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Higly dispersed Co sites in highly porous N-doped carbon are highly active for aerobic oxidation of C-H bond to corrosponding ketones under 60 $^{\circ}$ C and 1 atm O₂, which is 41.3 times more active in comparison to ZIF-67-derived Co catalyst.

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Aerobic oxidation of C-H bond under ambient conditions using highly dispersed Co over highly porous N-doped carbon⁺

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Highly dispersed Co sites in highly porous N-doped carbon (Co-NC) were synthesized by high-temperature pyrolysis of Zn/Co bimetallic zeolitic imidazolate framework-8 (Co_xZn_{100-x} -ZIF). Wide characterizations indicated that the pyrolysis atmosphere and temperature play crucial roles in the metal dispersion and pore structure of the resulting materials. A hydrogen treatment at elevated temperatures is found to favour the Zn volatilization and restriction the pore-shrink of the ZIF precursor, thus yielding efficient catalysts with highly dispersed Co, high surface area (1090 m²/g) and pore volume (0.89 cm³/g). When using as a catalyst for aerobic oxidation of ethylbenzene (EB), Co_1Zn_{99} -ZIF-800-H₂ contributes to 98.9 % EB conversion and 93.1 % ketone selectivity at mild conditions (60 °C, 1 atm O₂), which is 41.3 times more active in comparison to ZIF-67-derived Co catalyst. Co-NC is stable and could be reused for four times without obvious deactivation. This catalyst displays good chemoselectivity to the corresponding ketones when using a broad scope of hydrocarbon compounds.

Introduction

The selective oxidation of hydrocarbons is of great importance in the production of valuable building blocks such as alcohols, ketones, aldehydes and epoxides.^{1, 2} Compared with traditional oxidants, undoubtedly, molecular oxygen is the most atom-economical and environmentally benign oxidant. A large number of noble metals, such as Pd, Au, and Ru, are active for aerobic oxidation.³⁻⁸ However, the scarcity and high cost of noble metals hinder their large-scale practical applications. Searching for earth-abundant yet efficient catalysts to replace noble metals has, therefore, become one of the most exciting topics in the aerobic oxidation chemistry.

N-doped carbon materials have attracted much attention due to their feasibility for the selective oxidation with oxygen as the oxidant.⁹⁻¹³ The combination with early transition metals (Co, Fe, Mn, etc.) is believed to be the promising non-noble catalysts owing to their low price and large availability.¹⁴⁻²⁸ The way of activation of the N-doped carbon support is similar to the function of a ligand in homogeneous catalysts, in which the electron density of metal centres can be adjusted by special N species.²³ This electronic effect can be much stronger than any ligand effect and finally promotes the activity of metal NPs for specific catalytic reactions.²¹ Nevertheless, the traditional methods typically do not endow much manipulation over the dispersion of the metal and often results in its severe aggregation, which deteriorates the catalytic efficiency and stability of catalysts. Consequently, these catalysts are required to be operated in organic solvents under high temperatures, a large excess of base additives or high O₂ partial pressures (0.5-3 MPa) in order to achieve a high yield of desired products. These harsh conditions often lead to the over-oxidation of products, environmental pollution, and the risk of explosion.^{24, 25, 29} Therefore, designing highly dispersed active centres that are easily reachable by reactants is highly desirable to solve the above problems and thereby improve their catalytic performance.

Zeolitic imidazolate frameworks (ZIFs), composed of tetrahedrallycoordinated transition metal ions (e.g., Fe, Co, Cu, Zn) connected by N-containing imidazolate linkers, have received a lot of attention since they possess permanent porosity, three-dimensional (3D) structure and diversity of metals and organic linkers.³⁰ Pyrolysis of ZIFs serves as an important route to metal-supported N-doped carbon materials, in which metal species were confined in a CN matrix for recycling.^{17, 19, 31} However, several important issues are still unresolved, such as pore shrinkage and metal aggregation during the pyrolysis, which unfavour the molecular diffusion and trasformation.³² Herein, the bimetal-organic frameworks (Co_xZn_{100-x}-ZIF) were used to tune the spatial distribution of Co in the precursor, thereby realizing the control in dispersion of Co atoms for the final pyrolyzed catalysts (Co-CN). Compared with pyrolization in an Ar atmosphere, the hydrogen-pyrolytic approach leads to a high specific surface area and generates mesoporosity in the N-doped carbon matrix. These Co sites in the mesoporous N-doped carbon matrix

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exhibit superior activity for aerobic oxidation of C-H bond under very mild conditions. The catalysts also displayed abroad versatility and good stability.

Results and discussion

Characterization of Co-based materials



Fig. 1 (a) XRD patterns, (b) nitrogen sorption isotherms, (c) pore size distribution and (d) micropore size distribution of Co_xZn_{100-x} -ZIF materials. The micropore size distribution is calculated using the Horvath-Kawazoe method.

Co/Zn bimetallic ZIF was prepared by mixing of Co(NO₃)₂ and Zn(NO₃)₂ in methanol, denoted as Co_xZn_{100-x}-ZIF. The powder X-ray diffraction (XRD) pattern (Fig. S1) of the bimetallic Co_xZn_{100-x}-ZIF matches well with ZIF-8 and ZIF-67, confirming the successful synthesis of Co, Zn co-doped ZIF structure.³³ Moreover, Both ZIF-8 and Co_xZn_{100-x}-ZIF showed similar type I isotherms with a high nitrogen adsorption capacity at very low relative pressures (Fig. S2),³⁴ Table S1 shows that Co₁Zn₉₉-ZIF processes high surface area (1450 m²/g), similar as ZIF-8 (1410 m²/g) and ZIF-67 (1560 m²/g).

The addition of Co²⁺ can replace a certain proportion of Zn²⁺ sites in ZIF-8. Meanwhile, the Zn²⁺ sites serve as a "fence" to isolate the adjacent Co atoms.³⁴ The XRD patterns show that, utilizing Co₁Zn₉₉-ZIF as a precursor, no peaks characteristic of Co crystals emerged even when the pyrolysis temperature was raised to 800 °C under a hydrogen atmosphere (Fig. 1a). The detected Co contents in the Co_xZn_{100-x}-ZIF-800-H₂ increase with the pyrolysis temperature as measured by ICP-MS due to the loss of C and N from the support (Table S2). The measured Co content of Co₁Zn₉₉-ZIF-800-H₂ is 0.93 %. The aberration-corrected TEM (Fig. 2a and b) and HRTEM (Fig. S3) images of Co₁Zn₉₉-ZIF-800-H₂ show amorphous support, on which white dots can somewhat be identified. Big clusters or nanoparticles were



Fig. 2 (a and b) Aberration-corrected TEM images of Co_1Zn_{99} -ZIF-800-H₂ and (c and d) TEM images of $Co_{10}Zn_{90}$ -ZIF-800-Ar.

not observed. According to the STEM Z-contrast, those white dots are likely heavier than the support, and hence could be the highly dispersed Co atoms. In contrast, considerable Co NPs could be observed in $Co_{10}Zn_{90}$ -ZIF-800-Ar (Fig. 2c and d).

When temperature was raised to 900 °C, the crystallized metallic Co phase was emerged, as confirmed by the appearance of diffraction peaks from metallic Co (Fig. 1a). The presence of Zn plays a pivotal role in the formation of highly dispersed Co species, for which the spatial interval between two Co atoms can be finely controlled.³⁵ For example, Fig. S4 shows that decreasing the Co content would significantly weaken the Co diffractions of $Co_xZn_{100-x^-}$ ZIF-800-Ar, indicating the improved dispersion of Co species in the final N-doped carbon framework when x < 1.0. The low boiling point and high vapor pressure of Zn (bp 907 °C, 1 atm) can be evaporated away at high temperatures, and the removing of Zn²⁺ sites generates free N sites during pyrolysis, which could be beneficial for the formation of highly porous structure.³⁶ As shown in Fig. 1b, under the H₂ atmosphere, although the surface area of Co₁Zn₉₉-ZIF-800-H₂ (1090 m²/g) declines after pyrolysis in comparison to ZIF-8



Fig. 3 (a) Nitrogen absorption isotherms and (b) pore size distribution of Co_1Zn_{99} -ZIF-T-H₂ treated under different temperature.

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Entry	Catalysts	t/h	Conv./%	() OH	\land	TOF/h ⁻¹
1	No catalyst	4	0	-	-	-
2	Co ₁ Zn ₉₉ -ZIF	4	0	-	-	0
3	Co12n99-ZIF-600-H2	4	0	-	-	0
4	Co12n99-ZIF-700-H2	4	11.4	42.1	57.9	10.8
5	Co12n99-ZIF-800-H2	4	79.7	31.1	68.9	63.1
6	Co12n99-ZIF-900-H2	4	90.8	21.8	78.2	55.3
7	Co1Zn99-ZIF-800-Ar	4	44.2	31.4	68.6	50.1
8	ZIF-67-800-Ar	4	89.5	23.8	76.2	1.6
9	Co12n99-ZIF-800-H2	8	98.9	6.9	93.1	39.2
10 <i>^b</i>	Co12n99-ZIF-800-H2	4	0	-	-	-
11 ^c	Co12n99-ZIF-800-H2	4	17.1	30.5	69.5	13.5
12 ^d	Co12n99-ZIF-800-H2	4	33.3	34.3	65.7	26.4
13 <i>°</i>	Co12n99-ZIF-800-H2	4	9.6	14.3	85.7	7.6
14 ^f	Co ₁ Zn ₀₀ -ZIF-800-H ₂	17	57.0	6.5	93.5	424.7

^{*a*} Reaction condition: EB (0.25mmol), catalyst (5mg), H₂O (3mL), TBHP (0.28 equiv.), 60°C, O₂ (1 atm). ^{*b*} No TBHP was added. ^{*c*} Reaction in N₂ atmosphere. ^{*d*} Reaction in air atmosphere. ^{*e*} Hydroquinone was added. ^{*f*} 10 mmol EB (1.06g) was added.

(1410 m²/g), its pore volume keeps almost constant (Table S1), indicating the reserved pore-structure after hydrogen-mediated pyrolysis. In control experiment (Fig. 1b), Ar atmosphere gave rise to Co_1Zn_{99} -ZIF-800-Ar with much lower BET surface area (610 m²/g) and pore volume (0.40 cm³/g). Meanwhile, increasing the Co content in ZIF would aggravate the collapse of the pore structure. For example, $Co_{10}Zn_{90}$ -ZIF-800-Ar and ZIF-67-800-Ar afford low surface area (350 and 260 m²/g) as well as small pore volume (0.51 and 0.44 cm³/g). The BJH pore-size distribution of Co_1Zn_{99} -ZIF-800-H₂ shows two peaks at 1.5 and 100 nm, corresponding to micropore and macropore of Co_1Zn_{99} - and $Co_{10}Zn_{90}$ -ZIF-800-Ar closed obviously, confirmed by the corresponding micropore size distribution curves (Figs. 1c and d).

Table 2 Selectvie oxidation EB with O₂ over Co₂Zn_{100,2}-ZIF catalysts.^a



Fig. 4 (a) Zn 2p and (b) Co 2p XPS spectra of Co_1Zn_{99} -ZIF-800-H₂, Co_1Zn_{99} -ZIF and Co_5Zn_{95} -ZIF.

The metal contents measured by ICP-MS (Table S2) show that the total Zn of Co_1Zn_{99} -ZIF-800-H₂ (6.24 %) is lower than that of Arderived Co_1Zn_{99} -ZIF-800-Ar (9.53 %), indicating that H₂ is favor the evaporation of Zn.³⁷ As showing in Table S1, decreasing the pyrolysis temperature affords samples with low BET surface area (500-800 m²/g) and high Zn content (10-25 %). When the temperature was raised to 900 °C (Fig. 3), Co_1Zn_{99} -ZIF-900-H₂ still afforded high surface area (1100 m²/g) and pore volume (0.88 cm³/g) as well as further expanding of pore size. These results indicate that H₂ atmosphere

accelerates the evaporation of Zn (Table S2 and S3) and favors the mesopore generation (Table S1). These results suggest that controlling catalyst morphology with large surface areas is critical to achieving enhanced catalytic performance.

N1s XPS spectra (Fig. S5) show that, after pyrolysis, most N species are removed as indicated by the dramatically decreased peak intensity (Table S3). The residual imidazole-N could be deconvoluted into four types of N species with binding energy around 398.5, 399.8, 400.8, and 402.3 eV, which can be attributed to pyridinic-N (55.1 at.%), pyrrolic-N (6.1 at.%), quaternary-N (30.0 at.%) and oxidized-N (8.9 at.%), respectively.²⁰ As shown in Fig. 4a, Zn 2p_{3/2} peaks in the XPS spectra of Co1Zn99-ZIF and Co5Zn95-ZIF are located at ~1021.0 eV, which could be assigned to Zn²⁺ that is coordinated with imidazole. After pyrolysis, this XPS peak in Co₁Zn₉₉-ZIF-800-H₂ weakens significantly and shifts to 1021.6 eV, which could be ascribed to oxidized Zn (Zn $^{\delta +})$ that is strongly interacted with N-doped carbon. Co 2p XPS spectrum of Co1Zn99-ZIF (Fig. 4b) shows that nearly no Co signal could be detected, indicating Co2+ ions are mainly embedded in inside the ZIF due to the relatively fast nucleation between Co²⁺ and 2-methylimidazole.^{29,38} After pyrolysis of Co₁Zn₉₉-ZIF at 800 °C, Co₁Zn₉₉-ZIF-800-H₂ affords a relatively strong Co 2p_{3/2} signal at ~780 eV. After deconvolution, nearly no metallic Co could be observed at ~778 eV.

Catalytic property of Co-based catalysts

In a preliminary study, screening of catalysts for EB oxidation using TBHP as the oxidation agent was studied. As presented in Table S4, the ZIF-8 exhibited negligible activity for oxidation compared with the Co-doped catalysts (entry 1), indicating that the activity of Co-based catalysts could largely be ascribed to Co-N-C sites rather than N-C sites (entry 10).²⁹ Especially, for unpyrolysed sample, the oxidation activity was much lower than that of Ar-treated catalysts (entries 1-3). Then, catalysts with different Co-doping demonstrated a significant difference in activity (entries 4-10). It is noted that the Co content increased from the Co_{0.2}Zn_{99.8}-ZIF-800-Ar to the Co₅₀Zn₅₀-ZIF-800-Ar sample, the oxidation activity increased from 1.5 to 75.6

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%. However, further increasing Co content (ZIF-67-800-Ar) decreased the EB conversion obviously to 62.5 %. In order to further demonstrate the activity difference, the turnover frequency (TOF) based on total Co atoms were calculated. As the Co content increased, the catalytic activity increased first and then decreased, the highest TOF (32.2 h⁻¹) was achieved on Co₁Zn₉₉-ZIF-800-Ar catalyst (entry 5).

In order to further explore the effect of pyrolysis atmosphere and temperature, H₂-treated Co₁Zn₉₉-ZIF catalysts were synthesized and tested for catalyzing the oxidation of EB. Interestingly, Co₁Zn₉₉-ZIF-800-H₂ afforded much higher EB conversion (57.4 %) and TOF value (90.9 h⁻¹) than that of the Ar-treated counterpart (32.2 h⁻¹, entry 11). Co₁Zn₉₉-ZIF-400-H₂ and Co₁Zn₉₉-ZIF-600-H₂ had nearly no activity for EB oxidation (entries 12 and 13). Further increasing the temperature to 700 °C brought a boost for oxidation activity (entry 14). When the temperature was raised to 900 °C (entry 15), the TOF decreased slightly to 72.2 h⁻¹. When increasing reaction temperature to 60 °C (Table S5), Co₁Zn₉₉-ZIF-800-H₂ could afford 97.4 % conversion and 94.9 % selectivity at 4h.

The excellent catalytic performance of Co₁Zn₉₉-ZIF-800-H₂ toward EB oxidation with TBHP inspired us to study the aerobic oxidation of EB with readily available oxygen molecular (Table 2). A blank test shows that no EB was transformed when no catalyst was added (entry 1). Similarly, the Co₁Zn₉₉-ZIF and low-temperature-treated Co samples exhibited negligible activity for aerobic oxidation compared with other Co-doped catalysts. Among those catalysts, Co₁Zn₉₉-ZIF-800-H₂ and Co₁Zn₉₉-ZIF-900-H₂ gave conversions of 79.7 and 90.8 % as well as TOF of 63.1 h⁻¹ and 55.3 h⁻¹, respectively (entries 5 and 6). Comparatively, Co₁Zn₉₉-ZIF-800-Ar afforded relatively low conversion (44.2 %) and TOF value (50.1 h⁻¹). When the reaction time was prolonged at 60 °C, Co₁Zn₉₉-ZIF-800-H₂ afforded 98.9% EB conversion and 93.1 % ketone selectivity at 8 h (entry 9).

In control experiments, no EB was transformed when no TBHP was used (entry 10), suggesting that TBHP is functioning as the initiator for EB oxidation.³⁹ When the EB oxidation was carried out in N₂ atmosphere (entry 11), the conversion was found to be only 17.1%. When using air (entry 12) as the alternative of pure O₂, we



Fig. 5 Recycle of Co_1Zn_{99} -ZIF-800-H₂ for selective oxidation of EB with O_2 at low conversion.

Reaction condition: EB (0.25mmol), catalyst (5mg), H_2O (3mL), TBHP (0.28 equiv.), O_2 (1 atm), 60°C, 15 min.

obtained 33.3 % EB conversion. When hydroquinone (entry 13), a free radical scavenger, was added into the reaction system, the

oxidation rate was dropped significantly, which implied that then EB oxidation proceeded through a radical CMain 1630 may 403 FRE oxidation of EB at a gram scale (1.06 g, entry 14) also preceded efficiently in comparison with the small-scale transformation and acetophenone was produced with 93.5% selectivity and 53.3% yield. In fact, in comparison to reports in the literature (Table S6), our Co_1Zn_{99} -ZIF-800-H₂ catalyst has the superior catalytic performance for aerobic oxidation of EB at relatively low temperature.

Table 3 Selectvie oxidation C-H bonds with O_2 over Co_1Zn_{99} -ZIF-800- H_2 .^{*a*}

Entry	Reactants	t/h	Conv./%	Selectivity/%	
1	\bigcirc	8	98.9	\bigcirc	93.1
					6.9
2	\bigcirc	6	95.9		83.0
				С—он	17.0
3	\neg	4	98.4	\prec	61.4
				-	17.9
				но	10.7
4	\bigcirc	4	100	-	62.9
				но-	23.9
				\bigcirc	7.2
5	\bigcirc	8	81.5		71.8
				\bigcirc	27.1
6	\bigcirc	6	94.8	\bigcirc	68.8
				СООН	31.2
7	\bigcirc	4	92.6		58.2
				ОН	23.0
				\bigcirc	5.2
8		6	83.2	R S	47.0
				K → OH	21.2
9	ОН	15	27.8	СССООН	70.1
				\bigcirc	29.9
10	Он	15	28.3	ОН	48.4
				\sim	39.9
				\square	6.7

 a Reaction condition: substrate (0.25mmol), catalyst (0.008mol% Co), $\rm H_2O$ (3mL), TBHP (0.28 equiv.), 60°C, O_2 (1 atm).

The stability and reusability of the Co₁Zn₉₉-ZIF-800-H₂ catalyst were also investigated. Under the studied conditions, the Co₁Zn₉₉-ZIF-800-H₂ catalyst exhibits a EB conversion of 79.7 % after 4 h and can be reused at least four times with EB conversion still above 66 % after the fourth run (Fig. S6). In order to further test the stability of the catalyst, the recycling Co₁Zn₉₉-ZIF-800-H₂ at low conversion (~18%) was carried out. The catalyst shows no significant deactivation for 4 runs (Fig. 5). XRD pattern (Fig. S7) of the spent

 Co_1Zn_{99} -ZIF-800-H₂ after the fourth run shows that no cobalt diffraction peaks can be observed. The pore structure of the spent Co1Zn99-ZIF-800-H2 catalyst is still well preserved as revealed by the nitrogen sorption in Fig. S8, in which the BET surface area is about 980 m²/g. No Co metal is detected in the reaction solvent after the completion of the reaction, showing that Co₁Zn₉₉-ZIF-800-H₂ is highly active and stable in aerobic oxidation of EB under this mild condition.

To further demonstrate the versatility of Co1Zn99-ZIF-800-H2, we investigated aerobic oxidation of C-H bonds of a broad scope of substrates under the same condition. As shown in Table 3, good to excellent yields of the corresponding ketones were obtained. It can be found that 95.9% cyclohexene conversion was obtained at 60 °C in 6 h with 83 % cyclohexenone selectivity (entry 2). In the case of macromolecule-cyclooctene (entry 5), the reaction gave 81.5 % of conversion and 71.8 % of cyclooctenone selectivity. Apart from simple cycloalkenes, cyclodiolefins and terminal olefins were also selectively oxidized with relatively high ketone/aldehyde selectivities (entries 6-8). For example, cyclooctadiene (entry 7) afforded the corresponding ketone and enol with 92.6 % conversion without overoxidized products. Other substituted alcohols (entries 9 and 10), such as benzyl alcohol and phenylpropanol, afforded the corresponding aldehydes in relatively low yields.

Conclusion

In summary, we demonstrate an effective approach to construct highly dispersed Co in highly porous N-doped carbon for the selective oxidation C-H bond under mild conditions. It can achieve excellent product yield in aqueous solution at low temperatures (60 °C) and ambient-O₂-pressure (1 atm), affording 41.3 times higher activity than those of Ar-treated ZIF-67 catalyst. The catalytic system can also be adopted for aerobic oxidation of macromolecule hydrocarbons (e.g. cyclooctene and cyclodiolefin) with high yield of ketones. This catalyst is stable and easy to catalyze substrate with large scale. The structure results indicate that, in contrast of Ar, hydrogen-pyrolysis environment for preparing the Co₁Zn₉₉-ZIF-800-H₂ is found to favour the Zn volatilization and beneficial for restricting the pore-shrink of the ZIF precursor, thus yielding N-doped carbon matrix with high surface area and pore volume. The highly porous carbon frame and highly dispersed Co sites are the two key factors for this catalyst to show the excellent performance in the aerobic oxidation of C-H bond.

Experimental

Catalyst preparation

Co_xZn_{100-x}-ZIF was prepared by a modified method from Li's work.⁴¹ Typically, 6.8 mmol mixture of Zn(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O was dissolved in 80 mL methanol with stirring. Then 80 mL methanol containing 36.5 mmol 2-methylimidazole was added with vigorous stirring for 24 h at room temperature. The obtained product was separated by centrifugation and washed with methanol and finally dried at 60 °C under vacuum for overnight, which was marked as Co_xZn_{100-x}-ZIF. For the synthesis of ZIF-8 or ZIF-67, no Co(NO₃)₂·6H₂O or no $Zn(NO_3)_2 \cdot 6H_2O$ was added, respectively. The powder of Co_xZn_{100-x}-ZIF was then transferred into a ceramic boat and placed in

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a tube furnace. The sample was heated to desired temperatures with a heating rate of 5 °C/min and kept for 2 h under 10% P2/AP and then naturally cooled to room temperature. The catalyst was denoted as Co_xZn_{100-x}-ZIF-T-H₂, where T is the pyrolysis temperature. For comparison, pyrolyzation under an Ar atmosphere afforded Co_xZn₁₀₀-_x-ZIF-T-Ar.

Catalyst evaluation

The catalytic reaction was conducted in a flask equipped with a O_2 balloon. Before the reaction test, 5 mg catalyst and 0.25 mmol substrate were added into the flask. Then water (3 mL) and TBHP (0.28 equiv.) were added. The reaction mixture was stirred under 1 atm O₂ balloon at 60 °C. After the reaction, the organic phase was extracted with 15 mL ethyl acetate (5 mL each time), the solid catalyst was recovered by centrifugation. The identification of products was conducted using an Agilent 6890N/5975 GC-MS system. The products were quantitatively analyzed by using gas chromatography (Hewlett Packard 5890 II, FID detector) equipped with a HP-5 capillary column. Dodecane was used as the internal standard.

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