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Research Note

The influence of ZnO on the differential heat of adsorption of CO on Cu catalysts: a microcalorimetric study

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Abstract

The differential heat of adsorption of carbon monoxide on carefully reduced copper catalysts employed in methanol synthesis was measured by means of a Tian–Calvet calorimeter to probe the influence of ZnO. A ternary catalyst ($Cu/ZnO/Al_2O_3$) and two binary catalysts (Cu/ZnO and Cu/Al_2O_3) were prepared by coprecipitation and characterized by N_2 physisorption (BET surface area), temperature-programmed reduction (TPR), N_2O-reactive frontal chromatography (N_2O RFC), and methanol synthesis activity measurements. The shape of the adsorption isotherms, the initial heat of adsorption, and the coverage dependence of the heat of adsorption were found to be different for the catalysts with and without ZnO. The initial heat of adsorption turned out to be inversely correlated with the activity for methanol synthesis: $Cu/ZnO/Al_2O_3$ had the lowest initial heat of adsorption of 68 $kJ\,mol^{-1}$ and was the most active catalyst for methanol synthesis. Cu/ZnO showed a somewhat higher heat of adsorption of 71 $kJ\,mol^{-1}$ and a lower activity, and Cu/Al_2O_3 had the highest initial heat of adsorption of 81 $kJ\,mol^{-1}$ and the lowest activity. The decrease in the heat of adsorption of CO induced by the presence of ZnO is rationalized by strong metal–support interactions (SMSI); i.e., ZnO_x species are assumed to cover the Cu metal surfaces presumably as $Zn + O$ coadsorbate under reducing conditions.

Keywords: Microcalorimetry; Differential heat of adsorption; Carbon monoxide; Copper; Zinc oxide; Strong metal–support interactions (SMSI)

1. Introduction

Copper catalysts are widely used for methanol synthesis and the water gas shift reaction. The industrially applied catalyst is a ternary system containing copper, zinc oxide, and alumina ($Cu/ZnO/Al_2O_3$) [1,2]. Several hypotheses concerning the nature of the active site are found in the literature. Klier [3] proposed Cu species to be incorporated in interstitial and substitutional sites in ZnO. Chinchen et al. [4] identified metallic Cu as the active component and ZnO as an inert support which stabilizes a high Cu surface area. Other researchers assumed that the active sites are located at the Cu/ZnO interface [5]. Nakamura and co-workers [6–8] reported that ZnO_x species migrated under reducing conditions onto the Cu surfaces forming Cu–Zn alloys and stabilizing Cu(I) species. Günter et al. [9] observed a structural interaction of Cu and ZnO resulting in highly active strained Cu particles.

Carbon monoxide is used extensively as a probe molecule to differentiate between Cu sites. Infrared spectroscopy has been applied extensively to investigate the nonactivated adsorption of CO on Cu catalysts and also on Cu single crystal surfaces [10,11]. Roberts and Griffin [12] determined the heat of adsorption of CO on copper catalysts quantitatively by processing TPD data. They reported two desorption states with energies of 37–40 and 50–67 $kJ\,mol^{-1}$ for several Cu-containing catalysts. Dulaurent et al. [13] derived isosteric heats of adsorption of CO on Cu/Al_2O_3 from FTIR spectroscopy experiments in the temperature range from 298 to 740 K. They report isosteric heats of 82 $kJ\,mol^{-1}$ for $\Theta_{CO} \to 0$ and 57 $kJ\,mol^{-1}$ for the equilibrium coverage dosing 1% CO in He [13]. Topsøe and Topsøe [14] observed

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a decrease of about 50 cm^{-1} in the vibrational frequency of on-top adsorbed CO on Cu/ZnO catalysts under severe reducing conditions. This decrease was assumed to be due to the migration of zinc species onto the Cu surfaces [14]. Low-energy ion-scattering experiments provided additional evidence for this hypothesis [15,16]. The DFT simulations presented by Greeley et al. [17] for the adsorption of CO on copper surfaces covered with Zn and Zn + O adatoms are in good agreement with these experimental findings. Furthermore, Greeley et al. [17] predicted a lowered heat of adsorption of CO for this case.

During the last decades, microcalorimetry has been developed into a powerful tool to probe catalytically active surfaces quantitatively [18–22]. The first reliable calorimetric measurements of the differential heat of adsorption of carbon monoxide on reduced copper were presented in 1934 by Beebe and Wildner [23]. They investigated the adsorption of CO on 40 g of reduced copper granules at 273 K in the pressure range up to 0.4 kPa. An initial value of about 80 $kJ\,mol^{-1}$ was obtained which decreased to about 52 $kJ\,mol^{-1}$ at an equilibrium pressure of 0.4 kPa. Giamello et al. [24] combined microcalorimetry and IR spectroscopy to derive the heats of adsorption of CO on copper in various valence states, i.e., 66–43 $kJ\,mol^{-1}$ for CO on Cu(0), 110–66 $kJ\,mol^{-1}$ for CO on Cu(I), and 300–70 $kJ\,mol^{-1}$ for CO on Cu(II). They detected the presence of Cu(I) in reduced Cu/ZnO samples and suggested that those copper species might be dissolved in the ZnO matrix. Borgard et al. [25] reported calorimetrically determined values of 64–46 $kJ\,mol^{-1}$ for the adsorption of CO on a reduced Cu/SiO_2 catalyst.

In the present contribution, the adsorption of CO on two reduced binary (Cu/ZnO and Cu/Al_2O_3) and one ternary catalyst ($Cu/ZnO/Al_2O_3$) was investigated by microcalorimetry as a quantitative tool to elucidate the interactions between Cu and ZnO. The catalysts were prepared by coprecipitation and characterized by static N_2 physisorption, TPR, N_2O RFC, and measurement of the methanol synthesis activity. The differential heat of adsorption of CO on the reduced Cu catalysts was measured in a homemade setup consisting of a volumetric dosing apparatus connected to a Tian–Calvet calorimeter. The main problem was to avoid oxygen poisoning of the reduced Cu surfaces during the transfer and the microcalorimetric measurement. Thus, the catalysts were sealed in small pyrex capsules immediately after the reduction in a flow setup. The capsules were crushed in the measurement cell after the calorimeter had reached thermal equilibrium. The employed measurement technique was adopted from the pioneering work by Spiewak and Dumesic [26].

To the best of our knowledge, the heat of adsorption of carbon monoxide on fully reduced and clean Cu surfaces was derived quantitatively for the first time as a function of coverage using well-characterized Cu catalysts employed in methanol synthesis.

2. Experimental

The Cu catalysts were prepared by coprecipitation using aqueous solutions of $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Al(NO_3)_3$. Na_2CO_3 was employed as precipitation agent. A detailed description of the preparation method is given in Ref. [27].

Static nitrogen physisorption experiments were used to determine the BET surface area of the samples. Prior to the measurements, the catalysts were outgassed in vacuum at 373 K for 2 h. For further characterization, 100 mg of the 250- to 355-μm sieve fraction was reduced in a fixed-bed microreactor using a mixture of 2.1% H_2 in He by raising the temperature from 300 to 513 K. The actual CuO content of the catalysts was calculated from the H_2 uptake during the reduction. The specific Cu surface area was determined by N_2O-reactive frontal chromatography [28] under moderate reaction conditions [29]. The methanol synthesis activity was measured in synthesis gas under steady-state conditions (i.e., holding the temperature for 1.5 h) at ambient pressure and at a temperature of 493 K. A modified space velocity of 500 $cm^3\,min^{-1}\,g_{cat}^{-1}$ (STP) was chosen. The synthesis gas was composed of 14% He, 72% H_2, 4% CO_2, and 10% CO.

Prior to the microcalorimetric measurements, 100–300 mg of the 250- to 355-μm sieve fraction was reduced ex situ in a flow setup equivalent to those described in Refs. [30,31]. The following gases of high purity were used: He (99.9999%), H_2 (99.9999%), and H_2/He (2.1% H_2, 99.9995%). The reduction of the samples was carried out in a specially designed homemade reactor with the H_2/He mixture ramping the temperature at 1 $K\,min^{-1}$ up to 448 K and in a second step with H_2 ramping the temperature at 1 $K\,min^{-1}$ up to 513 K. This UHV-tight reactor provided the possibility of sealing the reduced sample without any contact to air in a Pyrex capsule of about 80 mm length under an atmosphere of about 1 kPa of He.

The applied procedure allowed transfer of the completely reduced and clean catalyst into the calorimeter without any surface contamination by oxygen or carbon dioxide. An in situ reduction in the calorimeter was not possible under the controlled and reproducible conditions realized in the flow setup described above. Furthermore, a simple transfer from the pretreatment cell into the measurement cell in a glove box filled with inert gas was not favorable as the calorimeter needed a long time (i.e., overnight) to reach thermal equilibrium which is a necessary condition to start the measurement. Such a long waiting period would cause contamination of the Cu surfaces due to the leak rate of the complete apparatus. Therefore, the crushing of the Pyrex capsule took place after the calorimeter had reached thermal equilibrium and immediately before the measurement started.

The adsorption calorimetry setup consisted of a volumetric dosing apparatus connected with a specially designed measurement cell in a Tian–Calvet calorimeter (Setaram C 80 II). The volumetric dosing apparatus was made of four completely metal-tightened bellows valves and a Baratron capacity manometer (range: 0–100.00 Pa). The dosing appa-

Table 1
Characterization and catalytic data

Catalyst	$Cu/ZnO/Al_2O_3$	Cu/ZnO	Cu/Al_2O_3
BET surface area ($m^2\ g_{cat}^{-1}$)	73	64	51
Cu content (wt% CuO)	47	68	76
Specific amount of Cu surface atoms[a] ($\mu mol\ g_{cat}^{-1}$)	610	610	176
Specific Cu surface area[b] ($m^2\ g_{cat}^{-1}$)	25	25	7.2
Specific methanol production rate[c] ($\mu mol\ s^{-1}\ g_{cat}^{-1}$)	0.103	0.056	0.015
Turnover frequency ($10^{-5}\ s^{-1}$)	16.9	9.2	8.3

[a] Derived by N_2O RFC.

[b] Assuming that 1 m^2 of Cu surface area equals 24.41 µmol Cu atoms.

[c] Obtained at ambient pressure using 100 mg catalyst in synthesis gas (14% He, 72% H_2, 4% CO_2, and 10% CO) and a volumetric flow rate of 50 $cm^3\ min^{-1}$ (STP).

ratus was placed in a heated box and was held at a constant temperature of 313 K. One dose of gas in the dosing section (all valves closed) at a pressure of 100 Pa and a temperature of 313 K amounted to about 1 µmol. The dosing apparatus was connected to a personal computer which controlled the temperature of the heated box, operated the valves, and collected the pressure and temperature data. The measurement cell was a homemade cell fitting exactly into the calorimeter. It was equipped with a linear motion feedthrough to break the Pyrex capsules containing the samples. The dosing apparatus and the measurement cell were both completely metal-tightened and only built of UHV-suitable components. The maximum apparent leak rate of the dosing apparatus was about 10^{-10} Pa m^3 min^{-1}.

To measure the differential heat of adsorption, CO was dosed sequentially at 300 K until no further adsorption was detectable. The differential heat of adsorption was calculated for each dose by dividing the measured enthalpy by the quantity of adsorbed molecules. The heat was determined by integrating the calorimetric data, and the quantity of adsorbed molecules was calculated from the collected pressure data. In addition, the processing of the pressure data yielded the adsorption isotherms of CO in the range up to 100 Pa. Prior to the experiments in this study, the adsorption calorimetry setup was tested by successfully reproducing the results of the CO adsorption experiments on Pt/SiO_2 presented by Shen et al. [32]. For the initial heats of adsorption, an experimental degree of accuracy of about ±2 kJ mol^{-1} was estimated based on repeated measurements.

3. Results

Characterization data of the investigated catalysts are summarized in Table 1. The Cu surface area was derived from the amount of Cu surface atoms ($n(Cu_{surf})$) determined by N_2O-reactive frontal chromatography assuming that 1 m^2 of Cu surface area equals 24.41 µmol Cu atoms. The turnover frequency was obtained by dividing the specific methanol production rate ($\mu mol\ s^{-1}\ g_{cat}^{-1}$) by the specific amount of Cu surface atoms ($\mu mol\ g_{cat}^{-1}$).

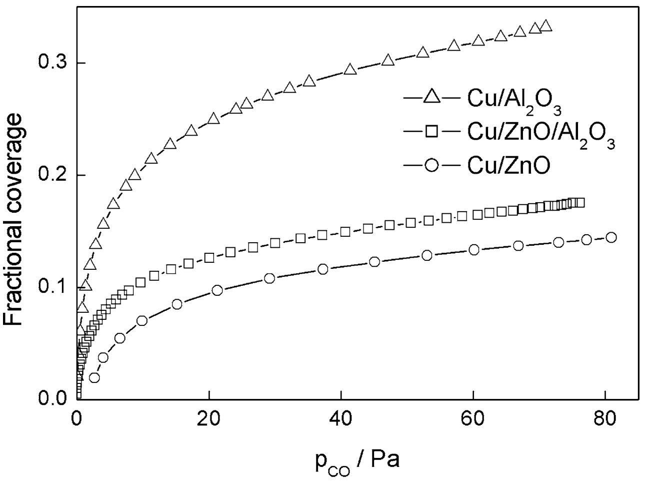

Fig. 1. Adsorption isotherms of CO on Cu catalysts at 300 K.

A simple estimation of the rate constant of desorption as proposed by Cardona-Martinez and Dumesic [18] yields a value of 0.12 s^{-1} for a heat of adsorption of 80 kJ mol^{-1} at 300 K. The order of magnitude of this rate constant is high enough to achieve a fast equilibration of CO with the Cu catalysts through an adsorption and desorption equilibrium. The fractional coverage of CO was calculated from the amount of adsorbed CO ($n_{ads}(CO)$) and the amount of Cu surface atoms (Table 1): $\Theta_{CO} = n_{ads}(CO)/n(Cu_{surf})$. Fig. 1 shows the adsorption isotherms of CO on the three investigated catalysts in the pressure range up to 80 Pa. A strong decrease in the fractional coverage of CO for a given equilibrium pressure in the presence of ZnO was observed. At $p_{CO} = 10$ Pa, the values of Θ_{CO} were 0.11, 0.07, and 0.21 for $Cu/ZnO/Al_2O_3$, Cu/ZnO, and Cu/Al_2O_3, respectively.

Parris and Klier [33] found that the equilibrium coverage of CO on Cu at a temperature of 293 K is $\Theta_{CO} = 0.18$ at a CO pressure of 16 kPa assuming single site adsorption, and that the adsorption is almost completely reversible. The maximum coverages on Cu/ZnO and $Cu/ZnO/Al_2O_3$ obtained in our experiments for equilibrium pressures of 80 Pa at 300 K are in good agreement with the work by Parris and Klier [33]. For Cu/Al_2O_3 somewhat higher coverages of $\Theta_{CO} = 0.33$ were found, indicating the simultaneous adsorption of CO on Cu and alumina at higher CO pressures. Correspondingly, as shown in Fig. 2, a decrease of the differential heat of adsorption was observed at fractional coverages of CO higher than 0.3. It is known that CO adsorbed on Al_2O_3 or ZnO is only weakly bound [18]. Additional irreversible adsorption or chemical reactions can be excluded because no heats high enough to be correlated with such processes were observed.

In Fig. 2 the measured differential heats of adsorption are presented with lines included to guide the eye. Cu/Al_2O_3 showed the highest initial value ($\Theta_{CO} \to 0$) of 81 kJ mol^{-1}. This value remained constant up to a fractional cover-

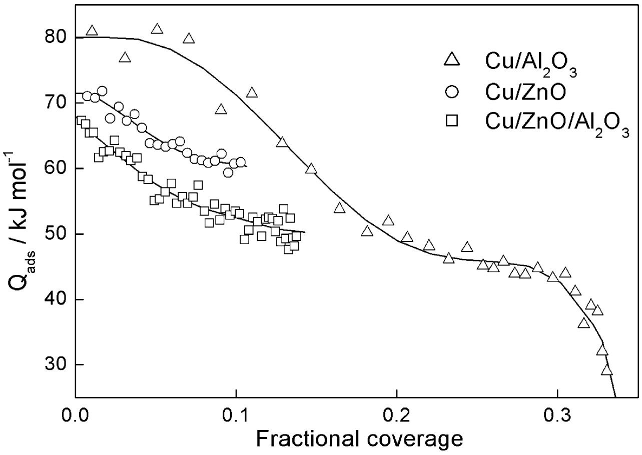

Fig. 2. Differential heats of adsorption of CO on Cu catalysts at 300 K.

age of about 0.1. In the range from 0.1 to 0.2 the heat of adsorption decreased with increasing coverage to about 45 kJ mol^{-1} remaining constant up to a fractional coverage of 0.3. For $\Theta_{CO} > 0.3$ the heat of adsorption decreased even further (30 kJ mol^{-1} at $\Theta_{CO} = 0.33$). For Cu/ZnO and Cu/ZnO/Al$_2$O$_3$, lower initial values of 71 and 68 kJ mol^{-1}, respectively, were obtained. Both catalysts showed a similar decrease with increasing coverage without the plateau observed for Cu/Al$_2$O$_3$. A final value of about 60 kJ mol^{-1} at $\Theta_{CO} = 0.1$ was found for Cu/ZnO. For Cu/ZnO/Al$_2$O$_3$, the final value was about 50 kJ mol^{-1} at $\Theta_{CO} = 0.14$.

4. Discussion

Tracy [34] investigated the coverage dependence of the isosteric heat of adsorption of CO on a Cu(100) single crystal plane in the temperature range from 77 to 300 K. An isosteric heat of adsorption of about 70 kJ mol^{-1} was reported for $\Theta_{CO} \to 0$, decreasing to about 55 kJ mol^{-1} for $\Theta_{CO} = 0.1$. The isosteric heat remained constant for the CO coverage range from 0.1 to 0.5. The initial value and the coverage dependence are in good agreement with the results obtained with Cu/Al$_2$O$_3$. Vollmer et al. [35] derived site-specific adsorption energies on single crystal faces and polycrystalline copper from thermal desorption spectroscopy (TDS) measurements. For the close packed surfaces Cu(111) and Cu(110), binding energies of 47 and 51 kJ mol^{-1}, respectively, were determined. Higher values of 58 kJ mol^{-1} were found for kinks, steps, and defect structures.

Dulaurent et al. [13] derived isosteric heats of adsorption of CO on Cu/Al$_2$O$_3$ from FTIR spectroscopy experiments in the temperature range from 298 to 740 K. The reported isosteric heats of 82 kJ mol^{-1} for $\Theta_{CO} \to 0$ and 57 kJ mol^{-1} for equilibrium coverage are in excellent agreement with our differential heats of adsorption of CO on Cu/Al$_2$O$_3$. Borgard et al. [25] reported calorimetrically measured values of 64–46 kJ mol^{-1} for the adsorption of CO on a reduced Cu/SiO$_2$ catalyst. These values are in good agreement with our measured values of the adsorption of CO on Cu/Al$_2$O$_3$ for $\Theta_{CO} > 0.1$. A further comparison of these measurements is not possible due to the lack of characterization data (copper content, specific copper surface area) in Ref. [25]. However, the total amount of adsorbed CO on the Cu/SiO$_2$ catalyst of less than 14 µmol g_{cat}^{-1} suggests a very small specific Cu surface area. Therefore, it seems unlikely that the initial heat of adsorption ($\Theta_{CO} \to 0$) was measured with the first dose of CO. In summary, the obtained differential heat of adsorption of CO on Cu/Al$_2$O$_3$ is in good agreement with literature results obtained with various methods on Cu single crystals and supported Cu catalysts including SiO$_2$ as non-interacting support.

The adsorption of carbon monoxide on Cu/ZnO systems was previously investigated by Giamello et al. [24]. Two different copper species (Cu(0) and Cu(I)) were reported for their reduced systems. The existence of both species was confirmed by IR data. They assigned differential heats of adsorption in the range of 110–70 kJ mol^{-1} to Cu(I) and values of 70 kJ mol^{-1} at low equilibrium pressures of CO decreasing to 40 kJ mol^{-1} at equilibrium pressures of 1.3 kPa to Cu(0). Our work shows that no Cu(I) species are present after complete and careful reduction of the catalysts. The differential heat of adsorption of CO on Cu/ZnO in our study is in excellent agreement with the values reported for the Cu(0) species. The lower values of 40 kJ mol^{-1} are only found at higher equilibrium pressures and fractional coverages of CO which were not investigated in our study.

A recent DFT study by Greeley et al. [17] showed that the calculated IR vibrational frequencies and the heat of adsorption of CO on Cu surfaces are strongly influenced by the presence of Zn adatoms and Zn + O adatoms as coadsorbate. The vibrational frequencies of CO adsorbed on top of the Cu atoms were lower by up to 72 cm^{-1}, and the decrease in the binding energy was in the range of 6 kJ mol^{-1} for $\Theta_{CO} = \Theta_{ZnO} = 1/9$ compared with unstrained Cu(111). At $\Theta_{Zn} = \Theta_{ZnO} = 1/4$, a strong decrease to 38.6 and 33.8 kJ mol^{-1}, respectively, was predicted for $\Theta_{CO} = 1/4$. The calculated decreases in the binding energy of CO are in good agreement with our work, since the observed difference of the initial heats of CO adsorption between Cu/Al$_2$O$_3$ and the Cu catalysts with ZnO is about 10 kJ mol^{-1}, and for $\Theta_{CO} > 0.1$ the observed differential heats of adsorption for Cu/ZnO and Cu/ZnO/Al$_2$O$_3$ were found to decrease to about 60 and 50 kJ mol^{-1}, respectively.

Wilmer and Hinrichsen [36] investigated the interaction of hydrogen with binary and ternary copper catalysts prepared and pretreated equivalently to our study. For Cu/ZnO/Al$_2$O$_3$, reversible changes as a function of the redox potential of the gas phase were observed. Stronger reducing conditions led to a reversible decrease of the specific Cu surface area as derived from H$_2$ TPD experiments indicating the migration of coadsorbed Zn + O species onto the Cu particles. Thus, it is assumed that under the highly reducing conditions of methanol synthesis several related phenomena occur: the Cu particles change their shape due to the wetting of the ZnO support [37], microstructural strain is induced [9], and the accessible specific Cu surface area is lowered by Zn + O adspecies [36].

In good agreement with our study, strong differences in the activity for methanol synthesis of Cu/Al_2O_3, Cu/ZnO, and $Cu/ZnO/Al_2O_3$ were reported [38]. However, only small differences in the interaction with hydrogen were observed indicating that the hydrogenation of CO_2-derived species is the rate-determining step in methanol synthesis [38]. Our results suggest an inverse correlation between the initial heat of adsorption of CO and the activity for methanol synthesis. Cu/Al_2O_3 had the highest initial heat of adsorption and the lowest activity while $Cu/ZnO/Al_2O_3$ had the lowest initial heat of adsorption and the highest activity (see Table 1). For a better understanding of the effects induced by ZnO on the catalytic properties of the Cu catalysts, further experiments are in progress including a systematic variation of the redox potential of the gas phase during the pretreatment in synthesis gas combined with a FTIR study under corresponding conditions.

In summary, the decrease in the heat of adsorption of CO induced by the presence of ZnO is rationalized by strong metal–support interactions (SMSI), i.e., ZnO_x species are assumed to cover the Cu metal surfaces presumably as Zn + O coadsorbate. Based on this hypothesis, new routes to highly active $Cu/ZnO/Al_2O_3$ catalysts were developed using the chemical vapor deposition of diethyl zinc onto Cu/ Al_2O_3 [39].

5. Conclusions

The presented technique and setup allowed investigation of the adsorption of CO on clean Cu surfaces of supported catalysts. It was possible to measure the differential heat of adsorption and adsorption isotherms for small coverages on metallic Cu.

The differential heat of adsorption and the adsorption isotherms of the investigated catalysts Cu/Al_2O_3, Cu/ZnO, and $Cu/ZnO/Al_2O_3$ revealed significant differences. In the presence of ZnO a decrease in the initial heat of adsorption of about 10 $kJ\,mol^{-1}$ and a decrease of the fractional coverage at a given equilibrium pressure of CO were observed. The differential heats of adsorption are in good agreement with experimental and theoretical data in the literature suggesting the presence of Zn + O adatoms on the Cu surfaces under reducing conditions. The presence of oxidic Cu species can be excluded after thorough reduction in H_2.

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