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NO Adsorption on Ag/Pt(110)-(1×2) Bimetallic Surfaces: Unexpected Formation of Nitrite/nitrate Surface SpeciesJin-bing Li^a, Zhi-quan Jiang^b, Wei-xin Huang^{b*}*a. Yanshan Branch of SINOPEC Beijing Research Institute of Chemical Industry, Beijing 102500, China**b. Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key-Laboratory of Materials for Energy Conversion and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China*

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NO adsorption on Ag/Pt(110)-(1×2) bimetallic surfaces at room temperature was investigated by means of Auger electron spectroscopy, X-ray photoelectron spectroscopy and thermal desorption spectroscopy. An unexpected formation of nitrite/nitrate surface species on Ag/Pt(110)-(1×2) bimetallic surfaces is observed, then decompose at elevated temperatures to form N₂. However, such nitrite/nitrate surface species do not form on clean Pt(110) and Ag-Pt alloy surfaces upon NO exposure at room temperature. The formation of nitrite/nitrate surface species on Ag/Pt(110)-(1×2) bimetallic surfaces is attributed to high reactivity of highly coordination-unsaturated Ag clusters and the synergetic effect between Ag clusters and Pt substrate.

Key words: Nitric oxide, Ag-Pt bimetallic surface, Nitrite/nitrate surface species, Synergetic effect

I. INTRODUCTION

The fundamental investigations of gaseous nitrogen oxides on metal surfaces are essential for the understanding of relevant catalytic processes, including automobile emissions control and manufacture of certain chemicals. Supported silver catalysts have been demonstrated to be catalytically active in DeNO_x reactions and nitrite/nitrate surface species on silver surfaces have been often observed as the intermediates during the catalytic reactions. The adsorption of NO and NO₂ on various well-defined silver model surfaces have been previously investigated to fundamentally understand the relevant catalytic reactions by various surface science techniques. The formation of surface nitrate species was observed on oxygen-precovered Ag(110) and Ag(111) after NO₂ adsorption at room temperature [1, 2]. Exposures of NO₂ onto clean silver single crystals could also lead to the formation of surface nitrate species, mostly likely in a mixed adsorption layer with other nitrogen-containing species [3–7]. The surface nitrate species is also reported to be formed on silver surfaces via the exposure of NO and O₂ mixtures, but only at high pressures. The formation of a AgNO₃ layer was observed upon exposure of the Ag(111) surface to

a NO/O₂ mixture with pressures in the 100 Pa range at 330 K; but at lower pressures no N-containing complexes form [8]. Similar experimental phenomena were also observed on Ag(110) and a silver polycrystalline foil after exposures of NO/O₂ mixtures at atmospheric pressure [9–12].

Pt(110) has a well-known (1×2) reconstructed surface phase and a (1×2) unreconstructed surface phase [13]. The surface reconstruction of a clean Pt(110) plane from the (1×1) to the (1×2) structure was observed by a field-ion microscope and low-energy electron diffraction (LEED), which can be understood by a missing-row model [14, 15]. The Pt(110)-(1×1) surface can be prepared only as a metastable phase and it is easily switched into the stable Pt(110)-(1×2) surface by thermal activation [16]. The deposition of Ag on Pt(111) has been extensively investigated, however, that on clean Pt(110)-(1×2) was rarely reported. The growth mode of a silver ultrathin film on a Pt(110)-(1×2) reconstructed surface up to 2.5 ML was investigated at room temperature by means of Auger electron spectroscopy (AES), LEED, and ultraviolet photoelectron spectroscopy (UPS), and the results indicated that the growth of this system follows the Stranski-Krastanov mode in which Ag deposition on Pt(110)-(1×2) initially follows a layer-by-layer growth mode up to 1.5 ML and then switches to a three-dimensional growth mode [17]. We have further investigated in detail the growth mode of Ag thin film on Pt(110)-(1×2) up to 1.5 ML at room temperature and at 600 K

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by means of AES, X-ray photoelectron spectroscopy (XPS) and CO thermal desorption spectroscopy (TDS) and found that the first 0.5 ML silver atoms fill in the missing-row sites of Pt(110)-(1×2) and form a pseudo Pt(110)-(1×1)-0.5 ML Pt-0.5 ML Ag surface structure, then the subsequent and the final 0.5 ML silver atoms grow on the Ag sites and the Pt sites of the pseudo (1×1) surface, respectively [18, 19].

In this work, we have investigated the adsorption of NO on such Ag/Pt(110)-(1×2) bimetallic surfaces at room temperature. An unexpected formation of nitrite/nitrate surface species on Ag/Pt(110)-(1×2) bimetallic surfaces was observed after exposures of NO at 1 μPa pressures. However, such nitrite/nitrate surface species do not form after the adsorption of NO on clean Pt(110) and Ag-Pt alloy surfaces at room temperature. These results demonstrate the high reactivity of highly coordination-unsaturated Ag clusters and the synergetic effect between Ag clusters and Pt substrate towards the activation of NO on Ag/Pt(110)-(1×2) bimetallic surfaces.

II. EXPERIMENTS

Experiments were performed in a UHV system with a base pressure of 0.02 μPa, equipped with facilities for AES, XPS, LEED, and TDS [18–21]. The AES were recorded through a hemispherical energy analyzer, with an incident electron energy of 3 keV at a pass energy of 150 eV. The XPS were taken with Mg K α radiation (1253.6 eV) at a pass energy of 50 eV. A Pt(110) single crystal was fixed on the sample holder through two Ta wires, and the temperature was monitored by a chromel-alumel thermocouple spot-welded on the back side of the sample. The Pt(110) was cleaned by the standard procedures including oxidation, sputtering and annealing at a high temperature, until AES and XPS detected no contaminants and LEED gave a sharp Pt(110)-(1×2) pattern. In the TDS experiments, the sample was heated at a rate of 8 K/s, and four signals, accounting for NO ($m/z=30$), N₂ ($m/z=28$), N₂O ($m/z=44$) and O₂ ($m/z=32$), were monitored simultaneously by a quadrupole mass spectrometer. The deposition of silver was accomplished through a home made evaporator. The coverage of deposited Ag in monolayer was determined from the Auger signal versus deposition time plot of silver thin film growth on Pt(110)-(1×2) at room temperature established in our previous papers [18, 19]. High-purity NO was exposed to Ag/Pt(110) surfaces by backfilling the UHV chamber. In this work, 2 L NO was dosed onto clean Pt(110) and Ag/Pt(110) bimetallic surfaces at room temperature, since the exposure of 2 L NO was large enough to saturate clean Pt(110)-(1×2) [21].

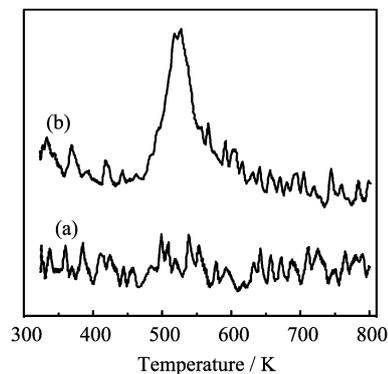


FIG. 1 The background desorption traces of CO from the clean Pt(110)-(1×2) surface during two successive TDS measurements with (a) and without (b) liquid nitrogen cooling down to room temperature.

III. RESULTS AND DISCUSSION

Due to the same m/z ratio between N₂ and CO and the same m/z ratio between N₂O and CO₂, it is rather difficult to distinguish these species in mass spectrometer. CO is one of the major residual gases in a UHV chamber and thus its influence on our experiments needs to be minimized. Firstly, we found that cooling the sample with liquid nitrogen can effectively suppress the adsorption of residual CO in the UHV chamber on our samples by shortening the cooling time. Figure 1 comparatively illustrates the background desorption traces of CO from the clean Pt(110)-(1×2) surface during two successive TDS measurements with and without liquid nitrogen cooling down to room temperature. No obvious CO desorption trace was observed when liquid nitrogen cooling was employed. Secondly, since the preparation of Ag/Pt(110)-(1×2) bimetallic surfaces took quite a long time in our experiments, the TDS experiments were designed as follows to minimize the adsorption of residual CO: Ag with various coverages was deposited onto the clean Pt(110) substrate at room temperature; then the fresh Ag/Pt(110) bimetallic surface was annealed at 700 K for 2 min, and the AES were recorded for the determination of Ag coverage after the sample was cooled down to room temperature; then the model surface was flashed to 700 K and cooled down to room temperature, and subsequently 2 L NO was dosed to the Ag/Pt(110) bimetallic surface at room temperature and the corresponding TDS spectra were then taken.

Figure 2 shows a series of thermal desorption spectra of NO, N₂, and N₂O from Ag/Pt(110) bimetallic surfaces with various Ag coverages exposed to 2 L NO at room temperature. No obvious desorption signal for O₂, which should be expected as a product of NO decomposition, was detected by the mass spectrometer for all investigated Ag/Pt(110) bimetallic surfaces. The likely reason is that the resulted O(ads) might dissolve into

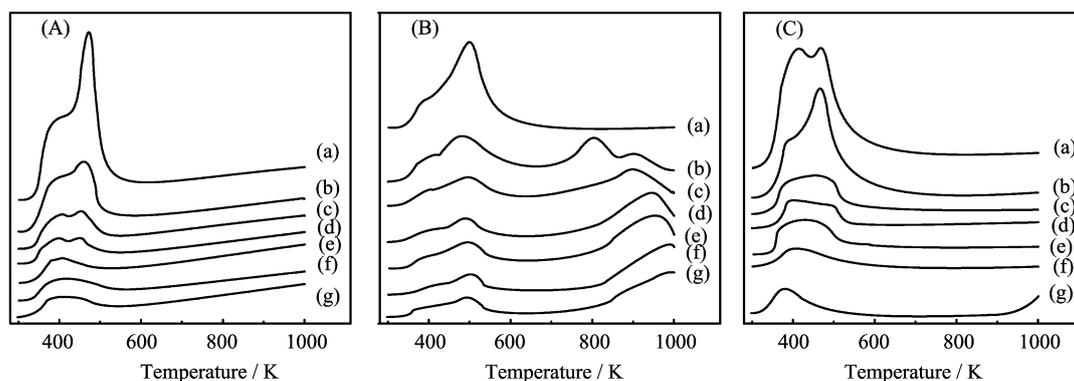


FIG. 2 Thermal desorption spectra following the exposure of 2 L NO to Ag/Pt(110) bimetallic surfaces with various Ag coverages for (A) 30 amu (NO), (B) 28 amu (N_2), and (C) 44 amu (N_2O) at room temperature. (a) 0 ML, (b) 0.10 ML, (c) 0.48 ML, (d) 0.65 ML, (e) 0.87 ML, (f) 1.25 ML, and (g) 1.42 ML.

the bulk of Pt(110), as proposed on the clean Pt(110) substrate upon NO exposure [21]. The similar case has also been reported for NO dissociation on a stepped Pd surface: no desorption of oxygen was observed below 1200 K, although NO dissociation and desorption of nitrogen resulted from NO dissociation were evidenced at around 500 K [22]. On clean Pt(110)-(1×2), the peaks at high and low temperatures are assigned to desorption of bridged and linear NO(ads), respectively [21, 23]. The desorption trajectories of N_2 and N_2O follow that of NO, however, the desorption temperatures of N_2 and N_2O are slightly higher than that of NO. It can be seen from Fig.2 that the desorption intensities of NO, N_2 and N_2O decrease with increasing Ag coverage on Ag/Pt(110) bimetallic surfaces. It suggests that the sticking coefficient and saturation coverage of NO on Ag are both lower than those on clean Pt(110)-(1×2). It was reported that the initial sticking coefficient of NO was 0.1 on Ag(110) at 300 K with the saturation coverage of 0.04 ML and a single NO desorption feature appeared at 390 K [24]. For Ag/Pt(110) bimetallic surfaces with Ag coverages below 0.87 ML, the desorption feature of NO from Pt(110) could be observed; however, for those with Ag coverages higher than 0.87 ML, only a broad desorption peak of NO centering at ~410 K could be observed.

Unexpectedly but interestingly, besides the N_2 desorption trace resulted from the decomposition of NO adsorbed on bare Pt(110) prior to 600 K, a clear desorption signal appears at above 700 K in the TDS for 28 amu after the Ag/Pt(110) bimetallic surfaces were exposed to NO at room temperature, as shown in Fig.2(B). This novel desorption feature on Ag/Pt(110) does not appear on the clean Pt(110) surface upon the same NO exposure. It shifts toward higher temperature with increasing Ag coverage on Ag/Pt(110) bimetallic surfaces. It is certain that this high-temperature desorption feature is not likely from desorption of CO on the catalyst surfaces. A likely origin for this feature could be desorption of CO chemisorbed on the sam-

ple rod made of copper. The temperature of the sample rod is low due to the use of liquid nitrogen cooling and the residual CO might adsorb on the sample rod, and the temperature of the sample rod is much lower than that of the sample during the heating ramp in the TDS measurements. When the sample temperature exceeds 700 K, the temperature of the sample rod could be high enough for desorption of adsorbed CO, consequently resulting in the high-temperature desorption signal in the TDS for 28 amu. However, this possibility can be excluded by the following experimental results. Firstly, under the same experimental conditions, no high-temperature desorption feature is observed in the TDS for 28 amu on clean Pt(110)-(1×2). Secondly, this feature changes in both desorption temperature and intensity with increasing Ag coverage, clearly suggesting that this desorption signal is correlated with the Ag/Pt(110) bimetallic surface. Thirdly, a comparative investigation of NO adsorption on 0.38 ML Ag/Pt(110) bimetallic surface was performed without cooling by liquid nitrogen. Under this case, the sample rod was at room temperature and CO could not adsorb on the sample rod. However, as shown in Fig.3, the high-temperature desorption feature still appears at approximately 880 K in the TDS for 28 amu, meanwhile, an additional desorption peak emerges at approximately 510 K which could be attributed to desorption of CO from the sample surface resulted from the adsorption of residual CO because liquid nitrogen cooling was not employed.

Therefore, we propose that high-temperature desorption feature in the TDS for 28 amu should come from N_2 desorption from Ag/Pt(110) bimetallic surfaces. Since chemisorbed NO species can not stabilize at such high temperatures, a very likely route to produce high-temperature N_2 is the thermal decomposition of nitrite/nitrate surface species. It was reported that the Ag- NO_x species formed on Ag(110) by the coadsorption of NO and O_2 at atmospheric pressure underwent decomposition at approximately 625 K [9, 10]. As

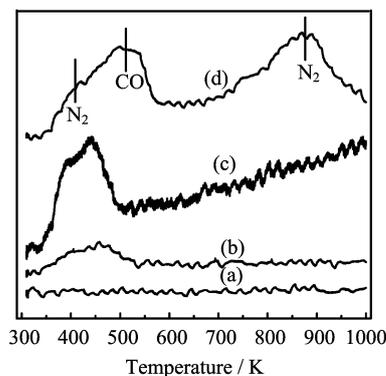


FIG. 3 Thermal desorption spectra following the exposure of 2 L NO to 0.38 ML Ag/Pt(110) bimetallic surface at room temperature without liquid nitrogen cooling. (a) 32 amu (O_2), (b) 44 amu (N_2O), (c) 30 amu (NO), and (d) 28 amu (N_2).

mentioned above, we have established the initial growth mode of silver thin film on Pt(110)-(1 \times 2) [18, 19]: the first 0.5 ML silver atoms fill in the missing-row sites of Pt(110)-(1 \times 2) and form a pseudo Pt(110)-(1 \times 1)-0.5 ML Pt-0.5 ML Ag surface structure, then the subsequent and the final 0.5 ML silver atoms grow on the Ag sites and the Pt sites of the pseudo (1 \times 1) surface, respectively. It can be deduced from the above surface structure that the deposited Ag is highly coordination-unsaturated on the Ag/Pt(110) bimetallic surfaces. We propose that such surface structures of Ag/Pt(110)-(1 \times 2) bimetallic surfaces make silver atoms reactive toward NO chemisorption. In addition, both theoretical calculations and experimental results showed that platinum transferred electron to silver for silver thin film grown on Pt single crystal surfaces [19, 25, 26]. Meanwhile, some adsorbed NO molecules undergo decomposition on clean Pt(110)-(1 \times 2) upon heating, forming adsorbed oxygen adatoms [21]. Synergetic effect might occur between Ag and Pt in which NO adsorbed on Ag atoms and oxygen adatoms on adjacent Pt substrate react to form nitrite/nitrate surface species. Therefore, the high reactivity of highly coordination-unsaturated Ag and the synergetic effect between Ag and Pt lead to the formation of nitrite/nitrate surface species on Ag/Pt(110)-(1 \times 2) upon NO exposure at room temperature followed by heating. It was reported that the NO_3 species on the Ag(110) surface, which was formed by the reaction of NO_2 with the oxygen adatoms produced from the partial dissociation of NO_2 , decomposed below 500 K [3]; the nitrate on Ag(111) decomposed into $NO_2(g)$ and $O(ads)$ at 396 and 497 K, and oxygen underwent desorption limited evolution as $O_2(g)$ at 578 K [2]. When NO_2 was dosed to Ag(111) at 90 K, it was found by reflection-absorption infrared spectroscopy that the resulting surface $NO_3(ads)$ decomposed between 165 and 320 K, and all surface species except $O(ads)$ desorbed below 500 K [7]. However,

it was also reported that the Ag- NO_x species formed on Ag(110) by the coadsorption of NO and O_2 at atmospheric pressure can stabilize up to approximately 625 K [9, 10]. The nitrate adlayer on Ag(110) was observed by scanning tunneling microscope to form coadsorbed $N(ads)$ and $O(ads)$ upon annealing to 485 K; at the same time, strong stabilization of adsorbed oxygen was proposed by coadsorbed nitrogen, consequently losing the reactivity with CO at 300 K [1].

In our case, the N_2 desorption feature, corresponding to the thermal decomposition of nitrite/nitrate surface species on Ag/Pt(110)-(1 \times 2), appears at above 750 K, and it changes in both desorption temperature and intensity with increasing Ag coverage. The synergetic effect between Ag clusters and Pt substrate could result in the higher stability of surface intermediate species on the bimetallic surface than on Ag single crystal surfaces. We propose that, upon heating, the surface nitrite/nitrate species firstly decompose into $NO(ads)$ and $O(ads)$, then the resulting $NO(ads)$ further decomposes into $N(ads)$ and $O(ads)$ likely catalyzed by the platinum substrate, and eventually the resulting $O(ads)$ diffuses into the bulk of Pt(110), and the resulting $N(ads)$ recombines into $N_2(g)$ desorbing from the surface. This recombinative desorption of $N_2(g)$ at above 750 K is reaction-limited, not desorption-limited, since pure adsorbed nitrogen can not be stable at such high temperatures. It was reported that the recombinative desorption of N_2 from adsorbed atomic nitrogen on Ag(111) was observed at temperatures between 350 and 500 K [27], and on Pt(110) at temperatures between 350 and 600 K [28]. Although direct spectroscopic evidence are needed to further confirm the formation of nitrite/nitrate surface species, this model can reasonably explain observed TDS experimental results.

Since the formation of nitrite/nitrate surface species is derived from the high reactivity of the highly coordination-unsaturated Ag, it is thus reasonable that the appearance of the N_2 high-temperature desorption feature depends on the surface structure of Ag/Pt(110) surface. We prepared 1.25 ML Ag/Pt(110) bimetallic surface and performed the TDS measurement after the exposure of 2 L NO at room temperature up to 1000 K; after the surface was cooled down to room temperature, a second cycle of TDS experiment after the exposure of 2 L NO was performed. Figure 4 comparatively illustrates the TDS results of these two cycles. It can be seen that obvious N_2 high-temperature desorption feature appears in the first cycle of TDS experiment but does not in the second cycle of TDS measurement. We found that the surface structure of 1.25 ML Ag/Pt(110) bimetallic surface changes after the first cycle of TDS measurement (Fig.5). Firstly, the Ag coverage determined by AES substantially decreases from the original 1.25 ML to 0.5 ML, indicating the desorption of Ag from the surface during the TDS experiment up to 1000 K; more importantly, the Ag3d XPS results show that the Ag3d_{5/2} binding energy shifts from

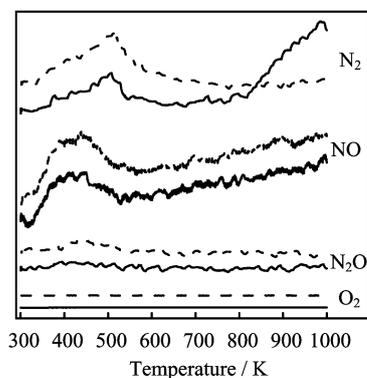


FIG. 4 Thermal desorption spectra of the first cycle of 2 L NO TDS experiment for 1.25 ML Ag/Pt(110) bimetallic surface at room temperature (solid line). TDS of the second cycle of 2 L NO TDS experiment for 1.25 ML Ag/Pt(110) bimetallic surface at room temperature (dash line), *i.e.*, TDS of 2 L NO TDS experiment for 0.50 ML Ag/Pt(110) alloy surface at room temperature.

367.75 eV for 1.25 ML Ag/Pt(110) bimetallic surface to 367.55 eV after the first cycle of TDS measurement. This could be taken as the evidence for the alloying of Ag and Pt on 1.25 ML Ag/Pt(110) bimetallic surface after heating to 1000 K. Therefore, after the first cycle of TDS experiment up to 1000 K, the original 1.25 ML Ag/Pt(110) bimetallic surface becomes 0.5 ML Ag/Pt(110) alloy surface. Ag atoms on the alloy surface lose its highly unsaturated coordination environment, as compared to those on the bimetallic surfaces deposited at room temperature. Therefore, Ag atoms on the 0.5 ML Ag/Pt(110) alloy surface only act to modify the surface property of Pt substrate and lose their high reactivity, thus the adsorption behavior of NO on 0.5 ML Ag/Pt(110) alloy surface is similar to that on clean Pt(110) surface.

The formation of nitrite/nitrate surface species on silver single crystal and polycrystalline foil has been reported only by the exposure of NO and O₂ mixtures at 100 Pa pressures at room temperature [9–12]. However, in our case, NO exposure at 1.0 μPa pressures to Ag/Pt(110) bimetallic surfaces at room temperature could form nitrite/nitrate surface species. These results demonstrate the high reactivity of Ag clusters on Pt(110) surface and the synergetic effect between Ag clusters and Pt substrate of Ag/Pt(110) bimetallic surfaces towards the activation of NO, which might have important implications for the relevant catalytic systems.

IV. CONCLUSION

NO adsorption on Ag/Pt(110) bimetallic surfaces was investigated by means of AES, XPS, and TDS. Likely nitrite/nitrate surface species can form after the exposure of NO at room temperature on Ag/Pt(110)

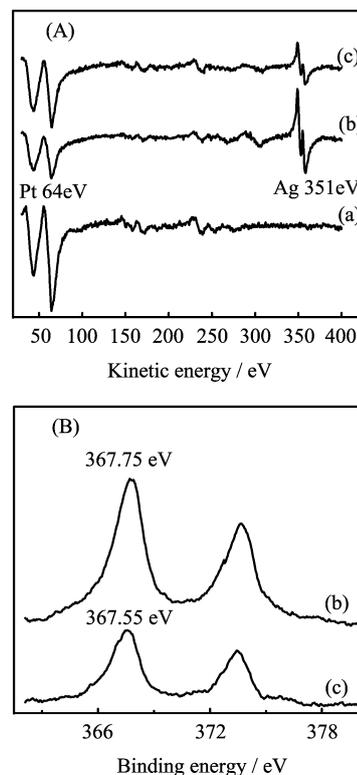


FIG. 5 AES (A) and Ag3d XPS (B) spectra of (a) clean Pt(110)-(1×2), (b) fresh 1.25 ML Ag/Pt(110) bimetallic surface, (c) fresh 1.25 ML Ag/Pt(110) bimetallic surface after one cycle of 2 L NO TDS experiment up to 1000 K, *i.e.*, the 0.50 ML Ag/Pt(110) alloy surface.

bimetallic surfaces followed by heating, but not on clean Pt(110) and Ag/Pt(110) alloy surfaces. These results demonstrate the high reactivity of highly coordination-unsaturated Ag clusters and the synergetic effect between Ag clusters and Pt substrate on Ag/Pt(110) bimetallic surfaces, providing insights into the relevant catalytic systems.

V. ACKNOWLEDGMENTS

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