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Kinetics of phenol hydroxylation reaction of open mesoporous TS-1 with high backbone titanium content

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Abstract

High skeletal titanium content, open mesoporous TS-1 titanosilica molecular sieves with more accessible active centres exhibit higher catalytic activity, target product selectivity and resistance to coking deactivation in green catalytic oxidation reactions using hydrogen peroxide as oxidant. In this paper, TS-1 titania-silica molecular sieves without anatase, with the highest theoretical skeletal titanium content (2.0 wt%) and open mesopores (mesopore volume 0.71 cm³/g) were synthesised based on the ageing dry gel limited domain conversion method invented in previous research work. The intrinsic kinetics of the catalytic reaction of phenol with hydrogen peroxide for direct hydroxylation of benzenes was investigated. The effects of stirring rate, phenol concentration, hydrogen peroxide concentration, catalyst dosage and reaction temperature on the initial conversion rate of phenol were investigated, and the experimental data were fitted with a power function equation to obtain the intrinsic kinetic equation of the catalyst ($r = 2.98 \times 10^6 \exp\left(-\frac{56.43 \times 10^3}{RT}\right) c^{1.07}(\text{Phenol})c^{0.10}(\text{H}_2\text{O}_2)$). Under the condition of eliminating the effect of internal and external diffusion, the reaction was 1.07 and 0.10 for phenol and hydrogen peroxide, respectively, with a reaction activation energy of 56.43 kJ/mol. This study provides a theoretical basis for the reactor and process design of hydroxylation of phenol to benzenediol based on this new catalyst.

Keywords: TS-1; Aged dry gel domain-limited transformation; Phenol hydroxylation; Intrinsic kinetics.
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1 Introduction

Dihydroxybenzene (DHB) is an important organic intermediate and has three main isomers: catechol, resorcinol and hydroquinone. Among them, catechol and hydroquinone have important industrial value and are widely used in dyestuffs, pharmaceuticals, pesticides, fragrance antioxidants, fungicides, photographic materials, rubber materials and other fields [1]. Traditional methods for the industrial production of catechol and hydroquinone include [2-3], electrolytic benzene method [4], Brichima method [5], Ube method [6], cyclohexanediol dehydrogenation method [7], p-diisopropylbenzene oxidation method [8], etc. These methods are gradually being phased out due to their complex processes, high production costs and serious environmental pollution.

Since the discovery of TS-1 titanosilica molecular sieve in 1983, research on the direct hydroxylation of catechol and hydroquinone from phenol using hydrogen peroxide (H_2O_2) as the oxidant and TS-1 as the catalyst has gradually gained attention. The reaction has the advantages of a simple process, high H_2O_2 utilisation and low environmental pollution, and is considered the most promising production process for the industrial application of hydroquinone [9]. However, TS-1 is a microporous molecular sieve, and the reactants have a high diffusion resistance within the microporous pores, resulting in a low utilization rate of its active sites; in addition, titanium skeleton is the active centre of TS-1, but the synthesis conditions of titania-silica molecular sieve are harsh, and the synthesis process inevitably produces anatase TiO_2 , which can lead to ineffective decomposition of H_2O_2 and side reactions during the reaction process [10]. Therefore, how to prepare titania-silica molecular sieve TS-1 with good mass transfer characteristics and high skeletal titanium content without anatase TiO_2 is the key to its industrial application. In order to enhance the mass transfer characteristics of TS-1, post-treatment of hydrothermally synthesised TS-1 with alkali is the most common method used in industry [11]. Although this method can etch secondary pore channels in TS-1 crystals and improve the utilisation of active sites inside the molecular sieve crystal, it usually reduces the hydrothermal stability of TS-1 and produces anatase TiO_2 . based on the conventional alkali post-treatment, Lin Min et al [12] from Sinopec Research Institute invented a new method for the preparation of graded pore TS-1 by tetrapropylammonium hydroxide (TPAOH) post-treatment. The TS-1 parent phase undergoes dissolution and recrystallisation during the post-treatment process, which not only forms closed hollow cavities in the TS-1 crystals, but also the recrystallisation process reinserts the non-skeletal titanium into the molecular sieve skeleton [13-15]. The above method can simultaneously improve the mass transfer performance and skeletal titanium content of TS-1 and has become the mainstream technology for the production of high performance TS-1 in China. However, as the resulting TS-1 has a closed mesoporous structure, the contactable external surface area provided is small and the improvement of the catalytic performance of the large molecules involved in the reaction is limited.

Recently, we [16] proposed a synthetic method for the domain-limited conversion of aged dry gels to synthesise open mesoporous TS-1 with high skeletal titanium content, which gives open mesoporous TS-1 without anatase TiO_2 in one step by treating aged dry gels with a TPAOH solution, obtaining the highest phenol conversion per titanium active site reported in the literature so far in the phenol hydroxylation reaction rate (TOF of 414) in the phenol hydroxylation reaction. Compared to the process based on the TPAOH treatment of the fully crystalline TS-1 powder, which is currently commonly used in the domestic industry, this method omits the process of synthesizing the molecular sieve powder and has the advantage of simplicity of operation and better catalytic performance of the resulting product, which is promising for industrial application. The study of the reaction kinetics of this catalyst is of great importance for its practical application. In this paper, the intrinsic kinetics of the catalytic reaction of phenol with H_2O_2 for direct hydroxylation of benzenes was investigated. The effects of stirring rate, reactant concentration and temperature on the reaction were investigated, and the corresponding kinetic parameters were derived. The kinetic equations were obtained using a

power function equation fitting method, which provides a theoretical basis for the design of a reactor and process for the hydroxylation of phenol to benzenediol based on this new catalyst.

2 Experimental component

2.1 Reagents and instruments

Tetraethyl orthosilicate (TEOS), AR, tetrapropylammonium hydroxide (TPAOH), 25 wt.%, isopropyl alcohol (IPA), AR, hydrogen peroxide (H₂O₂), 30 wt.%, methanol, AR, acetone, AR, Sinopharm Chemical Reagent Co. Esha (China) Chemical Co.

X'Pert multi-purpose X-ray diffractometer, PANalytical, The Netherlands; Agilent 8890 gas chromatograph, Agilent Technologies Ltd.; 3Flex fully automatic physisorption analyzer, Micromeritics, USA; Tecnai G2 F20 high-resolution transmission electron microscope (TEM), Philips-FEI, The Netherlands; Apreo field emission scanning electron microscope, Thermo Fisher Scientific, USA; JASCO V-770 UV-Vis spectrometer, Japan Spectroscopy Co.

2.2 Catalyst preparation

The TS-1 catalyst was synthesized according to the aging dry gel limited domain conversion method proposed by the group [16], the molar composition of the precursor was 1.0SiO₂: 0.025TiO₂: 0.33TPAOH:0.83IPA: 30H₂O. After clarification and transparency, the solution was stirred and added dropwise to the mixture of TBOT and IPA for 30 min and then aged at 90 °C under condensation and reflux for 24 h. After aging, the solution was transferred to an oven at 100 °C and dried for 48 h until the solution became dry and the quality of the solution did not change. An appropriate amount of the ground dry gel was then transferred to a PTFE-lined autoclave (100 mL) together with 0.1 mol/L TPAOH aqueous solution and crystallised at 170 °C for 11 h. After crystallisation, the solution was washed by centrifugation and dried overnight in an oven at 100 °C. After drying, the samples were calcined in air at 550 °C for 6 h (heating rate 1 °C/min) to obtain an open mesoporous TS-1 sample without anatase and with the highest theoretical titanium skeleton content, denoted ST-20-0.1-11H.

2.3 Material characterisation

2.3.1 X-ray diffraction spectroscopy testing (XRD)

An X-ray diffractometer (D8 A) was used to characterise the physical phase composition and structure of the samples. The target material was Cu, the tube voltage 40 KV, the tube current 30 mA and the scanning range 5 ~ 50°.

2.3.2 Transmission electron microscopy (TEM)

A transmission electron microscope was used to observe the microscopic morphology of the samples and to analyse them. The working voltage was 200 KV.

2.3.3 Ultraviolet-visible spectroscopy test (UV-vis)

A UV-Vis absorption spectrometer was used to characterise the Ti coordination state in the sample. The scanning range was 200 ~ 700 nm with a resolution of 2 nm.

2.3.4 Pore structure and pore size distribution tests

The pore structure and pore size distribution of the samples were characterised using an N₂ physisorber. The test temperature was -196.15 °C and the samples were degassed at 350 °C for 8 h prior to analysis.

2.4 Phenol hydroxylation reactions

The main reaction for the TS-1-catalyzed synthesis of phenol into hydroquinone is shown in Figure 1:

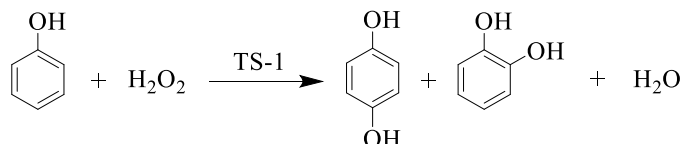


Figure 1. The main reaction of TS-1 catalyzed phenol synthesis of hydroquinone

The reaction was carried out in a 50 mL double-necked round-bottom flask equipped with a reflux condenser. The catalyst, solvent (deionised water) and phenol were added sequentially, heated to a set temperature in a constant temperature oil bath and maintained for a period of time, then a measured amount of H₂O₂ was added at one time, and samples were taken for analysis at regular intervals after the reaction had started. The intrinsic kinetics of the phenol hydroxylation reaction was investigated by controlling for variations in single factors such as catalyst dosage, phenol concentration, H₂O₂ concentration and temperature. The initial rate method [17] was used to find the initial conversion rate of phenol as the reaction proceeded and the product, benzenediol, continued to be deeply oxidised and the product was extremely complex.

The products were analysed by gas chromatography (GC Agilent 8890) equipped with a 30m capillary column (HP-5) and an FID detector.

2.5 Dynamical models

The power function kinetic equation is simple in form and can visualise the effect of factors such as reactant concentration and reaction temperature on the reaction rate with fewer parameters, therefore the power function equation is used to fit the experimental data in this paper.

The main reaction rate equation for the phenol hydroxylation reaction is expressed as follows:

$$r = -\frac{dc(\text{Phenol})}{dt} = kc^{\alpha}(\text{Phenol})c^{\beta}(\text{H}_2\text{O}_2) \quad (1)$$

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

3 Results and Discussion

3.1 Analysis of the physicochemical properties of the catalyst

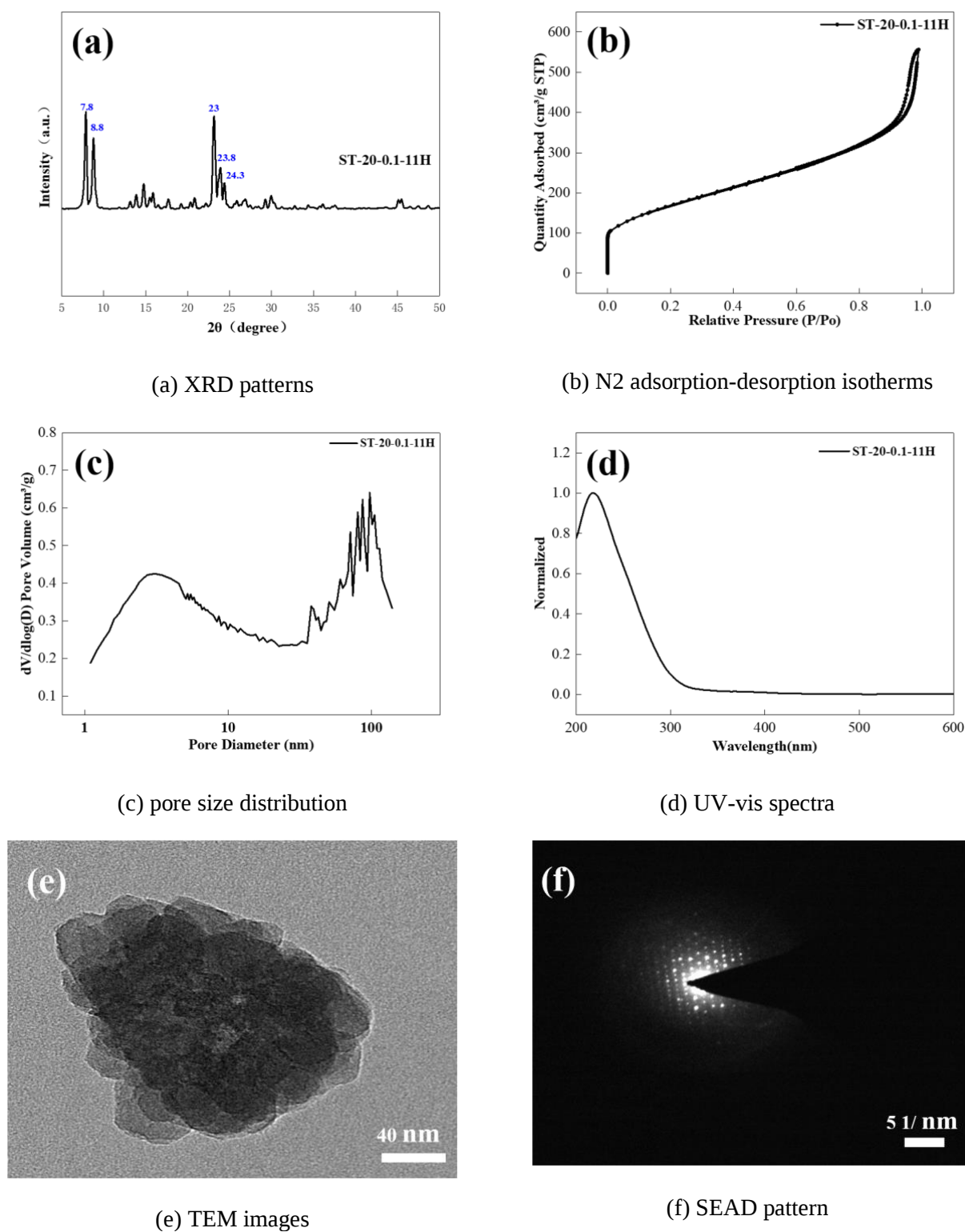


Figure 2. ST-20-0.1-11H

Table 1. Compositions and structure properties of ST-20-0.1-11H.

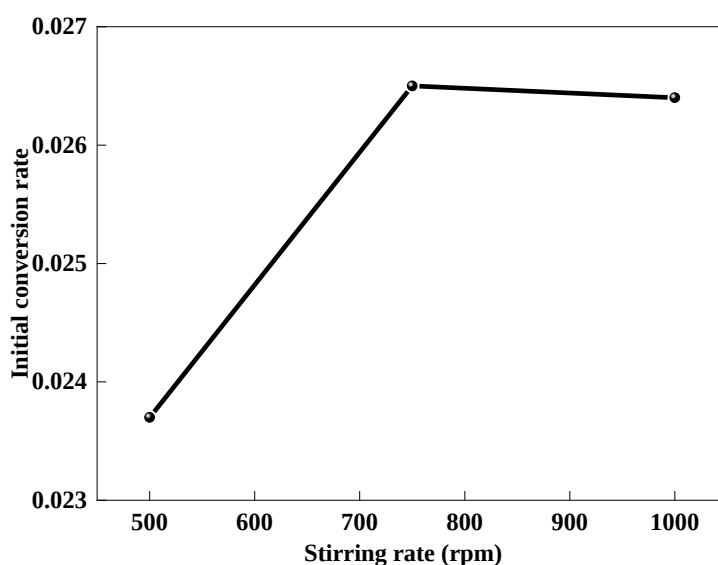
	Si/Ti ^a	Ti wt.% ^a	$S_{\text{BET}}^{\text{b}}$ (m ² /g)	$S_{\text{micro}}^{\text{c}}$ (cm ³ /g)	$V_{\text{meso}}^{\text{d}}$ (cm ³ /g)
ST-20-0.1-11H	39	2.0	608	0.15	0.71

^a by ICP; ^b by the BET method; ^c by the t-plot method; ^d by the BJH method (using the adsorption isotherm)

As shown in Figure 2a, the main characteristic diffraction peaks of 2θ at 7.8° , 8.8° , 23° , 23.8° and 24.3° can be observed in the XRD pattern of the sample, corresponding to the (011), (200), (051), (033) and (133) crystal planes, respectively, indicating that the sample has a typical MFI structure. From the N₂ sorption and desorption curves (Figure 2b), it can be seen that the sample has a Type IV isothermal curve with a significant increase in nitrogen adsorption in the medium pressure region ($0.2 < P/P_0 < 0.8$) and a significant hysteresis loop can be observed in the high pressure region ($0.8 < P/P_0 < 0.99$) with mesopores in the surface molecular sieve crystals. From the BJH pore size distribution diagram (Figure 2c), it can be seen that the mesopores are distributed in the range of 1 ~ 10 nm. The external surface area and mesopore volume of the samples were 309 m²/g and 0.71 cm³/g respectively (see Table 1). The UV-vis spectrum of the sample (Figure 2d) shows a strong absorption band at 210 nm and essentially no absorption at 310 nm, indicating that the coordination of titanium in the sample is tetra-coordinated skeletal titanium. The elemental composition of the sample was analysed by ICP and the resulting sample had a silicon-to-titanium ratio of 39 and a titanium atomic mass percentage of 2 wt.% (see Table 1), which is consistent with the highest tetra-coordinated skeletal titanium Ti content that TS-1 molecular sieves can have [18]. It is clear from the TEM (Figure 2e) image that the sample is formed by the assembly of small crystals in the range of 20 ~ 30 nm, and the SEAD (Figure 2f) indicates that the sample has a single crystal structure. In summary, the analysis shows that ST-20-0.1-11H is an essentially anatase free TS-1 with the highest theoretical skeletal Ti content and open mesopores.

3.2 Factors influencing catalytic performance

3.2.1 Elimination of outward diffusion

**Figure 3.** Effects of stirring-rate on initial conversion rate of phenol

The TS-1-catalyzed phenol hydroxylation reaction is a liquid-solid reaction where mass transfer between the two phases affects the reaction rate, so the effect of internal and external diffusion must

be eliminated when performing the reaction intrinsic kinetics. The resistance to the effect of external diffusion is concentrated in the hysteresis layer on the outer surface of the solid catalyst and can be eliminated by varying the speed of the reaction [19]. Controlling other reaction conditions constant, the initial conversion rate of phenol was measured for reactions at different stirring rates (500 rpm, 750 rpm and 1000 rpm) and the results are shown in Figure 3. When the stirring rate was higher than 750 rpm, the phenol conversion rate no longer changed, indicating that the effect of external diffusion had been largely eliminated. Therefore, the stirring speed for this work was set at 750 rpm.

3.2.2 Elimination of internal diffusion

The main factor affecting the rate of internal diffusion is the catalyst particle size. The average particle size of the TS-1 catalyst used in this experiment was about 150 nm, and the Mears criterion [20] can be used to determine the effect of internal diffusion for small particle sizes. Meanwhile, both Lu Changjuan [19] and Tyablikov [21] investigated the effect of internal diffusion in the hydroxylation reaction of phenol with TS-1 molecular sieve particle size and found that the Thiele modulus was much smaller than $(1/n)$ for molecular sieves with particle size around 200 nm. Therefore, the effect of internal diffusion can be neglected.

3.2.3 Effect of phenol concentration

The effect of phenol concentration on the reaction rate was first investigated. The initial reaction rate was measured at different concentrations of phenol, holding other reaction conditions constant. The results are shown in Table 2. It was found that as the phenol concentration increased, the initial reaction rate of phenol increased similarly and the reaction was characterised as a primary reaction.

Table 2. Phenol concentration and initial reaction rate

c(Phenol)/(mol/L)	r/(mol/L·min)
0.4962	5.54×10^{-3}
0.9924	1.076×10^{-2}
1.5878	2.342×10^{-2}
1.985	2.548×10^{-2}
2.3817	3.075×10^{-2}
2.9771	3.397×10^{-2}

At the beginning of the reaction, $c(\text{H}_2\text{O}_2)$ is constant, so that $k_m = kc^\beta(\text{H}_2\text{O}_2)$, then the reaction rate equation (1) can be expressed as

$$r = k_m c^\alpha(\text{Phenol}) \quad (3)$$

Taking the logarithm of both sides yields

$$\ln r = \ln k_m + \alpha \ln c(\text{Phenol}) \quad (4)$$

The data in Table 2 were substituted into equation (4) and plotted against $\ln c(\text{phenol})$ against $\ln r$. The results are shown in Figure 4. The slope of this fitted line is the number of reaction steps α . From the results in Figure 4, it is known that $\alpha = 1.07$, i.e. the number of reaction steps for this TS-1 catalyzed phenol hydroxylation reaction for phenol is 1.07.

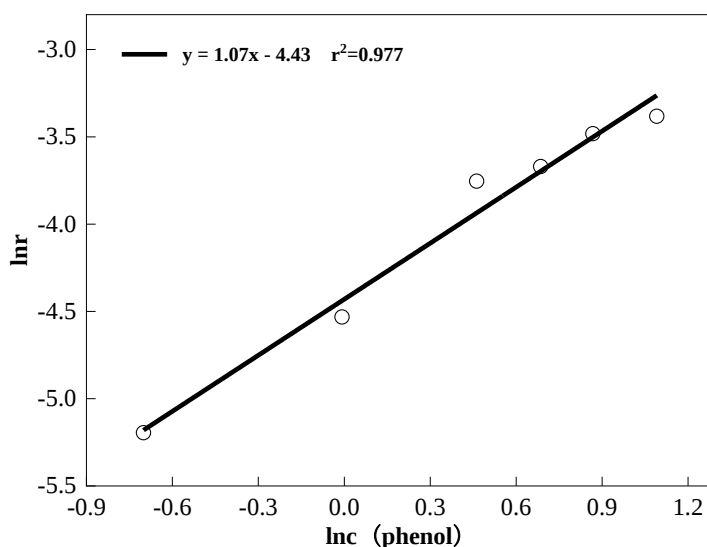


Figure 4. Effect of phenol concentration on initial reaction rate

3.2.4 Effect of H₂O₂ concentration

Similarly, the effect of H₂O₂ concentration on the reaction rate was investigated. Fixing other reaction conditions constant, the initial reaction rates were measured over a range of different H₂O₂ concentrations. The results are shown in Table 3. It was found that the initial reaction rate increased with increasing hydrogen peroxide concentration, but the range of variation was small and the reaction characteristics were close to that of a zero-level reaction.

Table 3. Hydrogen peroxide concentration and initial rate of reaction

c(H ₂ O ₂)/(mol/L)	r/(mol/L·min)
0.5926	2.64×10^{-2}
0.8642	2.74×10^{-2}
1.1935	2.82×10^{-2}
1.7696	2.95×10^{-2}

Similarly, let $k_n = kc^\alpha(\text{Phenol})$, then the reaction rate equation (1) can be rewritten as:

$$r = k_n c^\beta(\text{H}_2\text{O}_2) \quad (5)$$

Taking the logarithm of both sides yields:

$$\ln r = \ln k_n + \beta \ln c(\text{H}_2\text{O}_2) \quad (6)$$

The data in Table 3 were substituted into equation (6) and plotted against $\ln c(\text{H}_2\text{O}_2)$ against $\ln r$. The results are shown in Figure 5. The slope of this fitted line is the reaction step β . From the results in Figure 5, we can learn that $\beta = 0.10$, i.e. the reaction step of this TS-1 catalyzed phenol hydroxylation reaction for H₂O₂ is 0.10.

Combining the above analysis, the rate equation for this reaction can be expressed as

$$r = kc^{1.07}(\text{Phenol})c^{0.10}(\text{H}_2\text{O}_2) \quad (7)$$

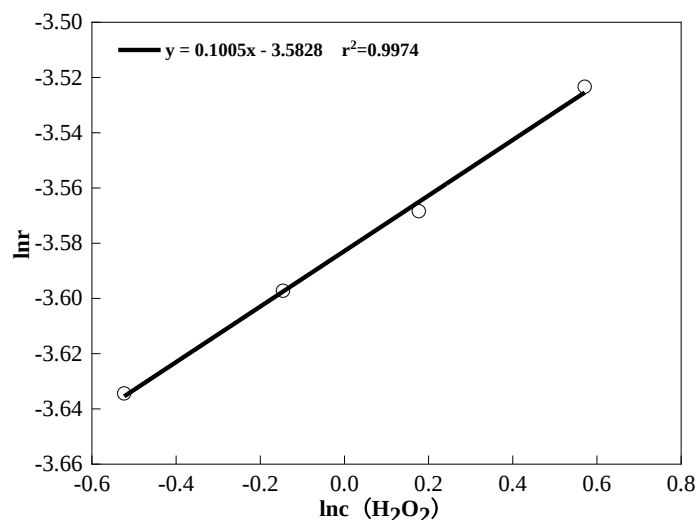


Figure 5. Effect of hydrogen peroxide concentration on initial reaction rate

3.2.5 Relationship between catalyst dosage and reaction rate

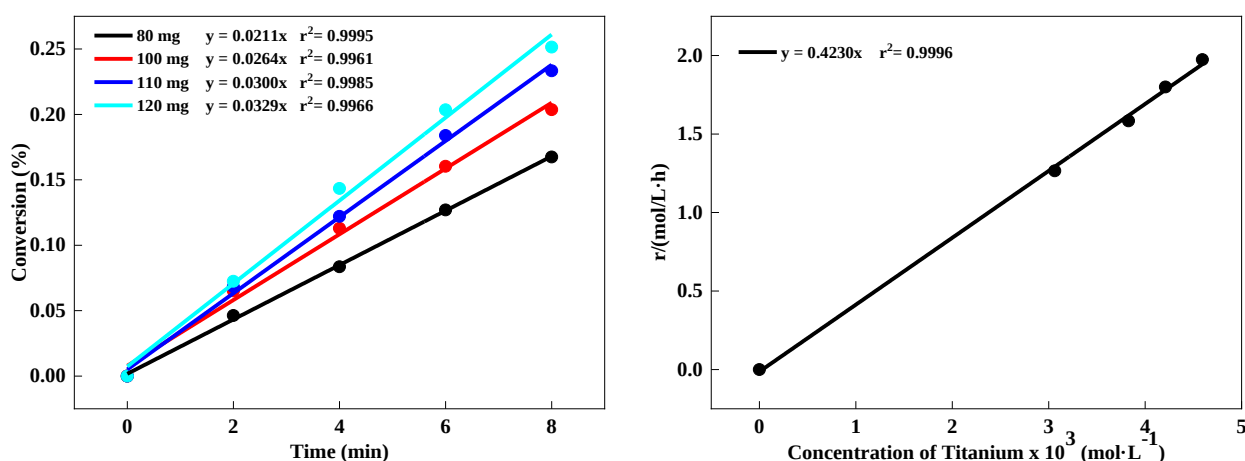


Figure 6. Reaction rate constant versus the amount of catalyst

Fixing other conditions constant, the effect of catalyst dosage on the reaction rate was investigated. The results are shown in Figure 6, with the increase of catalyst dosage, the initial reaction rate of phenol hydroxylation reaction increased significantly. The above results show that the conversion rate of the phenol hydroxylation reaction has a first order dependence on the catalyst dosage when the concentration of phenol and hydrogen peroxide is certain.

3.2.6 Relationship between temperature and reaction rate

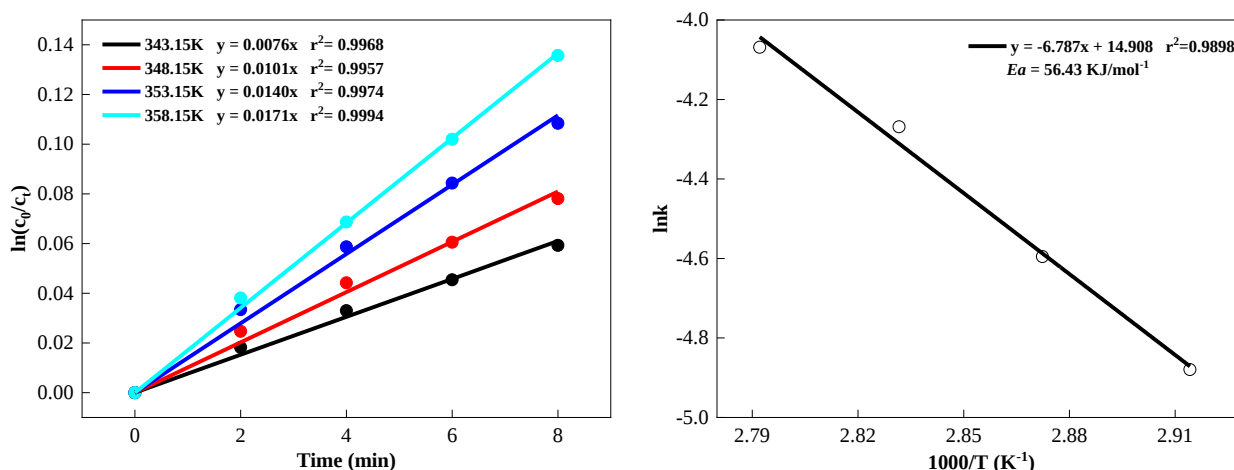


Figure 7. Reaction rate constant versus temperature

As shown in Figure 7, the reaction temperature has a significant effect on the initial reaction rate. The slope of the line is the apparent rate constant k . The apparent rate constant k obtained for different temperatures is plotted against the reaction time t using $\ln(c_0/c_1)$ and increases in the following order: 343.15 K < 348.15 K < 353.15 K < 358.15 K, indicating that the reaction follows pseudo-first order kinetics [22]. The apparent activation energy E_a of the reaction was calculated from the Arrhenius formula to be 56.43 kJ/mol, with a pre-factor $A = 2.98 \times 10^6$, further revealing that the reaction is kinetically controlled. Compared to the activation energy reported by Klawekla et al [23] for the catalytic hydroxylation of phenol using the fully crystalline raw powder TS-1 as a catalyst (E_a of 63.5 kJ/mol), the TS-1 catalyst used in this experiment catalyzed the hydroxylation of phenol with a lower value of activation energy, indicating that the reaction proceeded more easily and the initial reaction rate of phenol was faster, suggesting that the catalyst had superior catalytic performance.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (8)$$

Substituting all the data into equations (1) and (2), the regression equation for the phenol hydroxylation reaction can be derived as:

$$r = 2.98 \times 10^6 \exp\left(-\frac{56.43 \times 10^3}{RT}\right) c^{1.07}(\text{Phenol}) c^{0.10}(\text{H}_2\text{O}_2) \quad (9)$$

3.3 Model validation

In order to verify the accuracy of the empirical kinetic equations and regression parameters, it was necessary to compare the model calculated values with the experimentally measured values and the results are shown in Figure 8. It can be seen from the figure that the model calculated reaction rate values are in relatively good agreement with the actual measured values, with an average relative error of 5.95 %. Therefore, it can be concluded that within the experimental range, the intrinsic kinetic equation (9) derived in this paper can well describe the reaction characteristics of TS-1 molecular sieve catalysed phenol preparation of benzenes.

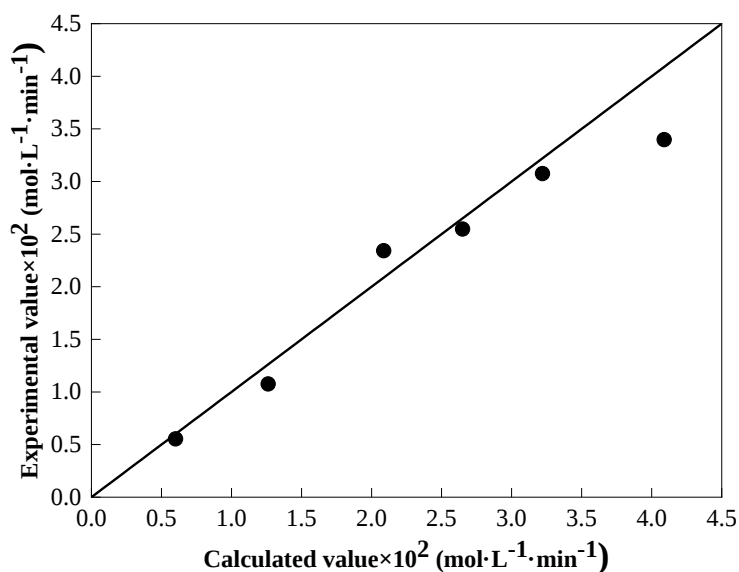


Figure 8. Comparison between calculated and experimental initial reaction rate of phenol

4 Results and Discussion

In summary, a new anatase-free TS-1 catalyst with the highest theoretical skeletal titanium content and open mesopores was prepared by the TPAOH post-treatment aging dry gelation method, and the intrinsic kinetics of the catalytic hydroxylation reaction of phenol with H_2O_2 was investigated, and it was found that:

- 1) When TS-1 was used as the catalyst for the phenol hydroxylation reaction with a controlled stirring speed greater than 750 rpm and an average catalyst particle size of 150 nm, the effect of internal and external diffusion was largely eliminated.
- 2) The initial reaction rate of the phenol hydroxylation reaction catalyzed by TS-1 accelerated with increasing reactant concentration and increased with increasing temperature. In the experimental range, the reaction is a 1.07 level reaction for phenol and a 0.1 level reaction for hydrogen peroxide, with an activation energy E_a of 56.43 kJ/mol.
- 3) The intrinsic kinetic equation for the TS-1 molecular sieve-catalyzed hydroxylation of phenol was established in the experimental range as $r = 2.98 \times 10^6 \exp\left(-\frac{56.43 \times 10^3}{RT}\right) c^{1.07}(\text{Phenol}) c^{0.10}(\text{H}_2\text{O}_2)$. The initial rate of phenol production calculated from the kinetic model is consistent with the experimental results.
- 4) This study provides a theoretical basis for the design of a reactor and process for the hydroxylation of phenol to benzenes based on this novel catalyst.

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