH)_2(c) + H_2O(l) \tag{6}$$

$$p - C_6H_4(OH)_2(c) + H_2O_2(l) \rightleftarrows p - C_6H_4O_2 + H_2O(l) \tag{7}$$

$$H_2O_2(l) \longrightarrow H_2O(l) + 1/2 0_2(g) \tag{8}$$

where c represents crystalline state, ι represents liquid state and g represents gaseous state, p- represents material p-position.

The hydroxylation of phenol belongs to electrophilic substitution reaction. H_2O_2 forms peroxide intermediate on catalyst zeolite as electrophilic reagent. The electrophilic reagent attacks o-and p-position of phenol, generates hydroquinone, dehydrates the catalyst surface, and restores the initial state. Because -OH is o-and p-position base, when

Table 2. The effect of temperature on the conversion of phenol.

Reaction temperature (ºC)	X_{phenol} (%)	S_{DHB} (%)	Y_{DHB} (%)	$E_{H_2O_2}$
40	48.25	87.54	42.24	52.84
50	51.64	92.74	47.89	59.88
60	51.82	92.47	47.92	59.91
70	51.48	91.21	46.95	58.69
80	50.11	88.63	44.41	55.52

Table 3. Effect of reaction time on hydroxylation of phenol with hydrogen peroxide.

t (min)	t' (min)	X_{phenol} (%)	S_{DHB} (%)	Y_{DHB} (%)	$E_{H_2O_2}$
5	45	51.79	87.66	45.40	56.80
10	45	51.68	91.26	47.16	58.95
15	45	51.71	93.46	48.33	60.41
20	45	51.55	93.67	48.29	60.36
15	5	51.54	93.60	48.24	60.30

the original position base on benzene ring is h, the physical proportion of o-p binary substitution should be However, due to the special pore structure of zeolite, the shape selection of pore system has an effect on the catalytic reaction to some extent, and the result is not entirely due to the actual catalytic ability. As shown in Fig. 4, it is generally considered to be the free radical reaction mechanism involving Fe(3)/Fe(2) redox pair.

It can be seen from the reaction process should include (a) the transformation from Fe(3) to Fe(2), (b) the formation of hydroxyl radicals, (c) the attack of hydroxyl radicals on reactant molecule A to form active intermediate B, (d) the formation of active intermediate B by electron transfer to form product C, (e) the formation of oxygen with hydroxyl radicals and H_2O_2 in the presence of Fe(3). In the above steps, the formation of hydroxyl radicals directly affects the reaction rate, while the formation of hydroxyl radicals is affected by step (a), so step (a) is the decisive step. We have observed that the induction period is limited by the concentration of Fe(3) in the solution, so increasing the amount of catalyst and the reaction temperature can shorten the induction period, which is consistent with the hypothesis. The hydroxyl radicals produced in step (b) can attack the product molecule C in addition to the reactant molecule A, as shown in Fig. 5.

Based on the above conclusion, the influence of catalyst amount, hydrogen peroxide amount, temperature and reaction time on the catalytic process can be determined.

(a) Influence of catalyst quantity: with the increase of catalyst quantity, the conversion of phenol also increases. However, the selectivity of hydroquinone and the effective utilization ratio of hydrogen peroxide are decreasing, which may be caused by the deep oxidation of hydroquinone when the amount of catalyst is too large.

(b) Effect of hydrogen peroxide content: as a hydroxylation agent, the concentration of H_2O_2 has a great influence on the performance of the reaction. When the amount of hydrogen peroxide is lower than the stoichiometric ratio, the conversion rate of phenol and the selectivity of hydroquinone are lower, but the effective utilization rate of H_2O_2 is higher. When the amount of hydrogen peroxide is higher than the stoichiometric ratio, the conversion rate of phenol and the selectivity of product are higher, but the effective utilization rate of H_2O_2 is lower. When discussing the effect of the amount of H_2O_2 on the reaction performance, it was noted that when the amount of H_2O_2 was equal to

Table 4. Experimental reagents used.

Reagents Name	Specifications	Manufacturer or place of origin
P-tert-butyl phenol	CP	Sinopharm Group Chemical Reagent Co., Ltd.
Hydrogen peroxide	AR, 30%	Tianjin Guangfu Fine Chemical Research Institute
Catechol	AR	Sinopharm Group Chemical Reagent Co., Ltd.
Acetonitrile	AR	Tianjin Guangfu fine Chemical Research Institute
Methanol	Chromatographically pure	Tianjin Guangfu Fine Chemical Research Institute
Ethanol	AR	Tianjin North Tianyi Chemical Reagent plant
Acetone	AR	Tianjin North Tianyi Chemical Reagent plant
Glacial acetic acid	AR	Shanghai chemical reagent plant economic and trade company
Iron nitrate	AR	Tianjin Guangfu Fine Chemical Research Institute
Magnesium nitrate	AR	Xian Chemical reagent plant
Iron oxide	AR	Wuxi prospect Chemical Reagent Co., Ltd
Copper nitrate	AR	Sinopharm Group Chemical Reagent Co., Ltd.
Copper acetate	AR	Sinopharm Group Chemical Reagent Co., Ltd.
Nickel nitrate	AR	Shanghai Mingyi Chemical Co., Ltd.
Sodium thiosulfate	AR	Sinopharm Group Chemical Reagent Co., Ltd.
Potassium iodide	AR	Sinopharm Group Chemical Reagent Co., Ltd.

Table 5. Solubility of reactants and products

Solvent	Phenol	Hydrogen peroxide solution	Catechol	Hydroquinone
Water	Mutually dissolvable	Mutually dissolvable	80.8	26.0
Acetone	Mutually dissolvable	Mutually dissolvable	96.3	45.9
Ethanol	Mutually dissolvable	Mutually dissolvable	97.3	45.7

the theoretical stoichiometric ratio, the conversion rate of phenol was lower. However, when H_2O_2 is excessive, the conversion rate of phenol increases significantly, but this increase is accompanied by a significant increase in the selectivity of hydroquinone as the main product and the utilization rate of H_2O_2. This phenomenon is different from the conventional bimolecular reaction, because excessive H_2O_2 not only promotes the conversion of phenol, but also may trigger further oxidation of hydroquinone, resulting in reduced selectivity. In addition, H_2O_2 may self-decompose at experimental temperatures, which may affect its effective utilization in the reaction. Therefore, in order to achieve the balance of high selectivity and high utilization, the amount of H_2O_2 is optimized in practical applications to ensure the high efficiency and economy of the reaction.

(c) Temperature effect: under the catalysis of H-ZSM-5 supported iron cobalt mixed oxidation, phenol hydroxylation can be carried out at $40\,^\circ$C, but the conversion rate of phenol, selectivity of hydroquinone, yield of hydroquinone calculated by phenol and effective utilization rate of hydrogen peroxide are low. The low conversion of phenol is due to the low reaction rate of hydroxylation at low temperature, as shown in Table 2.

There are two possible reasons for the low selectivity of hydroquinone: one is that the oxidation of hydroquinone to p-benzoquinone is a reversible exothermic reaction, and low temperature is conducive to the deep oxidation of phenol; the other is that when the temperature is low, the consumption rate of hydrogen peroxide is slow, resulting in a large amount of accumulation in the reaction system, and when it accumulates to a certain amount, it will cause the instantaneous content of hydroxyl radicals in the reaction system Too much of it results in the deep oxidation of phenol. When the reaction temperature is $50\,^\circ$C and $60\,^\circ$C, all the indexes are greatly improved and reach the maximum value in the temperature range. The reaction temperature continued to rise, and all inspection indexes decreased, which may be

due to the high temperature promoting the decomposition of hydrogen peroxide and the formation of phenol tar, reducing the hydrogen peroxide participating in the hydroxylation reaction, and aggravating the phenomenon of deep oxidation of products [18, 19].

(d) Effect of reaction time: the effect of reaction time on the hydroxylation of phenol with hydrogen peroxide is shown in Table 3. The reaction time refers to the time from the continuous dripping of hydrogen peroxide to the stop of heating and stirring, including the dripping time (t) of hydrogen peroxide and the continuous reaction time (t') after the dripping. The reaction temperature is $50\,^\circ$C, the molar ratio of phenol to hydrogen peroxide is 1.25, and the mass ratio of catalyst to phenol is 0.03.

It can be seen from Table 3 that the selectivity of hydroquinone is the largest when the time of dropping hydrogen peroxide is more than 15 min. The shorter the dropping time, the faster the dropping acceleration, the more hydrogen peroxide accumulated in the reaction system, the more serious the deep oxidation of phenol, and the lower the selectivity of hydroquinone. The hydroxylation reaction has been completed within 5 minutes after the addition of hydrogen peroxide, and the reaction speed is very fast.

After the completion of the above study, a control experiment was designed to verify the research results.

3. Experimental parts

3.1 Experimental reagents and instruments
The main types and information of reagents used in the study are shown in Table 4.

3.2 Experimental instruments
Constant temperature magnetic stirrer; 85-2 type; Shanghai sile Instrument Co., Ltd. PHS-4CT Shanghai Dapu Instrument Co., Ltd. JJ-3 Jiangsu ronghua Instrument Manufacturing Co., Ltd. DHG-9053A Shanghai Yiheng Tech-

Table 6. Hydroxylation of phenol with different solvents.

Solvent	Phenol conversion (%)	Hydroquinone selectivity (%)	Yield of hydroquinone (%)	Product selectivity(%)			
				HQ	CAT	BQ	tar
Water	20.4	94.6	19.3	36.8	57.8	0	5.4
Acetone	1.6	0	0	0	0	100	0
Aceticacid	0	0	0	0	0	0	0
Ethanol	0	0	0	0	0	0	0

Table 7. Hydroxylation activity of different catalysts for phenol hydroxylation

Catalyzer	Phenol conversion (%)	Hydroquinone selectivity (%)	Yield of hydroquinone (%)	Product selectivity(%)			
				HQ	CAT	BQ	tar
Fe-Mg-O	20.4	94.6	19.3	36.8	57.8	0	5.4
Fe-Mg-O[1])	23.5	92.2	21.6	35.5	56.7	0	9.3
Fe-Mg-O[2])	56.5	90.5	50.9	36.9	53.6	0.2	9.3
α- Fe$_2$O$_3$	13.4	79.1	10.6	30.0	49.1	3.5	17.4
MgO	0	0	0	0	0	0	0
La1.9Sr0.1CuO4	-	-	40.8	23.2	16.6	1.0	-
(Cpyr)$_8$P$_2$Mo$_{16}$V$_2$O$_{62}$	-	-	8.12	78.6	0	21.4	-
TS-1	26	90	23.4	43.2	46.8	2.0	8.0

nology Co., Ltd. Vacuum pump; SHB-III Zhengzhou Great Wall Technology Industry and Trade Co., Ltd. DZF-6050 Shanghai Yiheng Technology Co., Ltd. Analytical balance; AL204; Shanghai Weiping Scientific Instrument Co., Ltd.

3.3 Experimental preparation

3.4 Preparation of magnesium ferrite catalyst

Magnesium ferrite catalyst was prepared by coprecipitation. Dissolve 86 g Fe(NO$_3$)$_3$9H$_2$O and 31 g Mg(NO$_3$)$_2$6H$_2$O in water, stir evenly, drop into 250 mL ammonia water, stir, age, filter repeatedly, wash, dry at 120 °C, put into muffle furnace and bake at 600 °C.

3.5 Phenol hydroxylation

The hydroxylation reaction is carried out in a glass reactor. The catalyst in the reaction should have high catalytic activity to promote the phenol hydroxylation reaction. The catalyst should maintain stability under reaction conditions and not be easily deactivated or degraded. The catalyst itself or its catalytic products should not be toxic to ensure the environmental friendliness of the reaction. Use standard catalytic activity testing methods to evaluate the activity of catalysts. Evaluate the selectivity of the catalyst by analyzing the content of HQ, CAT, BQ, and coke in the reaction products. Use a thermostat or heating/cooling system to maintain the required reaction temperature. The feeding system is used to accurately add catalysts and solvents to ensure the accuracy of the reaction. Analysis equipment: Use a chromatograph, mass spectrometer, or other analytical instruments to analyze reaction products to evaluate the performance of the catalyst. In the reactor, first add a catalyst, then add a certain amount of solvent and phenol for electromagnetic stirring, raise the temperature to the desired reaction temperature, and then add a metered amount of H$_2$O$_2$ (30%). The reaction conditions are: water/phenol (mass ratio): 8-12.5, H$_2$O$_2$/phenol (molar ratio): 3, catalyst/phenol (mass ratio): 0.05, reaction temperature: 60 °C: 0.05, reaction temperature: 60–70 °C.

3.6 Product analysis

The product analysis was completed on the liquid chromatograph. Chromatographic column: ODS Hypersil 5 μm, 4.6

mm × 100 m. Column temperature: 40 °C. Mobile phase: methanol water solution (methanol/water = 30/70, mass ratio). Flow rate of flushing agent: 0.4 mL/min. UV detector λ=280 nm. XRD analysis of catalyst samples showed that Cuk α was the source of X-ray and the diffraction peaks between (20–70 °C) were recorded. In IR analysis, samples were doped with KBr and the analysis range was (400-1300) cm-1.The formula for the conversion rate is shown in equation (9).

$$X = \frac{N_{A,0} - N_A}{N_{A,0}} \qquad (9)$$

In Equation (9), X represents the conversion rate; $N_{A,0}$ represents the number of moles of the substance A before the reaction; N_A represents the number of moles of the substance A remaining after the reaction. The formula for the yield is shown in equation (10).

$$Y = \frac{N_B}{N_{A,0}} \qquad (10)$$

In equation (10), Y represents the yield; N$_B$ represents the number of moles of product B. The formula for Selectivity is shown in equation (11).

$$S = \frac{N_B}{N_A} \qquad (11)$$

In equation (11), S represents selectivity.

3.7 Effect of solvent on hydroxylation of phenol

The hydroxylation reaction of phenol is usually carried out in the liquid phase, and solvent selection may have a significant impact on the reaction. Different solvents can affect the control of reaction rate, product selectivity, and reaction conditions. Water can usually reduce the activation energy of the reaction and promote its occurrence. This is because water molecules can form hydrogen bonds with reactants and intermediates, thereby stabilizing the reaction transition state and reducing the energy required for the reaction. This allows the reaction to proceed at lower temperatures or faster rates. And water is an excellent solvent that can dissolve many organic compounds in it. This is crucial for many organic reactions as it ensures effective mixing and

| (a) MgFe$_2$O$_4$ | (b) MgFe2O4 after the reaction |
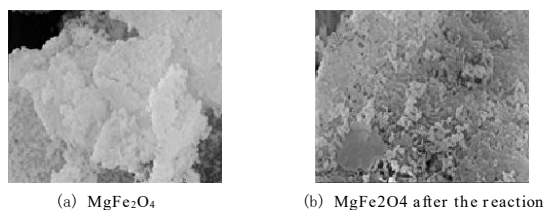
Figure 7. Scanning electron microscopy characterization.

| (a) MgFe$_2$O$_4$ | (b) MgFe2O4 after the reaction |

Figure 8. Transmission electron microscopy characterization.

contact of reactants, thereby increasing the chances of reactions occurring. Water is stable at room temperature and is not easily decomposed. This makes it an ideal reaction solvent as it does not interfere with the reaction or degrade into unwanted products. Water is stable at room temperature and is not easily decomposed. This makes it an ideal reaction solvent as it does not interfere with the reaction or degrade into unwanted products. The function of solvent in the reaction is to dissolve reactant and avoid coking of catalyst. For the hydroxylation of phenol with hydrogen peroxide, the basic requirement for the solvent is that it can dissolve both organic phenol and inorganic H_2O_2.

It can be seen from Table 5 that there is no difference in the solubility of water, acetone and ethanol to phenol and H_2O_2, but the solubility of reaction products (catechol and hydroquinone) is different. However, whether they can all be used in the hydroxylation of phenol with hydrogen peroxide needs to be investigated from the reaction results. Under the reaction conditions of solvent/phenol (mass ratio) = 12.5, H_2O_2/phenol (mole ratio) = 3, catalyst/phenol (mass ratio) = 0.05 and reaction temperature of 65 °C, the results of different solvents on phenol hydroxylation are shown in Table 6.

It can be seen from Table 6 that the solvent has a great influence on phenol hydroxylation reaction, and water is the best solvent found at present. The hydroxylation of phenol catalyzed by magnesium ferrite may be carried out by free radical mechanism. The presence of water is conducive to the formation of free radicals OH, thus promoting the hydroxylation of phenol. Although organic solvents such as methanol, ethanol and acetone can make phenol and hydrogen peroxide become mutually soluble systems, they are not conducive to the formation of free radicals ·OH, so they cannot promote the hydroxylation of phenol.

3.8 Effect of different catalysts on hydroxylation of phenol

Under the same reaction conditions, the phenol hydroxylation activities of different catalysts were investigated. The results are shown in Table 7.

Table 7 shows that MgO has no activity for phenol hydroxylation. This may be because its physical and chemical properties are not suitable for catalyzing this particular reaction, or it does not provide the necessary activation sites. This result highlights the importance of catalyst selection in reaction design, as unsuitable catalysts may not promote the desired reaction. Although α-Fe_2O_3 has a certain activity, it is still very low compared with the composite oxide
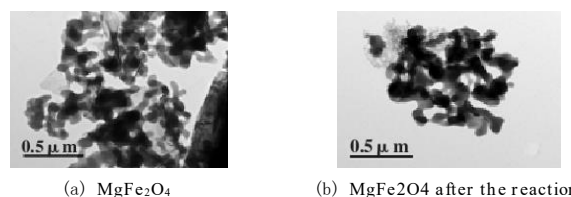
magnesium ferrite ($MgFe_2O_4$), which shows that the physical and chemical properties of the composite oxide have changed greatly compared with the simple oxide, resulting in the obvious difference of catalytic activity. It also has a relatively low conversion rate of phenol, while producing a large number of other products, such as catechol, benzoquinone and coke. This may indicate that α-Fe_2O_3 catalysts are not an ideal choice for highly selective hydroquinone production. Under the same reaction conditions, the catalytic activity of magnesium ferrite catalyst is close to that of TS-1 catalyst, which is superior to La-Sr-Cu-O catalyst and tungstate phosphorus heteropoly compound catalyst. This shows that the magnesite catalyst is one of the best catalysts in the hydroxylation of phenol. This comparison can help us select the most suitable catalyst for a particular reaction to achieve higher product selectivity and yield.

3.9 Results and discussions

The prepared $MgFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$ catalysts were characterized by XRD and compared with the XRD patterns of commercial Fe_2O_3. The characterization results are shown in Fig. 6.

The prepared $MgFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$ catalysts all show the characteristic peak of spinel structure, and magnesium ferrite ($MgFe_2O4_4$ shows high catalytic activity under the reaction conditions. Spinel structure is a kind of structure conducive to catalytic reaction, and a large number of metal sites in the structure act as the active site, thus increasing the reaction rate. Moreover, the high chemical stability of the spinel structure also enables the catalyst to maintain higher structural integrity during catalysis and prolonging the life of the catalyst. When $CuFe_2O_4$ is used as catalyst, the conversion is relatively low, only 17.7%. Although $NiFe_2O_4$ is slightly better than $CuFe_2O_4$, it still cannot meet the required standard. The scanning electron microscopy characterization of $MgFe_2O_4$ was observed, as shown in Figure 7. As can be seen from Figure 7, before the reaction, $MgFe_2O_4$ presents a relatively regular flake, which gathers together in the form of layer upon layer. After the reaction, the flake shape disappears and becomes a coral-like connected particle structure. The characterization of $MgFe_2O_4$ was observed by transmission electron microscopy, as shown in Figure 8. As can be seen from Figure 8, the morphology of $MgFe_2O_4$ observed by transmission electron microscopy did not change significantly before and after the reaction. The results showed that the surface struc-

ture of the catalyst was rearranged, but the internal structure of the catalyst did not change.

4. Conclusions

Magnesium ferrite is an excellent catalyst for hydroxylation of phenol to hydroquinone, which has a good prospect of development and application. Water is an excellent solvent, which can promote the hydroxylation of phenol. The hydroxylation of phenol catalyzed by magnesium ferrite may be carried out by free radical mechanism. The experimental results show that in the preparation of highly selective phenol hydroxylation catalyst, magnesium ferrite can effectively improve the conversion. Under the same reaction conditions, the catalytic activity of magnesium ferrite catalyst is close to that of TS-1 catalyst, which is superior to la-sr-cu-o catalyst and phosphotungstate heteropoly acid composite catalyst, making up for the defects of traditional catalyst. The $MgFe_2O_4$, $NiFe_2O_4$ and $CuFe_2O_4$ catalysts show the characteristic peak of spinel structure, and the $MgFe_2O_4$ shows high catalytic activity under the reaction conditions. Although the analysis results of the effect of Fe and Mg on the hydroxylation of phenol with high selectivity are obtained, there are some defects in the research process. The research is mainly conducted on a laboratory scale and has not yet involved large-scale production and practical applications. In the future, magnesium ferrite catalysts will be applied to larger scale phenol hydroxylation reaction systems to evaluate their performance and feasibility in actual production. Moreover, the study did not take into account the changes in the activity stability of magnesium ferrite catalysts after a large number of reactions. In the future, the number of experiments will be increased and the results will be enriched.

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