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Short Communication

Photocatalytic hydroxylation of phenol with Fe–Al-silicate photocatalyst: A clean and highly selective synthesis of dihydroxybenzenes

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ABSTRACT

Photocatalytic hydroxylation of phenol to catechol and hydroquinone in liquid phase over a novel heterogeneous photocatalyst Fe–Al-silicate was investigated with the assistance of UV irradiation at 365 nm at room temperature. The catalyst was characterized by BET, BJH, FT-IR, UV–vis DRS and XRD. The effects of various parameters (types and amount of co-solvent, amount of catalyst, reaction time and amount of H_2O_2) on photocatalytic hydroxylation of phenol were studied to explore the better reaction conditions. In this study, phenol conversion could reach high up to 64.9%, with a total selectivity of 95% and the yield of 39.3%, 22.3% for catechol and hydroquinone, respectively.

1. Introduction

The application of photocatalytic reactions to organic synthesis has attracted interest because of recent developments in environmentally benign synthetic processes. Notably, TiO_2 photocatalytic reactions for organic synthesis have recently been the subject of many reports [1–5]. It is widely accepted that •OH radicals can be generated on illuminated nanometer TiO_2 surfaces, which are considered to be efficient electrophillic substitution agents. Furthermore, the processes using H_2O_2 as oxidant are considered to be the better foreground technique, due to the easy acquirement of their feed, mild reaction condition, and water as main by-product without the environmental pollution.

The selective and one-step hydroxylation of phenol by H_2O_2 is an attractive and challenging subject from economical and environmental point of view. The dihydroxybenzenes viz. catechol and hydroquinone are two important products of phenol hydroxylation, widely used as photographical chemicals, antioxidants, polymerization inhibitors, pesticides, flavoring agent and medicine [6].

The choice and reaction conditions of catalysts are very important in the phenol hydroxylation using H_2O_2 as oxidant. Several attempts were made for this reaction using heterogeneous catalysts [7–16]. K. M. Parida [17] studied the phenol hydroxylation over molybdovanadophosphoric acid modified zirconia, and giving 49% conversion and 61% selectivity. V. Rives et al. [18] studied the phenol hydroxylation over CoNiAl ternary hydrotalcites, and the maximum conversion of phenol was 14.2%. K.M. Parida et al. [19] developed the Fe(III) salicylamide immobilized on MCM-41 for hydroxylation of phenol, and the highest conversion can reach 64.6% at 80 °C. However, all of the above reactions are thermocatalysis which requires high energy, and accompanies with the generation of undesirable by-products.

Samia Azabou et al. [20] studied the liquid-phase photooxidation of tyrosol to hydroxytyrosol via a new Fe–Al-montmorillonite photocatalyst, and the yield of hydroxytyrosol can reach 64.36%. In this study, a new type of photocatalyst based on silicate (Fe–Al-silicate) was prepared and characterized with a goal to effective utilizing in photocatalytic organic synthesis of dihydroxybenzenes from phenol. The catalyst showed high activity and selectivity on photocatalytic phenol hydroxylation, which was then pursued under various parameters in attempts to find the optimal reaction conditions, as well as to establish related fundamental studies for a future clean industrial application.

2. Experimental

2.1. Preparation of the catalyst (Fe–Al-silicate)

The silicate inorganic gel (the product brand is SMF-LV) is provided by Fenghong New Material Company (China). Its general formula is $(Mg, Na, Li, F)_3Si_4O_{10}(OH)_2 \cdot nH_2O$, which consists of SiO_2, (55–57)%; MgO, (23.5–25.0)%; Na_2O, (2.8–3.8)%; Li_2O, (1.2–1.5)%; and F, (5–5.8)%.

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Fe–Al-silicate was readily obtained by ion adsorption process according to the following procedure. 1.22 g of $FeCl_3 \cdot 6H_2O$ and 0.2 g of $AlCl_3$ ($mol_{Fe3+}/mol_{Al3+} = 3:1$) were mixed into 100 mL of H_2O with stirring until absolutely dissolved. 1.5 g of silicate was added to the above solution. Then 0.2 mol/L of NaOH (50 mL) solution was slowly added to the solution at 70 °C under stirring. After being aged for 24 h, the catalyst was washed with distilled water until total elimination of Cl^-, then dried in the oven at 60 °C and finally calcined at 500 °C for 5 h.

The sample Fe–Al was prepared by the same process above, but no silicate addition for the contrast test.

2.2. Characteristic of the catalyst

To determine the crystal phase composition of the Fe–Al-silicate, we carried out X-ray diffraction (XRD) measurements using a PANAalytical X'pert Por X-ray diffractometer with Cu Kα radiation. The diffraction spectrum was recorded in the 2θ range of 10–90° in steps of 0.017°. FT-IR spectra were recorded on NICOLET 380 (Thermo) using the KBr pellet technique. The specific surface area (BET method), and average pore diameter (BJH method) of the catalysts were determined by nitrogen adsorption–desorption isotherms using Quantachrome NOVA-2000 sorption analyzer, and the samples were analyzed at 77 K by nitrogen adsorption–desorption. The UV–vis diffuse reflectance spectra (UV–vis DRS) were performed with a Lambda 900 UV–vis spectrophotometer (Perkin-Elmer Co.).

2.3. Photocatalytic hydroxylation of phenol and product analysis

The photocatalytic hydroxylation of phenol by H_2O_2 was carried out in a standard photocatalytic reactor which consists of two parts: a pyrex glass cylindrical reactor (160 mL) with an outer jacket and a 125 W high pressure Hg lamp (main emission wavelength is 365 nm) placed parallel to the reactor as a light resource. The following solvents and reagents were used as purchased: phenol, H_2O_2 (30%), distilled water, and co-solvents (acetonitrile, *t*-butyl alcohol, acetone, acetic acid and methanol).

All the experiments were conducted at ambient pressure and the reaction temperature was kept at 25 ± 1 °C by the continuous circulation of water through the jacket around the reactor. The typical procedure follows. To a suspension of 0.1 g Fe–Al-silicate powder and 0.5 g phenol in 15 mL distilled water, and then added 4 mL acetonitrile as co-solvent, the reaction system was stirred until well mixed. Then 1 mL of H_2O_2 was added to the suspension to start the reaction.

The samples were collected at regular intervals during illumination. Phenol, catechol, and hydroquinone were analyzed with GC (Agilent 6890N) and GC–MS (gas chromatography–mass spectrometry; Hiden HPR20-QIC).

The term of reaction performance was defined as follows:

$$\text{Conversion of phenol} = \frac{\text{mole of phenol reacted}}{\text{initial mole of phenol}} \times 100\%$$

$$\text{Yield of catechol} = \frac{\text{mole of catechol produced}}{\text{initial mole of phenol}} \times 100\%$$

$$\text{Yield of hydroquinone} = \frac{\text{mole of hydroquinone produced}}{\text{initial mole of phenol}} \times 100\%$$

$$\text{Selectivity} = \frac{\text{yield of catechol} + \text{yield of hydroquinone}}{\text{conversion of phenol}} \times 100\%.$$

3. Results and discussion

3.1. Characterization of the catalyst

The XRD of Fe–Al-silicate, silicate and PDF 39-1425 are shown in Fig. 1. The XRD patterns of the prepared photocatalyst give some typical diffractions at $2\theta = 22°$, 28.2°, 31.3°, and 36.1°, which are identical to the typical pattern characteristic of cristobalite-like phase (PDF 39-1425). In addition, the XRD patterns of the catalyst are similar with the raw material silicate, which can infer that the main structure of the catalyst is not changed.

The catalyst is characterized using FT-IR with the goal to further investigate Fe^{3+} and Al^{3+} ions incorporated into the silicate. The FT-IR spectra of Fe–Al-silicate and silicate after calcination are shown in Fig. 2. The sharp and strength peak at 1060 cm^{-1} is the silicate characteristic peak. For Fe–Al-silicate, the peaks at 474 cm^{-1} and 796 cm^{-1} are from the M–OH stretching and M–O–M′ bending modes, wherein M and M′ represent the Fe and Al elements. So we preliminarily infer that the metal elements are incorporated into the silicate. But the main structure of the catalyst was not changed compared with the silicate, which is consistent with the XRD analysis results.

The N_2 adsorption–desorption isotherm and the pore size distribution curve measured from the adsorption branch of nitrogen isotherm by BJH method (inset) of the catalyst are shown in Fig. 3. The composite exhibits mesoporosity with an average pore size of approximately 9 nm and the BET specific surface area is 90 $m^2\,g^{-1}$ when calcined for 5 h at 500 °C. The large specific surface area confirms that the framework of the catalyst has high adsorption ability.

To investigate the optical absorption properties of the catalyst, the UV–vis DRS of the catalyst is measured and the result is shown in Fig. 4. The band gap of Fe–Al-silicate is 3.1 eV, so the absorption edge wavelength (λ_g) of the catalyst is 400 nm matched with the lamp emission (365 nm). It is a benefit for the photocatalytic reaction.

3.2. Preliminary experiments

Fe–Al-silicate can catalyze the phenol to catechol and hydroquinone in the presence of H_2O_2 with the assistance of UV irradiation at the wavelength 365 nm. This oxidation relies on the generation of the powerful oxidant •OH radicals as H_2O_2 reacts with a conduction band electron (Eq. 1) and the redox process in presence of iron ions (Eqs. 2

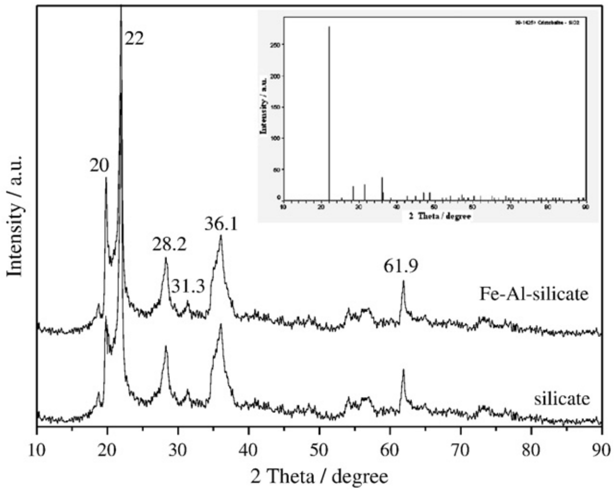


Fig. 1. XRD patterns of Fe–Al-silicate, silicate calcined at 500 °C for 5 h and the PDF 39-1425 (inset).

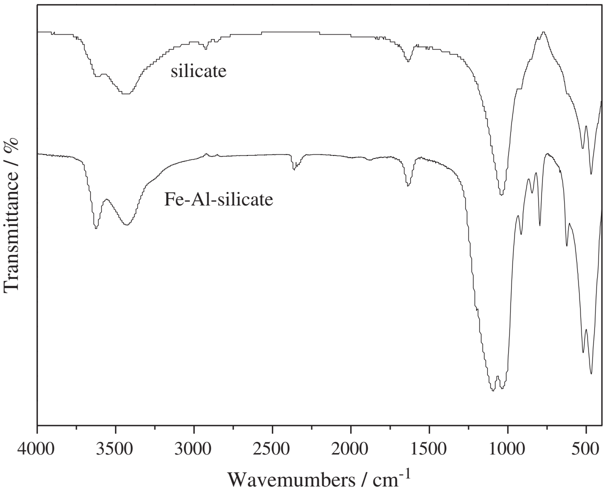


Fig. 2. FT-IR spectra of Fe–Al-silicate and silicate calcined at 500 °C for 5 h.

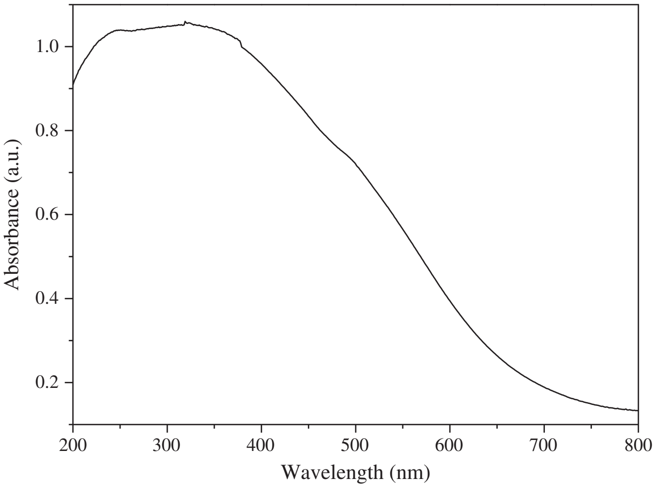


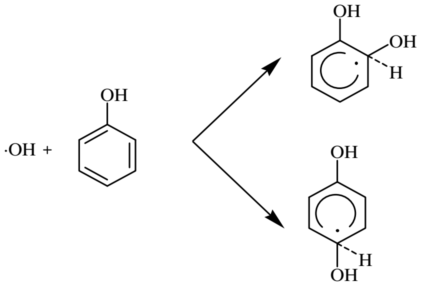
Fig. 4. UV–vis DRS of Fe–Al-silicate calcined at 500 °C for 5 h.

and 3), then phenol can be directly converted into catechol and hydroquinone by reacting with •OH (Eqs. 4 and 5).

$$H_2O_2 + e_{cb}^- \rightarrow \cdot OH + OH^- \quad (1)$$

$$e_{cb}^- + Fe^{3+} \rightarrow Fe^{2+} \quad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (3)$$



(4)

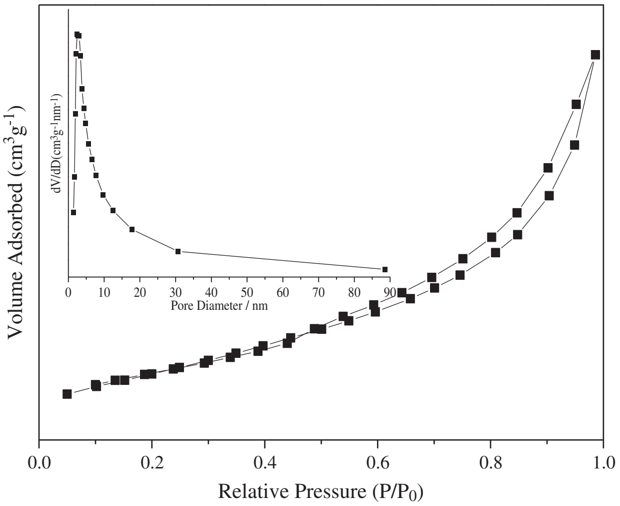
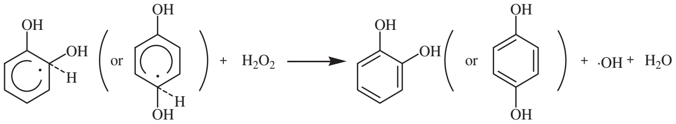


Fig. 3. N_2 adsorption–desorption isotherms and the pore size distribution curve calculated from the adsorption branch of nitrogen isotherm by BJH method (inset).



(5)

Blank controls (without catalyst) and dark controls (without UV irradiation) were run, and no significant catechol and hydroquinone were observed (Table 1). It should be noted that, in the absence of UV irradiation, phenol was not converted to catechol and hydroquinone even with adding excessive H_2O_2.

We also studied the phtotocatalytic hydroxylation reaction of phenol with the Fe–Al sample, but it has no photocatalytic activity with very low conversion, no catechol and hydroquinone production. So the silicate plays an important role for the Fe–Al-silicate in the photocatalytic reaction.

3.3. The effect of co-solvent

Selected solvents such acetonitrile, acetic acid, acetone, *t*-butyl alcohol and methanol as the co-solvent were studied respectively for the photocatalytic hydroxylation of phenol, and the results were shown in Table 2. When *t*-butyl alcohol and acetone were used as co-solvent, only a trace amount of catechol and hydroquinone was detected. Only 8.3% and 5% of phenol was converted, no significant catechol and hydroquinone was observed when acetic acid and methanol were the co-solvent, indicating that acetic acid and methanol surrounding was unfavorable for the reaction. The promotion effect of the co-solvent for the hydroxylation of phenol can be rated according to the following: acetonitrile > none > *t*-butyl alcohol > acetone.

Acetonitrile was a typical solvent in the hydroxylation reaction by thermocatalysis. Table 3 lists the terms of phenol hydroxylation performance with the effects of acetonitrile as a co-solvent. The

Table 1
Hydroxylation of phenol under different conditions.[a]

Entry	Catalyst (g)	UV	Phenol conversion (%)	Yield (%)		Selectivity (%)
				CAT	HQ	
1	No	Yes	31.7	3.4	N.D	10.7
2	0.1	No	8.0	N.D	N.D	–

CAT: catechol; HQ: hydroquinone; N.D: no detected.

[a] Phenol, 0.5 g; water, 15.0 mL; actetonitrile, 4.0 mL; H_2O_2, 1.0 mL; reaction time, 4.0 h.

Table 2
Effect of co-solvents on hydroxylation of phenol.[a]

Co-solvent	Phenol conversion (%)	Yield (%)		Selectivity (%)
		CAT	HQ	
None	72.0	24.5	13.6	52.9
Acetonitrile	64.9	39.3	22.3	95.0
t-butyl alcohol	67.4	3.6	1.9	8.2
Acetone	57.9	1.3	0.8	3.6
Acetic acid	8.3	N.D	N.D	–
Methanol	5.0	N.D	N.D	–

[a] Phenol, 0.5 g; catalyst, 0.1 g; water, 15.0 mL; co-solvent, 4.0 mL; H_2O_2, 1.0 mL; UV time, 4.0 h.

addition of acetonitrile up to 4 mL slightly increased the yield, the conversion of phenol has no obvious changes, but any further addition gradually reduced the conversion and yield. Therefore, 4 mL of solvent was used throughout the remainder of this work. The solvent effect of acetonitrile as co-solvent was in agreement with the results obtained by Park et al. [1], they studied the hydroxylation of benzene with modified TiO_2 photocatalyst and achieved the best yield of phenol with usage of 4 vol.% acetonitrile as co-solvent. Nevertheless, additional introduction of acetonitrile also lead to gradual reduction of yield, which is consistent with our findings in this study. The photocatalytic hydroxylation of phenol by H_2O_2 happened through a hydroxycyclohexadienly (HCHD) radical intermediate which formed by attacks of phenol with •OH radical. Then hydrogen atom abstraction of HCHD radical by oxidants (H_2O_2) gives catechol and hydroquinone subsequently (see Eqs. 4 and 5). The co-solvent of acetonitrile shared the properties of electron acceptor as •OH radical scavenger. Thus, both acetonitrile and phenol compete for •OH radical, which induced the reduction of both conversion and yield by decreasing the amount of •OH at the high concentration of acetonitrile. Nevertheless, herein we found acetonitrile effectively improve the reaction performance of photocatalytic hydroxylation of phenol with proper dosage in the presence of acetonitrile as a co-solvent because it can prevent the phenol in water from volatilization during the reaction [1].

3.4. Effect of reaction time

Table 4 shows the influence of reaction time on the phenol hydroxylation reaction. The reaction occurs similar to Fenton chemistry, through the participation of •OH in activating phenol toward the formation of catechol and hydroquinone accumulation. Longer reaction time directly increased the phenol conversion. During the first 4 h of reaction, accumulation of catechol and hydroquinone was concomitant with the removal of phenol. The yield of catechol and hydroquinone can reach 39.3% and 22.3%, respectively, the highest yields found in this study. Meanwhile, the selectivity can reach 95%. However, the reaction performance data in Table 4 indicated that the product yield and selectivity decreased gradually after 4 h due to the increase of byproducts in the system, which was proposed to be caused by oxidative degradation and mineralization [21,22].

Table 3
Effect of the acetonitrile amount.[a]

Acetonitrile (mL)	Phenol conversion (%)	Yield (%)		Selectivity (%)
		CAT	HQ	
1	67.6	14.9	5.2	29.7
2	69.5	22.0	12.4	49.5
3	65.6	21.3	13.1	52.4
4	64.9	39.3	22.3	95.0
5	53.7	29.1	20.8	92.9
6	51.2	24.8	15.5	78.8

[a] Phenol, 0.5 g; catalyst, 0.1 g; water, 15.0 mL; H_2O_2, 1.0 mL; UV time, 4.0 h.

Table 4
Time dependence of phenol hydroxylation reaction.[a]

Reaction time (h)	Phenol conversion (%)	Yield (%)			Selectivity (%)
		CAT	HQ	CAT/HQ	
1	33.0	3.5	2.1	1.67	17.0
2	46.0	7.8	4.8	1.63	27.4
3	66.5	26.4	16.5	1.60	64.5
4	64.9	39.3	22.3	1.76	95.0
5	66.9	33.4	19.8	1.69	79.5
6	72.3	11.5	6.8	1.69	25.3

[a] Phenol, 0.5 g; catalyst, 0.1 g; water, 15.0 mL; acetonitrile, 4.0 mL; H_2O_2, 1.0 mL.

It should be noted that the phenol conversion after 4 h of reaction (64.9%), in Table 4, was found to be slightly lower than that after 3 h of reaction (66.5%). It is additional evidence of reductive back reaction which happened while HCHD radical meets a conduction band (CB) electron and decreased conversion by regeneration of feed-in phenol [23].

3.5. Effect of the amount of H_2O_2

Table 5 shows that the yield of catechol and hydroquinone can reach up to 39.3% and 22.3%, respectively, as H_2O_2 concentration increases. This could be due to the increase in hydroxyl radical concentration upon photolysis of H_2O_2 (Eq. 1). A further increase of H_2O_2 concentration higher than 1 mL decreases the catechol and hydroquinone production; it was difficult to control the selective oxidation to produce catechol and hydroquinone at a high oxidant concentration. The phenol conversion was increased by a high concentration of oxidant but it decreased the selectivity. H_2O_2 is so reactive and non-selective that oxidative degradation and mineralization are prevalent. Therefore, minimizing unwanted pathways such as oxidative degradation is important to achieve selective hydroxylation.

3.6. Effect of catalyst amount

The influence of the catalyst loading on the conversion, yield and selectivity is illustrated in Table 6. The conversion of phenol increased when continuously increasing the amount of catalyst, but the yield and selectivity decreased when the catalyst loading was increased to 0.15 g. The active catalytic sites may be considered to have responsibility for these phenomena. The oxidation of the organic species adsorbed on the catalyst active sites may be associated with the delays for short reaction time, and the phenol was easy to be oxidized to other products. Therefore, the yield did not increase as adding more catalyst. 0.1 g of the catalyst was the optimum amount for photocatalytic hydroxylation of phenol in this case.

Table 5
Effect of H_2O_2 amount.[a]

H_2O_2 (mL)	Phenol conversion (%)	Yield (%)		Selectivity (%)
		CAT	HQ	
0.5	65.1	15.7	9.8	39.2
0.8	66.2	20.4	14.8	53.2
1.0	64.9	39.3	22.3	95.0
1.2	65.1	22.3	12.6	53.6
2.0	81.3	23.0	11.9	42.9

[a] Phenol, 0.5 g; catalyst, 0.1 g; water, 15.0 mL; acetonitrile, 4.0 mL; UV time, 4.0 h.

Table 6
Effect of catalyst loading.[a]

Catalyst (g)	Phenol conversion (%)	Yield (%)		Selectivity (%)
		CAT	HQ	
0.02	43.8	5.2	1.8	15.9
0.05	57.0	43.7	4.7	84.9
0.10	64.9	39.3	22.3	95.0
0.15	77.8	13.0	4.2	22.1
0.20	90.7	16.5	9.6	28.8

[a] Phenol, 0.5 g; water, 15.0 mL; acetonitrile, 4.0 mL; H_2O_2, 1.0 mL; UV time, 4.0 h.

4. Conclusion

The photocatalytic hydroxylation of phenol in liquid phase with a new type of Fe–Al-silicate was investigated under various conditions. Fe–Al-silicate showed high photocatalytic activity for hydroxylation of phenol. The selectivity, yield of catechol and hydroquinone and conversion of phenol are 95%, 39.3%, 22.3%, and 64.9% respectively. The selectivity of photocatalytic hydroxylation decreased while by-products increased at too long reaction time, large amount of catalyst and H_2O_2. Acetonitrile was found to be an effective co-solvent to facilitate the photocatalytic hydroxylation process. Through an improvement of the photocatalyst with the convenient preparation and cost-effectiveness, environmentally-friendly industrial production of dihydroxybenzenes utilizing photocatalytic techniques could be realized.

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