Solution combustion synthesis of Co oxide-based catalysts for phenol degradation in aqueous solution

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ABSTRACT

Solution combustion using urea as a fuel was employed to synthesise Co oxide and Al₂O₃-, SiO₂- and TiO₂-supported Co oxide catalysts. The catalysts were characterised using several techniques such as N₂ adsorption/desorption, XRD, FTIR, UV–vis diffuse reflectance and SEM–EDX, and their catalytic activity was evaluated in phenol degradation in aqueous solution with sulphate radicals. Solution combustion is a simple and effective method in preparation of supported Co catalysts. Co₃O₄ was the major Co crystal phase in the samples prepared via the combustion synthesis. Bulk Co₃O₄ particles were not effective in reaction, but supported Co oxides showed higher activity than unsupported Co oxide. The supports influenced Co dispersion and catalytic activity. Co/TiO₂ exhibited the highest activity, but it deactivated much faster than other two supported catalysts. Co/SiO₂ showed a comparable activity to Co/Al₂O₃ and the best stability among the three Al₂O₃-, SiO₂- and TiO₂-supported Co catalysts.

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1. Introduction

Wastewater discharged from various industrial processes contains many pollutants such as particles, organics and heavy metal ions. Many organic compounds are toxic and can cause significant health problem to humans and damage to the eco-environment. Removal of organic toxins can be achieved by several techniques, adsorption, flocculation, membrane separation and chemical oxidation, in which advanced oxidation can achieve complete destruction of organics. Currently, Fenton oxidation using OH radical is most commonly used, being proven a cost-effective advanced oxidation process [1]. However, Fenton reaction suffers from the requirements for acidic pH, large quantity of chemical reagents, large production of ferric hydroxide sludge and very slow catalysis of the ferrous ions generation [2].

Recently, sulphate radical produced by oxone (a patented product by DuPont [3]) has been proposed as an alternative to hydroxyl radical from Fenton oxidation. Co ion was found to be the most active metal ion reacting with oxone for sulphate radical generation [4–7]. However, homogeneous oxidation using Co²⁺/oxone will result in loss of Co and the toxicity of the metal, as cobalt is recognised as a priority aqueous pollutant that can cause several health problems such as asthma, pneumonia and other lung problems [8,9]. Therefore, heterogeneous Co-loading systems are

required. Several investigations have been reported in using Co oxides [10,11], Co²⁺ exchanged zeolites [12] or supported Co catalysts [2,13–17]. It was found that supported Co oxides could show good activity and stability [2,13,15,17].

Solution combustion synthesis is a convenient method to prepare metal oxide and composite nanopowders, which involves a self-sustained combustion reaction between a fuel and a metal precursor [18,19]. Several publications are available on the preparation of the supported catalysts by utilisation of the solution combustion approach [20,21]. However, few investigations reported synthesis of such catalysts in a controllable combustion mode in one step. Dinka and Mukasyan [22] demonstrated that the solution combustion could be used to produce different types of oxide-based supported catalysts. They prepared Al₂O₃- and ZrO₂-supported Fe oxide and tested them in steam reforming of heavy hydrocarbons. While so far, there is no investigation that reports one-step synthesis method for preparing supported Co oxides for the activation of oxone. In this paper, we report the synthesis of supported Co oxide by one-step solution combustion method and their catalytic behaviour in phenol degradation using oxone as an oxidant.

2. Experiment

2.1. Synthesis of Co oxide and supported Co oxide

All chemicals used for catalyst preparation were obtained from Sigma–Aldrich Chemicals. For Co oxide synthesis, 3 g of

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$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich, 99.0%) and 1 g of urea were dissolved in 7 mL of water solution and stirred for 30 min. The solution was then put in a preheated furnace at 773 K for 30 min. For synthesis of supported Co oxide catalysts, 0.3 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 g of urea were firstly dissolved in 7 mL of water and then mixed with 5 g of solid supports, activated $\alpha\text{-Al}_2\text{O}_3$ (99.0%, 105 μm), SiO_2 (99.5%, 12 nm) and anatase TiO_2 (99.5%, 25 nm). All the supports were used as received from Sigma–Aldrich Chemicals without further treatment. The mixture was stirred for 30 min and then put in a furnace at 773 K for 30 min.

2.2. Characterisation of catalysts

The textural structure of catalysts was determined by nitrogen adsorption/desorption at liquid nitrogen temperature. The nitrogen adsorption/desorption isotherm was measured on an Auto-sorb-1 (Quantachrome, USA) at 77 K. The samples were evaporated in vacuum at 473 K for 4 h prior to the adsorption measurements.

The crystalline structure of various samples was analysed using powder X-ray diffraction (XRD). The spectra were obtained on a Bruker D8-advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), with accelerating voltage and current of 40 kV and 40 mA, respectively.

UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was recorded on a Jasco V-570 equipped with an integrating sphere, in which BaSO_4 was used as a reference material. Scanning electron microscopy (SEM), performed on a Zeiss Neon 40EsB FIBSEM, was used to evaluate the morphology, size and texture information of the samples. The integrated energy dispersive X-ray spectroscopy (EDS) was applied to analyse the dispersion of Co in the samples.

2.3. Catalytic decomposition of aqueous phenol

Phenol degradation tests were carried out at 303 K in 1 L glass vessel with 500 mL of phenol solution at 25 mg/L with a constant stirring rate of 400 rpm. Firstly, 0.25 g catalyst was added into the phenol solution for 5 min, and then oxone ($2\text{KHSO}_5 \cdot \text{KH}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, PMS from Aldrich) was added into the solution at 2 g/L. At selected time interval, water sample (1 mL) was withdrawn into a HPLC vial, and 0.5 mL of pure methanol was injected into the vial to quench the reaction. The concentration of phenol was analysed using a Varian HPLC with a UV detector set at $\lambda = 270 \text{ nm}$. A C-18 column was used to separate the organics, while the mobile phase made of 30% CH_3CN and 70% water at a flow rate of 1.5 mL/min was used.

For the recycle test of used catalysts, after each run, the catalysts were collected by filtration and thoroughly washed with distilled water several times, then dried at 353 K for 2 h.

3. Results and discussion

The support of anatase TiO_2 had a S_{BET} of 55 m^2/g with particle size of 25 nm. Activated $\alpha\text{-Al}_2\text{O}_3$ had a particle size of 105 μm , S_{BET} of 155 m^2/g and pore size of 5.8 nm. SiO_2 had a particle size of 12 nm and S_{BET} of 220 m^2/g . Table 1 shows textural properties of Co oxide and supported Co catalysts. Compared with the supported catalysts, Co oxide synthesised by solution combustion method presented low surface area and high pore size. The lower S_{BET} was possibly due to the aggregation of particles. Moreover, supported catalysts had lower S_{BET} than pure supports except for TiO_2 , which had similar S_{BET} to pure Co_3O_4 . For three supported catalysts, Co/TiO_2 and Co/SiO_2 showed similar values in surface area and pore size, while $\text{Co}/\text{Al}_2\text{O}_3$ gave the highest surface area and pore volume.

Table 1

Textural properties of unsupported and supported Co oxide catalysts.

Catalyst	S_{BET} (m^2/g)	V (cm^3/g)	Pore size (nm)	Rate constant ($\text{mg}/\text{L min}$)	R^2
Co_3O_4	52	0.14	5.3	−0.060	0.987
Co/TiO_2	69	0.090	2.6	−0.496	0.963
$\text{Co}/\text{Al}_2\text{O}_3$	89	0.19	4.2	−0.289	0.993
Co/SiO_2	63	0.073	2.3	−0.179	0.991

Fig. 1. XRD patterns of Co oxide and supported Co catalysts.

XRD patterns of unsupported and supported Co oxide catalysts are illustrated in Fig. 1. For unsupported Co oxide, Co_3O_4 is the single crystalline phase. No peaks of CoO or Co_2O_3 were observed. For $\text{Co}/\text{Al}_2\text{O}_3$, crystallites of Co_3O_4 and $\alpha\text{-Al}_2\text{O}_3$ were found as two chemical phases. SiO_2 - and TiO_2 -supported Co oxide catalysts showed only support phase, and no Co oxide peaks could be seen, suggesting that Co oxide was highly dispersed on the supports.

SEM with EDS was used to determine the morphology and chemical phases. SEM images in Fig. 2a–d showed that unsupported Co oxide presented as sponge like particles. $\text{Co}/\text{Al}_2\text{O}_3$ presented in larger aggregates with particle size around 100 μm . Co/SiO_2 presented in irregular shape with particle size of 2–5 μm , while Co/TiO_2 showed as spherical particles with particle size of 0.2 μm . Fig. 2e showed EDX profiles of the catalysts. As shown, unsupported Co oxide presented strong signals of Co. Table 2 lists the chemical compositions of the catalysts in preparation and determined by EDS. It was found that Co/O from EDS was very close to that of Co_3O_4 . For supported Co catalysts, Co signals were also detected with similar intensities, but much weaker than those of unsupported Co oxide. Moreover, the chemical compositions, particularly Co-loadings from EDS, were consistent well to preparation parameters, indicating a good Co dispersion. Higher Co level in $\text{Co}/\text{Al}_2\text{O}_3$ from EDS was due to large particle size ca. 100 μm of the support.

UV–vis diffuse reflectance spectra of four samples are presented in Fig. 3. Unsupported Co oxide presented strong adsorption bands at visible range between 400 and 800 nm. Co^{2+} ions occupy the tetrahedral sites and Co^{3+} ions at octahedral sites. The first band at ca. 400 nm can be assigned to the ligand–metal charge transfer (i.e., $\text{O}^{2-} \rightarrow \text{Co}^{2+}$), while the band at about 700 nm is corresponding to the $\text{O}^{2-} \rightarrow \text{Co}^{3+}$ charge transfer [23,24]. The band peaked at 400 and 700 nm indicates the formation of Co_3O_4 [25], which is confirmed by XRD pattern. For Co/TiO_2 and Co/SiO_2 , two strong adsorption bands maximised at 420 and 720 nm are also attributed to Co_3O_4 , where a migration of Co^{2+} to octahedral sites occurs

Fig. 2. SEM images of Co_3O_4 (a), $\text{Co}/\text{Al}_2\text{O}_3$ (b), Co/SiO_2 (c), Co/TiO_2 (d) and EDS of the prepared catalysts (e).

[26,27]. For $\text{Co}/\text{Al}_2\text{O}_3$, adsorption peaks at 410, 540, 590 and 630 nm were observed, which is different from other two supported catalysts. The peaks at 540, 590 and 630 nm suggested the presence of Co^{2+} in tetrahedral coordination [28,29].

It has been believed that decomposition of $\text{Co}(\text{NO}_3)_2$ in air can produce CoO , Co_2O_3 and Co_3O_4 . A final product is Co_3O_4 . During the process of $\text{Co}(\text{NO}_3)_2$ decomposition, some pre-spinel structure will form with a co-existence of cobaltous ions in tetrahedral and octahedral sites [27]. XRD profiles and UV–vis diffuse reflectance spectra of supported Co catalysts demonstrated that Co_3O_4 was the major Co species and it was highly dispersed on TiO_2 and SiO_2 surface. In solution combustion with urea, decomposition of $\text{Co}(\text{NO}_3)_2$ can be shown in following equation.

Table 2

Chemical compositions of pure and supported cobalt oxides from preparation and EDS characterisation.

Sample	Preparation (at.%)			EDS (at.%)		
Co_3O_4	Co: 42.86		O: 57.14	Co: 41.79		O: 58.21
Co/TiO_2	Co: 0.54	Ti: 32.91	O: 66.55	Co: 0.53	Ti: 27.74	O: 71.74
$\text{Co}/\text{Al}_2\text{O}_3$	Co: 0.42	Al: 39.61	O: 59.97	Co: 0.67	Al: 32.67	O: 66.66
Co/SiO_2	Co: 0.41	Si: 33.02	O: 66.57	Co: 0.44	Si: 30.84	O: 68.72

(Please be noted that NO_2 is a toxic gas and the reaction needs to be carried out with good ventilation.)

Fig. 4 shows phenol degradation with time on various Co catalysts. Unsupported Co oxide showed slow degradation of phenol,

Fig. 3. UV-vis diffusion reflectance spectra of Co oxide and supported Co catalysts.

Fig. 4. Catalytic degradation of phenol on Co-based catalysts.

and the phenol degradation was about 50% in 4 h. However, supported Co oxides generally presented higher phenol degradation. Co/TiO₂ could degrade phenol at 100% in 50 min, while Co/SiO₂ exhibited slower phenol degradation than Co/Al₂O₃, achieving 100% degradation in 150 min.

Yang et al. [13] used an impregnation method to prepare supported Co oxide catalysts and studied the effect of support (Al₂O₃, SiO₂ and TiO₂) on heterogeneous degradation of 2,4-dichlorophenol in water using oxone. They found the activity follows the order of Co/SiO₂ > Co/TiO₂ > Co/Al₂O₃, which is due to the different metal-support interaction. Zhang et al. investigated MgO-, ZnO-, Al₂O₃-, ZrO₂-, TiO₂- and SBA-15-supported cobalt oxide with oxone for the degradation of organic dyes in dilute solutions [17]. They reported that Co/MgO showed the best activity, which can be attributed to basicity of the support and hydroxyl groups.

In this investigation, it has been shown that supported Co catalysts exhibited higher activity than unsupported Co oxide. XRD patterns showed that Co oxide was highly dispersive on SiO₂ and TiO₂, which would provide more sites for the activation of oxone for sulphate radical production. No correlation was observed between the catalytic activity and the BET surface area or particle size of catalysts, suggesting the physical properties would not be the major factors influencing catalytic activity. In general, homogeneous oxone activation for sulphate radical generation and phenol degradation could be shown in following reactions.

Fig. 5. Multiple tests of supported Co catalysts in phenol degradation. (a) Co/TiO₂, (b) Co/Al₂O₃ and (c) Co/SiO₂.

From Eqs. (3), and (4), it is seen that basic surface promotes the activation of permonosulphate by consuming H⁺. It is generally believed that the acidity of oxide supports follows the order of SiO₂ > Al₂O₃ > TiO₂. Thus, it is deduced that Co/TiO₂ exhibited the highest activity due to the high dispersion of Co oxide and high basicity of TiO₂.

Table 3

Reaction rate constant of phenol degradation on Co-based catalysts.

Catalyst	Rate constant (mg/L min)			Regression coefficients		
	First run	Second run	Third run	First run	Second run	Third run
Co/TiO ₂	−0.496	−0.169	−0.085	0.963	0.992	0.970
Co/Al ₂ O ₃	−0.289	−0.170	−0.066	0.993	0.982	0.984
Co/SiO ₂	−0.179	−0.140	−0.0914	0.991	0.991	0.988

From the curves shown in Fig. 4, it was found that phenol degradation showed almost linear correlation with time, suggesting that phenol degradation followed zero-order kinetics. Table 1 shows the rate constant values and regression coefficients. As seen, the regression coefficients are high (>0.96), suggesting a good fit to the zero-order model. We have investigated the kinetics of heterogeneous activation of oxone by different Co catalysts for phenol degradation and found that zero-order or first-order kinetics could occur depending on the catalyst systems [9,12,15,16]. Zeolite and SiO₂ supported Co oxide presented zero-order kinetics, while activated carbon supported Co oxide showed the first-order kinetics, which is due to strong adsorption of phenol on carbon support.

In heterogeneous Co oxide catalysts with oxone system, the redox cycle of Co oxide in Co₃O₄ will play the role for the activation of oxone. Due to the slow surface reaction between Co₃O₄ particles and oxone, production of sulphate radicals is the controlling step for phenol degradation and the effect of phenol concentration in solution will not be important, making phenol degradation showing as zero-order kinetics.

Fig. 5 further demonstrates the performance of Al₂O₃-, SiO₂- and TiO₂-supported catalysts in three-run tests. The supported Co catalysts presented different behaviour in recycling tests. Co/TiO₂ showed a fast deactivation in three performances. Phenol degradation was reduced from 100% to 34% in the second and further to 18% in the third run at 45 min. Co/Al₂O₃ also showed deactivation but at a lower rate. At 90 min, phenol degradation could be reduced from 93% to 55% in the second run and 32% in the third run. Compared with the above two catalysts, Co/SiO₂ presented much stable activity in phenol degradation. The phenol degradation was changed from 99% at 150 min to 83% in the second run and 63% in the third run. Based on the zero-order kinetics, the rate constants for the tests are given in Table 3. As shown that the reduction in rate constants in phenol degradation would follow an order of Co/TiO₂ > Co/Al₂O₃ > Co/SiO₂.

4. Conclusion

Synthesis of supported Co catalysts was achieved using a one-step solution combustion method. Catalytic activity of the supported Co oxide presents better performance than unsupported Co oxide. The order of catalytic degradation of phenol on supported Co catalysts followed Co/TiO₂ > Co/Al₂O₃ > Co/SiO₂; however, Co/SiO₂ exhibited better stable performance than the other two cata-

lysts. The catalytic activity could be related to acid–base property of supports and Co oxide dispersion on the supports.

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