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IR spectroscopy evidence of MoS_2 morphology change by citric acid addition on MoS_2/Al_2O_3 catalysts – A step forward to differentiate the reactivity of M-edge and S-edge



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Jianjun Chen, Francoise Maugé, Jaafar El Fallah, Laetitia Oliviero*

Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 bd du Maréchal Juin, 14050 Caen, France

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ABSTRACT

Citric acid was used as chelating agent to prepare a series of MoS₂/Al₂O₃ catalysts. CO adsorption followed by infrared spectroscopy characterization (IR/CO) was employed to probe the M-edge and S-edge of MoS₂ slabs on these catalysts. Addition of citric acid promotes the growth of S-edge, whereas it inhibits that of M-edge: The morphology of MoS₂ is progressively modified from a slightly truncated triangle with predominately M-edge to a hexagon with both M-edge and S-edge with increasing citric acid amount. Such morphology change is of great importance to the catalytic performance as M-edge and S-edge demonstrate different reactivity in hydrodesulfurization (HDS) reactions. Indeed, IR/CO data reveal that sulfur vacancy creation occurs more easily on M-edge, whereas at room temperature, thiophene tends to adsorb more strongly on S-edge. Moreover, parallel between IR/CO study and HDS test shows that S-edge has a higher intrinsic activity than M-edge in thiophene HDS reaction.

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1. Introduction

The presence of sulfur as impurity in fuels causes heavy pollutions around the world. Drastic regulations are thus put in place to limit the sulfur content in fuels. The more and more strict limitations of sulfur content allowed in fuels have resulted in continuous efforts to improve the activity of conventional hydrodesulfurization (HDS) catalysts, which are typically CoMo and NiMo supported by Al₂O₃. According to the structure model proposed by Topsøe et al. [1-4], the catalytic active sites on sulfided CoMo/Al₂O₃ catalyst are the so-called CoMoS structure located on the edge of MoS_2 slabs. It was well established [5–7] that MoS₂ slabs present, in their perfect crystallographic (100) plane, principally two types of edges: the Mo-terminated edge (M-edge) and the sulfur-terminated edge (S-edge). Both M-edge and S-edge can show different configurations with different sulfur coverage [8]. When the sulfur coverage on M-edge and/or S-edge is less than 100%, sulfur vacancies are created on the edges. Density functional theory (DFT) simulations [9–11] suggested that Co atoms have different affinities toward M-edge and S-edge. Moreover, it was proposed that the CoMoS sites located on M-edge and S-edge have different intrinsic activities in thiophene HDS [12] and toluene

hydrogenation [13,14]. These results suggest that the morphology of MoS₂ slabs, in particular the type and quantity of the edges exposed, has significant influence on both the CoMoS site concentration and their intrinsic activity.

The morphology of MoS₂ slabs has been first investigated by DFT calculations [6,7,15] under different sulfidation conditions. The MoS₂ morphology is determined, according to the Wulff construction [16], by the total lowest edge-free energy, i.e. the relative free energy of M-edge and S-edge. It was suggested that the edgefree energy of MoS₂ can be expressed as a function of a pseudo chemical potential of sulfur, which is determined by sulfidation temperature and H₂S/H₂ partial pressure. A high chemical potential of sulfur leads to a triangular-shaped MoS₂ terminated by Medge, while an intermediate chemical potential of sulfur favors the formation of hexagonal MoS₂ terminated with both M-edge and S-edge. Then, it was recently imaged by scanning tunneling microscopy (STM) that the morphology of MoS₂ nanoparticles supported on Au substrate can vary from a triangle to a hexagon with sulfo-reductive conditions, the sulfidation agent or the presence of promoters [17–21]. In addition, it was found by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) that unpromoted MoS₂ slabs supported on graphite are majorly present as slightly truncated triangular clusters, while the addition of promoters leads to more heavy truncated hexagonal slabs [22,23].



^{*} Corresponding author. E-mail address: laetitia.oliviero@ensicaen.fr (L. Oliviero).

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Although the morphology of MoS₂ was predicted by DFT simulations [6,7,15] and imaged by STM [17-21] and HAADF-STEM [22,23] on model catalysts, the gap between model system and real catalyst remains, calling for experimental evidence for the relevance of these studies on Al₂O₃-supported catalyst. As a proven technique, low-temperature CO adsorption followed by infrared spectroscopy (IR/CO) has been used to characterize MoS₂/Al₂O₃ catalysts since several decades. For a long time, it has been well recorded by IR/CO that there are distinctly two different CO adsorption bands on MoS_2 phase, which are located at ~2110 and \sim 2070 cm⁻¹ [24,25]. Combining experimental infrared spectra and theoretical DFT calculations, Travert et al. [26,27] well established that the v(CO) band at \sim 2110 cm⁻¹ was assigned to CO adsorption on M-edge of MoS_2 crystallites and the band at \sim 2070 cm⁻¹ to CO adsorption on S-edge. These band attributions were recently confirmed by Labruyere [28]. Furthermore, a quantitative evaluation of the M-edge and S-edge concentrations on MoS₂/Al₂O₃ catalysts can be obtained after the determination of the integrated molar extinction coefficient of CO adsorbed on each edge [Supplementary Material]. All in all, the above-mentioned preparatory work makes the IR/CO technique a good candidate for depicting the MoS₂ morphology on real Al₂O₃-supported catalysts.

In fact, the results of IR/CO studies on MoS₂/Al₂O₃ catalysts are essentially in good agreement with the DFT simulations. For instance, DFT simulation [6] has predicted that M-edge is energetically more stable than S-edge over a large range of sulfur chemical potential and therefore that the morphology of MoS₂ is truncated triangle terminated by mainly M-edge under typical HDS conditions. Accordingly in IR/CO studies [24-29], the CO adsorption band located at \sim 2110 cm⁻¹ (attributed to CO adsorption on Medge) was observed with massive intensity, while the v(CO) band at \sim 2070 cm⁻¹ (assigned to CO adsorption on S-edge) was always recorded as a broad shoulder. Nevertheless, previous IR/CO study [28] did not observe clearly MoS₂ morphology change with sulfidation temperature and/or H₂S partial pressure on MoS₂/Al₂O₃ catalyst, even though such morphology change has been predicted by DFT calculations [6]. Alternatively, STM study by Walton et al. [21] found that MoS₂ morphology differs with supports (Au, graphite and TiO₂), which indicates that support interaction also plays important role in MoS₂ morphology change. Indeed, the free energy of M-edge and S-edge can vary with support interaction and the variation may not be in the same proportion [21]. In this manner, one may anticipate that changing the MoS₂-Al₂O₃ interaction may lead to different growth preference of M-edge and S-edge during sulfidation and thus result in the morphology change of MoS₂ on Al₂O₃ support.

Following this anticipation, we use herein citric acid as chelating agent to prepare a series of MoS_2/Al_2O_3 catalysts, as it was shown that using chelating agents such as citric acid in preparation of HDS catalysts can modify the slab-support interaction [30–32]. Interestingly, by IR/CO characterization of these catalysts, we observe that citric acid addition does modify the growth preference of M-edge and S-edge and thus changes the morphology of MoS_2 slabs on MoS_2/Al_2O_3 catalyst. In addition, we also confirm significant difference in sulfur vacancy creation and thiophene adsorption on M-edge and S-edge, allowing therefore a comparison with previous DFT predictions from literature. Finally, combining IR results and HDS activity test, we find that M-edge and S-edge have different intrinsic activity in thiophene HDS reaction.

This contribution provides, to our knowledge, the first experimental evidence of MoS₂ morphology change on Al₂O₃ supported catalysts, which strongly supports previous microscopy (STM and HAADF-STEM) and DFT studies of such MoS₂ morphology change on model catalysts. This work also reveals an important effect of citric acid on the morphology of MoS₂ phase, providing a new insight into the role of chelating agent on HDS catalysts. Moreover, it is shown that with exquisite experiment, IR spectroscopy can be employed to study not only the morphology of MoS_2 phase but also the adsorption and reaction characteristics of M-edge and S-edge on MoS_2/Al_2O_3 catalyst.

2. Experimental

2.1. Catalyst preparation

A series of Mo/Al₂O₃ catalysts with different amounts of citric acid (CA) was prepared by a one-step pore volume impregnation method. Firstly, the impregnation solutions were prepared with different amounts of citric acid (CA, $C_6H_8O_7 \cdot H_2O$, PROLABO) and a constant amount of ammonium heptamolybdate tetrahydrate (AHT, (NH₄)₆Mo₇O₂₄·4H₂O, MERCK). Afterward, the pretreated γ -Al₂O₃ support (SASOL, specific surface area of 252 m² g⁻¹ and pore volume of 0.84 mL g⁻¹, precalcined in air at 723 K for 2 h) was added into the solutions and strongly shaken for 2 h. Finally, the catalysts were dried at 383 K for 3 h. Note that these catalysts were not calcined in order to keep the chelating agent in its initial form. Hereinafter, the Mo/Al₂O₃ catalysts prepared with citric acid are denoted as Mo(CA/Mo = *x*)/Al₂O₃. *x* refers to the molar ratio of citric acid (CA) to Mo. *x* = 0, 0.5, 1.0, and 2.0 while the Mo content was kept at 0.19 mmol per gram of Al₂O₃ support.

2.2. Infrared (IR) spectroscopy characterization

IR characterization was performed on a newly designed setup called CellEx. The CellEx consists of three parts: (i) a stainless steel reactor for catalyst sulfidation and other treatment under different temperature, pressure, and gas phase; (ii) an IR cell equipped with a spectrometer for spectroscopic characterization; and (iii) a transfer connection for transferring sample from reactor into IR cell under inert gas. With the CellEx, the catalysts can be treated under different conditions and sequentially *in situ* characterized by IR spectroscopy without any air pollution. More details about CellEx were described in Ref. [33].

2.2.1. Catalyst sulfidation

Catalyst sulfidation was performed in the stainless reactor of CellEx. Catalyst sample was firstly grounded and pressed into self-supporting pellet of ~8 mg cm⁻² (precisely weighted). The pellet was introduced into the reactor, which was then evacuated to 1.33 Pa to remove the air. After that, the pellet was sulfided at 623 K (heating rate of 3 K min⁻¹) and 0.1 MPa under a 30 mL min⁻¹ 10%H₂S/H₂ for 2 h. Sequentially, the reactor was flushed with Ar at 623 K and then cooled down to room temperature under Ar. Finally, the sulfided pellet was transferred under Ar to the IR cell for IR characterization.

2.2.2. Low-temperature CO adsorption followed by IR spectroscopy characterization (IR/CO)

In the IR cell, the sulfided pellet was firstly heated at 6 K min⁻¹ up to 623 K and kept for 1 h under evacuation. The final pressure in the IR cell after evacuation should reach 10^{-3} Pa. After that, the pellet was cooled down by liquid nitrogen to 100 K for CO adsorption. CO adsorption was performed by introducing small calibrated doses of CO at different pressures (0.03–1.20 µmol of CO) and finally with 133 Pa CO at equilibrium in the IR cell. IR spectra of adsorbed CO were recorded with a Nicolet spectrometer equipped with a MCT detector with 256 scans. Note that the graphical resolution is 0.5 cm⁻¹. For comparison, all the spectra presented were normalized to a sulfided catalyst pellet of 5 mg cm⁻².

The concentration of each type of edge sites was obtained after spectral decomposition performed on Peakfit V4.12 using "Autofit peak II-Second derivative Methods". In spectral decomposition, the center and full width at half height (FWHH) of the generated peaks were allowed varying in fixed small range. The molar extinction coefficient of CO adsorbed on M-edge (ϵ_{M-edge}) was determined in the IR cell by introducing small doses of CO onto the sulfided $Mo(CA/Mo = 0)/Al_2O_3$ catalyst at liquid nitrogen temperature (100 K). The molar extinction coefficient of CO adsorbed on S-edge (ε_{S-edge}) was determined by subtracting the contribution of M-edge from the spectra obtained after introducing small doses of CO onto the sulfided Mo(CA/Mo = 2)/Al₂O₃ catalyst at liquid nitrogen temperature (100 K). The determined ϵ_{M-edge} and ϵ_{S-edge} are $20 \pm 3 \,\mu\text{mol}^{-1}$ cm and $35 \pm 9 \,\mu\text{mol}^{-1}$ cm, respectively. Details for spectral decomposition, $\epsilon_{M\text{-}edge}$ and $\epsilon_{S\text{-}edge}$ determination, and edge site concentration calculation are given as Supplementary material.

2.2.3. Thiophene adsorption followed by IR/CO characterization

Thiophene adsorption was performed in the IR cell after the evacuation at 623 K described in Section 2.2.2. Several calibrated doses of thiophene vapor were introduced into the IR cell at room temperature until the total introduced thiophene amount reached $3.5 \times 10^{-2} \,\mu$ mol/mg of catalyst. Then, the pellet was cooled down by liquid nitrogen and characterized by IR/CO as described in Section 2.2.2.

2.2.4. Catalyst sulfidation followed by H_2 treatment and IR/CO characterization

Catalyst sulfidation followed by H_2 treatment was carried out in the stainless steel reactor of CellEx. The catalyst pellet was firstly sulfided as described in Section 2.2.1 and then treated by 30 mL min⁻¹ pure H_2 at 623 K for 2 or 20 h. After this treatment, the pellet was transferred to the IR cell for IR/CO characterization as described in Section 2.2.2.

2.3. Thiophene hydrodesulfurization (HDS) test

Before thiophene HDS test, the catalyst was sulfided at 623 K (heating rate of 3 K min⁻¹) and 0.1 MPa for 2 h under a 30 mL min⁻¹ flow of 10%H₂S/H₂. Then, thiophene HDS test was carried out at 623 K and 0.1 MPa with around (but precisely weighted) 50 mg of sulfided catalyst. Thiophene was introduced into the reactor by passing 70 mL min⁻¹ of H₂ flow through a thiophene saturator maintained at 291 K and mixed with a flow of 20 mL min⁻¹ of 10%H₂S/H₂. The partial pressure of thiophene, H₂ and H₂S in the mixture is 8 kPa, 91.2 kPa, and 2.1 kPa, respectively. After 24 h reaction, the outlet gas was analyzed by a Varian 3900 chromatograph equipped with flame ionization (FID) detector. The reaction rate was calculated as $r_{HDS} = (F/m) * X$, where F/m is the molar flow rate of thiophene per gram of catalyst and X is the thiophene HDS conversion which is below 5%.

2.4. Transmission electronic microscopy

Transmission electron microscopy (TEM) was performed on a JEOL 2010 FEG operated at 200 kV. To limit detrimental exposure to air sulfided catalysts were unloaded from the sulfidation reactor under argon flow into ethanol. A few drops of a suspension of catalyst were put on a copper grid. Slab length and stacking degree distributions of sulfide slabs were determined manually by measuring at least 300 slabs per sample from the TEM images. All the TEM images were recorded at the same magnification and digitized using a 2k x 2k CCD camera. The image treatment was performed using the commercial software from GATAN (DIGITALMICROGRAPH).

3. Results

3.1. IR spectra of CO adsorption on MoS₂/Al₂O₃ catalysts prepared with and without citric acid

The spectra of increasing doses of CO (up to 133 Pa at equilibrium) adsorbed on sulfided Mo(CA/Mo = 0)/Al₂O₃ and Mo(CA/Mo = 2)/Al₂O₃ catalysts are shown respectively in Fig. 1(A) and (B). As previously reported [26,27], on sulfided Mo(CA/Mo = 0)/Al₂O₃ catalyst (Fig. 1(A)), adsorption of the first CO doses leads to the main band at 2112 cm⁻¹, corresponding to CO adsorbed on M-edge of MoS₂ phase. As CO coverage increases, two other main bands at 2189 and 2156 cm⁻¹ are observed, which are assigned to CO coordination on Lewis acid sites (Al³⁺) and OH groups of Al₂O₃ support, respectively. Meanwhile, a shoulder at 2068 cm⁻¹ is also recorded with increasing doses of CO, which is ascribed to CO adsorption on S-edge of MoS₂ slabs.

When the catalyst was prepared with citric acid, as shown in Fig. 1(B) on sulfided $Mo(CA/Mo = 2)/Al_2O_3$ catalyst, the first doses of CO introduction also lead to CO adsorption on M-edge (band at 2110 cm⁻¹). With increasing CO doses, v(CO) bands characterizing CO adsorption on Al₂O₃ support (bands at 2186 and 2155 cm^{-1}) are also recorded. These IR observations are similar to those on sulfided Mo(CA/Mo = 0)/Al₂O₃ catalyst. However, the v(CO) band at 2065 cm^{-1} attributed to CO adsorbed on S-edge, which is an illdefined shoulder on sulfided $Mo(CA/Mo = 0)/Al_2O_3$ catalyst, is clearly recorded with the increasing CO coverage and the final intensity of this band is comparable with that of the v(CO) band associated with CO adsorption on M-edge. Meanwhile, the v(CO)band intensity on M-edge (band at 2110 cm⁻¹) is significantly decreased on sulfided Mo(CA/Mo = 2)/Al₂O₃ catalyst. These results clearly demonstrate that the addition of citric acid during preparation increases the amount of S-edge while decreases that of Medge on MoS₂/Al₂O₃ catalyst.

3.2. IR spectra of CO adsorption on MoS_2/Al_2O_3 catalysts prepared with different amount of citric acid

In order to investigate the effect of citric acid amount on the morphology of MoS₂ slabs, the series of Mo(CA/Mo = x)/Al₂O₃ catalysts were sulfided under the same condition and characterized by IR/CO. The only parameter varied between these catalysts is the amount of citric acid used during preparation. The IR spectra of CO adsorption (100 K, 133 Pa CO at equilibrium) on these catalysts are shown in Fig. 2. In all cases, mainly four v(CO) bands located at 2186, 2155, 2110 and 2065 cm^{-1} are detected on these catalysts, which are attributed to CO adsorption on Lewis acid sites and OH groups of Al₂O₃ support, M-edge and S-edge of MoS₂ phase, respectively. Nevertheless, big differences in the intensity of CO adsorption bands on MoS₂ phase are evident. As shown in Fig. 2, with the increase of citric acid addition, the CO adsorption band on Sedge (band \sim 2065 cm⁻¹) is gradually increased, from an ill-defined shoulder to a well-defined band. Meanwhile, the v(CO) band intensity on M-edge (band \sim 2110 cm⁻¹) is gradually decreased.

The concentration of M-edge and S-edge on this series of sulfided $Mo(CA/Mo = x)/Al_2O_3$ was calculated after spectral decomposition. (Details are given in Supplementary Material). The calculated concentration of M-edge, S-edge and total edge sites is shown in Fig. 3. A large concentration of M-edge together with a very small concentration of S-edge was recorded on sulfided $Mo(CA/M = 0)/Al_2O_3$ catalyst, in accordance with the DFT prediction [6] that the morphology of MoS_2 under typical HDS conditions is truncated triangle with predominantly M-edge. With the addition of citric acid, the concentration of S-edge gradually increases while that of M-edge stepwise decreases. These results clearly indicate that the



Fig. 1. IR spectra of increasing doses of CO (up to 133 Pa at equilibrium) adsorbed at 100 K on (A) $Mo(CA/Mo = 0)/Al_2O_3$ catalyst and (B) $Mo(CA/Mo = 2)/Al_2O_3$ catalyst sulfided with $10\%H_2S/H_2$ at 623 K and 0.1 MPa.



Fig. 2. IR spectra of CO adsorption (100 K, 133 Pa at equilibrium) on Mo(CA/ Mo = x)/Al₂O₃ catalysts sulfided with 10%H₂S/H₂ at 623 K and 0.1 MPa.



Fig. 3. Concentration of M-edge, S-edge and total edge sites determined by low temperature CO adsorption on sulfided $Mo(CA/Mo = x)/Al_2O_3$ catalysts; slab morphology according to the M-edge/S-edge ratio.

addition of citric acid promotes the growth of the S-edge while inhibits that of M-edge on MoS_2 slabs. Moreover, the increase of S-edge overcomes the decrease of M-edge, and thus, the total edge site (M-edge + S-edge) concentration, as shown in Fig. 3, is increased.



Fig. 4. Positions of v(CO) band on M-edge and S-edge on sulfided $Mo(CA/Mo = x)/Al_2O_3$ catalysts.

Presuming that the ratio of M-edge and S-edge for a single MoS_2 slab is in line with the overall ratio of each edge detected by IR/CO, a schematic diagram of MoS_2 morphology on this series of catalyst was drawn. As shown in Fig. 3, the truncation degree of MoS_2 slabs is steadily increased with the addition of citric acid and thus, the morphology of MoS_2 slabs is progressively changed from a slightly truncated triangle presenting predominantly M-edge to a hexagonlike shape with both M-edge and S-edge.

Besides the effect on v(CO) band intensity, a gradual downward shift of v(CO) band position on both M-edge and S-edge with increasing citric acid amount is also observed, as shown in Fig. 4. The position of v(CO) band is the results of sigma donation and Pi back-donation between CO and MoS₂ edge sites. The sigma donation (electronic density from CO to MoS₂) shifts the vibration frequency to higher wavenumbers (upward-shift), while the Pi back-donation (electronic density from MoS₂ to CO) shifts it to lower wavenumbers (downward-shift) [34]. An increase of the electron density of the MoS₂ adsorption sites decreases the sigma donation and increases the back-donation, both leading to a downward shift. In this way, the observed downward shift of v(CO) bands with addition of citric acid indicates an increase of electronic density on MoS₂ phase on both edges after citric acid addition.

3.3. Reaction of H_2 with M-edge and S-edge sites

Hydrogen being one of the reactant during HDS process, its reactivity on HDS catalysts is of great importance [35]. Molecular

hydrogen can dissociatively adsorb on MoS₂ edges, leading to the creation of sulfur vacancy by removing sulfur in the form of H₂S and resulting in the MoS₂ edges with lower sulfur coverage. The edge ability for sulfur vacancy creation can be evaluated by IR/ CO characterization because the elimination of sulfur atoms by H₂ increases the accessibility of CO to Mo sites, which intensifies the CO adsorption on MoS₂ edges [36]. In order to evaluate the ability for sulfur vacancy creation on M-edge and S-edge, the sulfided Mo(CA/Mo = 2)/Al₂O₃ catalyst, on which the MoS₂ slabs present both M-edge and S-edge, was exposed to pure H₂ at 623 K and 0.1 MPa for certain time and sequentially characterized by IR/CO without any air contact [37]. The IR spectra obtained under 133 Pa of CO at equilibrium after 2-h and 20-h H₂ treatment are shown in Fig. 5. The corresponding IR spectrum after sulfidation is also drawn in Fig. 5 for comparison.

As shown in Fig. 5, sulfur vacancy can be readily created on Medge, since the v(CO) band attributed to CO adsorption on M-edge (band around 2110 cm⁻¹) is drastically increased after a 2-h H₂ treatment and a 20-h H₂ treatment further increases its intensity. Meanwhile, sulfur vacancy creation can also occur on S-edge, as the v(CO) band attributed to CO adsorption on S-edge (band around 2065 cm⁻¹) is also enhanced after a 2-h H₂ treatment. Nevertheless, the v(CO) band intensity on M-edge increases much more significantly than that on S-edge after H₂ treatment. The CO adsorption band on S-edge is only slightly increased by a 2-h H₂ treatment, and a 20-h H₂ treatment does not further intensify the v(CO) band on this edge. These results indicate that sulfur vacancy creation occurs more easily on M-edge and only limited S atoms can be removed from S-edge by H₂ treatment.

Besides the increased intensity after H_2 treatment, another important result displayed in Fig. 5 is the v(CO) band shift, which is closely related to the sulfur coverage at the edges. On M-edge, the v(CO) band initially presents at 2110 cm⁻¹ on the sulfided sample is shifted to 2107 cm⁻¹ after H_2 treatment. Such band shift indicates that sulfur coverage on M-edge is reduced by H_2 treatment. By contrast, the v(CO) band position on S-edge is not shifted after H_2 treatment, indicating that the sulfur coverage on this edge is not significantly changed in H_2 treatment. Such conclusion of unchanged sulfur coverage on S-edge is reinforced by the fact that the 20-h H_2 treatment does not further enlarge the v(CO) band intensity on this edge (spectrum B and C in Fig. 5).

In addition to the variation in v(CO) band intensity and position, another v(CO) band located at 2098 cm⁻¹ appears after H₂ treatment. This band has been previously observed and assigned to CO adsorption on M-edge with lower sulfur coverage [28,38]. In fact, a careful IR spectrum analysis suggests that this band is



Fig. 5. Effect of H₂ treatment at 623 K on CO adsorption (100 K, 133 Pa at equilibrium) on sulfided Mo(CA/Mo = 2)/Al₂O₃ catalyst. IR/CO spectrum obtained. (A) After sulfidation; (B) after 2-h H₂ treatment; and (C) after 20-h H₂ treatment.

already present as a shoulder in the IR/CO spectrum obtained on sulfided sample (spectrum A in Fig. 5). This v(CO) shoulder band becomes more pronounced after H₂ treatment. This result indicates that there is probably not only one kind of site but rather different sites with gradual sulfur coverage on the M-edge.

3.4. Thiophene adsorption on M-edge and S-edge

In order to investigate the interaction of thiophene with M-edge and S-edge, the freshly sulfided Mo(CA/Mo = 2)/Al₂O₃ catalyst was exposed to small amount of thiophene molecules $(3.5 \times 10^{-2} \,\mu\text{mol}/\text{mg} \text{ of catalyst})$ at room temperature and then characterized by IR/CO. The IR/CO spectra after thiophene adsorption are shown in Fig. 6(A). After introducing small amount of thiophene onto the catalyst surface at room temperature, the first spectrum only presents the band associated with CO adsorption on the M-edge (band at 2112 cm⁻¹). With increasing CO coverage, v(CO) bands of CO adsorbed on Al³⁺ and OH (bands at 2186 and 2155 cm⁻¹) are also recorded. However, the v(CO) band associated with CO on S-edge is always recorded as a shoulder located at 2074 cm⁻¹.

The IR spectra under 133 Pa of CO at equilibrium obtained before and after thiophene adsorption on sulfided Mo(CA/ Mo = 2)/Al₂O₃ catalyst are compared in Fig. 6(B). The v(CO) band intensity corresponding to CO adsorption on Al³⁺ and OH is slightly decreased after thiophene adsorption, showing that part of thiophene molecules adsorbs on the Al₂O₃ surface via Al³⁺ sites and hydroxyl groups in accordance with previous results of Trabuck et al. [39]. Moreover, this conclusion consists well with the investigation of thiophene adsorption on γ -Al₂O₃ by Quigley et al. [40],



Fig. 6. (A) IR spectra of increasing doses (up to 133 Pa at equilibrium) of CO adsorbed at 100 K on sulfided Mo(CA/Mo = 2)/Al₂O₃ catalyst after adsorption of 3.5×10^{-2} µmol thiophene/mg of catalyst at room temperature; and (B) comparison of IR spectra of CO adsorption (133 Pa at equilibrium) before (spectra a) and after (spectra b) thiophene adsorption.

in which three kinds of adsorbed thiophene species were identified on the alumina surface at saturation coverage: One is thiophene interacting with hydroxyl groups presumably via hydrogen bonding, the second is thiophene coordinated via its sulfur atom to coordinately unsaturated Al³⁺ sites, and the third species is multilayered thiophene presents only at high thiophene coverage.

More pronounced effect shown in Fig. 6(B) is the intensity decrease of the v(CO) bands associated with CO adsorption on both M-edge and S-edge (bands at 2112 and 2074 cm^{-1}), which is in accordance with thiophene adsorption on both M-edge and S-edge. Since the v(CO) band of CO adsorbed on S-edge (band at 2074 cm⁻¹) decreases more strongly than the one of CO adsorbed on M-edge (band at 2112 cm^{-1}), it is also suggested that thiophene probably adsorbs more strongly on S-edge than M-edge. For comparison, adsorption of thiophene molecules on M-edge and S-edge was studied by DFT simulations, but it seems that consensus was difficult to achieve in the literature. Cristol et al. [41] proposed that thiophene adsorbs on the stable S-edge in reductive conditions, which corresponds to the HDS reaction condition. By contrast, Moses et al. [42] showed that thiophene molecules preferably adsorb at the Mo edge brim sites by calculating the binding energy of thiophene adsorption on M-edge and S-edge. In another way, Lauritsen et al. [43] using STM imaged that thiophene can adsorb on the H-activated M-edge of triangular-shape MoS₂ slabs. However, this study did not rule out the adsorption of thiophene on S-edge as the synthesized MoS₂ slabs only expose M-edge.

Besides the variation in v(CO) band intensity, what of more interest is that both v(CO) bands associated with CO adsorption on M-edge and S-edge are upward-shifted after thiophene adsorption and the upward-shift is much bigger on S-edge than on Medge $(9 \text{ cm}^{-1} \text{ versus } 2 \text{ cm}^{-1} \text{ as shown in Fig. 6(B)})$. The upward shift of v(CO) band is closely related to a decrease of electron density on M-edge and S-edge induced by thiophene adsorption. thus providing important indication on the electron interaction between MoS₂ edges and thiophene molecules. Such electron interaction may involve both electron donation and back-donation between the MoS_2 phase and thiophene molecules [44]. Generally, the electron donation from S lone pair of thiophene molecule into the acceptor Mo d-state increases the electron density on MoS₂ surface, while the back-donation lowers the electron density of MoS₂ phase by transferring electrons from occupied Mo d-states to thiophene (probably the π bond in the molecule) [44]. Apparently, the decrease of electron density on M-edge and S-edge indicates that the back-donation prevails over the donation process. Thus, the net electron transfer is from MoS₂ edges to thiophene molecules. Furthermore, the larger upward shift of v(CO) band on S-edge indicates that the electron back-donation is much stronger between S-edge and adsorbed thiophene molecule. This result is of great importance since the strong electron back-donation may significantly reduce the aromatic character of thiophene ring [45], which efficiently activate the molecule toward the subsequent HDS reaction.

3.5. Thiophene HDS activity of the sulfided Mo(Mo/CA=x)/Al_2O_3 catalysts

Fig. 7 reports the catalytic activity in thiophene HDS reaction of sulfided $Mo(CA/Mo = x)/Al_2O_3$ catalysts. The sulfided $Mo(CA/Mo = 0)/Al_2O_3$ catalysts exhibit the lowest HDS rate, and a general trend of increasing activity with the addition of citric acid was observed. However, this improvement of activity cannot be simply attributed to the increase of total MoS_2 edge sites (M-edge + S-edge). For example, comparing the sulfided $Mo(CA/Mo = 0)/Al_2O_3$ and $Mo(CA/Mo = 2)/Al_2O_3$ catalysts, the total MoS_2 edge sites are enhanced by + 27% (73–93 μ mol/g, Fig. 3) whereas the HDS rate



Fig. 7. Thiophene HDS rate on sulfided $Mo(CA/Mo = x)/Al_2O_3$ catalysts measured at 623 K and 0.1 MPa.

is increased by + 40% (1.7–2.4 mol h^{-1} kg⁻¹, Fig. 7). Taken into account the error in determining edge site concentration and HDS rate, the disproportion between the total MoS₂ edge sites and HDS rate is significant. Since both the total edge sites and the relative concentration of each edge sites are changed, probably M-edge and S-edge have different intrinsic activity in thiophene HDS reaction.

In order to compare the intrinsic activity of M-edge and S-edge in HDS reaction, the TOFs (*Turn Over Frequency*) of M-edge and S-edge are calculated by presuming that thiophene HDS reaction proceeds independently on both M-edge and S-edge and that these TOFs are constant on the four catalysts. The overall activity of the catalyst can be mathematically expressed as the sum of activity contributions of each edge, which is the number of the edge site multiplied by its intrinsic activity (TOF):

$$r_{\rm HDS} = n_{\rm M-edge} \times \rm{TOF}_{\rm M-edge} + n_{\rm S-edge} \times \rm{TOF}_{\rm S-edge}$$
(1)

where r_{HDS} is the overall thiophene HDS rate; $n_{\text{M-edge}}$ and $n_{\text{S-edge}}$ are the concentration of M-edge and S-edge, respectively; TOF_{M-edge} and TOF_{s-edge} are the intrinsic activity of M-edge and S-edge, respectively.

The overall thiophene HDS rate can be obtained from thiophene HDS test, and the concentration of each edge can be calculated according to the respective CO adsorption band area. To calculate the TOFs of M-edge and S-edge, a set of four equations with only the two TOF values as unknown is obtained on the four sulfided $Mo(CA/Mo = x)/Al_2O_3$ catalysts and must be solved. The solution of the set of equations was obtained on Microsoft Excel 2010 with the multifactor line regression tool. It is found that the TOF_{M-edge} is $22 \pm 2 h^{-1}$ and TOF_{S-edge} is $35 \pm 5 h^{-1}$ with the $R^2 = 0.999$. The detailed regression procedure and parameters are provided in the Supplementary Material. Indeed, the TOF result shows that S-edge is about 60% more active than M-edge in thiophene HDS reaction.

3.6. TEM analysis

The length and stacking distributions of the sulfide phase obtained on $Mo(CA/Mo = 0)/Al_2O_3$ and $Mo(CA/Mo = 2)/Al_2O_3$ catalysts are shown in Fig. 8A and B respectively.

The addition of citric acid leads to a decrease of the average slab length from 3.0 to 2.4 nm and to a slight increase of the average stacking number (1.5-1.7).



Fig. 8. TEM analysis of the morphology (A) slab length and (B) stacking number of Mo(CA/Mo = 0)/Al₂O₃ and Mo(CA/Mo = 2)/Al₂O₃ catalysts.

4. Discussions

4.1. The MoS_2 morphology revealed by IR/CO and the effect of citric acid addition

As a preferred support material, the γ -Al₂O₃ allows a good dispersion of MoS₂ phase but also has strong interaction with MoS₂ slabs. The strong MoS₂-Al₂O₃ interaction may explain why it is difficult to observe clearly the MoS_2 morphology change on Al_2O_3 support by varying the sulfidation temperature and/or H₂S partial pressure [28]. In our work, as shown in Fig. 3, it is clearly recorded by IR spectroscopy that the addition of citric acid progressively increases the concentration of S-edge while decreases that of Medge on the series of $Mo(CA/Mo = x)/Al_2O_3$ catalyst. Although the IR study cannot provide directly the information of a single MoS₂ slab, the stepwise increase of S-edge at the expense of M-edge does suggest that the morphology of MoS₂ slabs on these catalysts is changed from a truncated triangle to a hexagon-like shape. This conclusion is drawn based on the statistic assumption that the ratio of M-edge and S-edge on a single MoS₂ slab is in line with the overall ratio of each edge detected by CO adsorption. Moreover, this conclusion is hardly affected by other MoS₂ slab characteristics such as length and stacking. As far as we know, this is the first experimental evidence of such MoS₂ morphology change on MoS₂/Al₂O₃ catalyst, providing the strong support on the relevance of previous microscopy (STM [17-21] and HAADF-STEM [22,23]) and DFT [6,7,15] studies of MoS₂ morphology on model catalysts.

This effect of chelating agents on the slab morphology has never been proposed previously. One most reported effect of the addition of chelating agent is the delayed sulfidation of promoter that allows cosulfidation of Mo and promoters and leads to higher concentration of promoted site [46]. Even if this effect is not always observed [47], it cannot be totally discarded that the rate or temperature range of sulfidation is involved in the morphology change. However, as previously said, on Al_2O_3 , the sulfidation temperature has only a limited effect on slab morphology [28]. Previous study [48] has proposed that the MoS₂-Al₂O₃ interaction originates from the linkages between Mo atoms and surface OH groups (Mo-O-Al). Here, the effect of citric acid on the morphology change of MoS₂ slabs is tentatively interpreted as lessening the amount of OH groups available to interact with Mo atoms during the formation of MoS₂ phase [49] and thus reducing the MoS₂-Al₂O₃ interaction. The reduction of MoS₂-Al₂O₃ interaction presumably changes the relative free energy of M-edge and S-edge and thus changes the MoS_2 morphology [20]. In this manner, the MoS_2 - Al_2O_3 interaction can be stepwise reduced by varying citric acid addition because the amount of consumed OH groups should correlate with the amount of citric acid used. The MoS₂-Al₂O₃ interaction could also be

modified by the formation of Mo complexes upon citric acid addition [50]. In fact, the v(CO) band position on M-edge and S-edge in IR/CO spectra does provide the implication of the stepwise reduction of MoS₂–Al₂O₃ interaction. As shown in Fig. 4, the v(CO) bands on both M-edge and S-edge are progressively downward-shifted, which originates from a stepwise increase of electron density on MoS₂ phase with the addition of citric acid. Such increase of electron density on MoS₂ may be understood in terms of a gradual reduction of MoS₂–Al₂O₃ interaction. Upon the addition of citric acid, the slight increase of stacking number measured by TEM is also consistent with a decrease of slab-support interaction.

The different growth preferences of M-edge and S-edge due to the change of $MoS_2-Al_2O_3$ interaction also indicate that these two edges interact differently with Al_2O_3 support. Indeed, DFT study by Hinnemann et al. [51] suggested that the Mo–O–Al linkages between $MoS_2-Al_2O_3$ are located on the S-edge, thus that the S-edge interacts much more strongly with Al_2O_3 support. By contrast, Costa et al. [52] proposed in another periodic DFT study that S-edge interacts more weakly with Al_2O_3 support than Medge. Here, our experimental results suggest that M-edge interacts more strongly with Al_2O_3 support, as we observed predominantly M-edges on the MoS_2 slabs with the strongest $MoS_2-Al_2O_3$ interaction.

One may argue that using citric acid will leave carbonaceous deposits on the catalyst surface, which may replace sulfur at MoS₂ edges, giving rise to a carbide-type phase at the particle edges [53]. Indeed, TPR experiments by Valencia et al. [54] revealed that citric acid can be reduced during sulfidation to leave carbon on the catalytic materials. Meanwhile, the C-C vibrations can also be recorded by IR spectroscopy on the sulfided MoS₂/ Al₂O₃ prepared with citric acid in our experiments. However, we did not observe any v(CO) band characterizing CO adsorption on MoS_xC_y phase on our samples. Accordingly, previous studies by Tuxen et al. [55] revealed that incorporation of carbon in MoS₂ phase is thermodynamically unfavorable. Therefore, we suggest that the carbonaceous deposits on the MoS₂/Al₂O₃ surface is more like a by-product of the addition of citric acid, which may be involved in the lowering of slab-support interaction [56] rather than giving rise to a new phase on MoS₂ edges. Finally, Rinaldi et al. have proposed that this carbonaceous deposit is responsible for a decrease of pore volume and an increase of surface area [57] which could also play a role in the modification of the slabsupport interaction.

A more general proposition is that any effect reducing MoS₂support interaction may change the MoS₂ morphology by changing the relative free energy of M-edge and S-edge. For example, previous study [28] showed that increasing sulfidation temperature can also lead to small MoS₂ morphology change on γ -Al₂O₃. This may be interpreted as that higher sulfidation temperature reduces the $MoS_2-Al_2O_3$ interaction by breaking Mo–O–Al linkages, as observed by Candia et al. [58] in 1980s. In the same idea, it was imaged by Lauritsen et al. [20] with STM that incorporation of Co promoters in MoS_2 phase can shift the triangular MoS_2 slabs into a hexagon shape. Such effect of promoters on MoS_2 morphology may also be explained by a lessening of the interaction between MoS_2 edge and support due to the promoter incorporation on the MoS_2 edge, as suggested by DFT calculations [52]. However, it cannot be ruled out that the incorporation of promoter on the edge itself may change the relative free energy of M-edge and S-edge independently of the support.

4.2. The reactivity of M-edge and S-edge

4.2.1. The reactivity of M-edge and S-edge in H_2 treatment

To start with, it is worthy to note that previous IR/CO studies [38,59] identified that the effect of H₂-treatment on MoS_2/Al_2O_3 is completely reversible; the IR/CO spectrum is similar to that obtained directly after sulfidation if the H₂-treated catalyst is resulfided under the same condition. Further, STM studies by Helvg et al. [17] showed that reactive atomic hydrogen treatment at 600 K on MoS₂ nanoparticles creates sulfur vacancies on the fully sulfur-coordinate M-edge without changing the morphology of MoS₂ nanoparticles. Moreover, it is suggested that the MoS₂ morphology transformation involves quite large activation barriers [18], and thus, one may not expect reversible morphology changes for MoS_2/Al_2O_3 catalysts. Therefore, we consider that the H₂ treatment experiment performed on MoS_2/Al_2O_3 catalysts does not change the morphology of the already formed MoS_2 slab.

Although not being expected to affect MoS₂ morphology, H₂ is found to change the MoS₂ edge structure in two ways [21]. First, hydrogen can react with edge sulfurs to form H₂S, which creates sulfur vacancies on the edges. Secondly, hydrogen can also dissociate on the edge sites and lead to the formation of SH groups, which may provide the source of active H for HDS process. With H₂ treatment experiment, as shown in Fig. 5, we find that sulfur vacancy creation more easily occurs on M-edge than S-edge, which is in accordance with previous DFT calculations [44,60,61]. Furthermore, it is found that only limited amount of S atoms can be removed from S-edge. In particular, the 20-h H₂ treatment does not result in further formation of sulfur vacancies on S-edge (spectra b and c in Fig. 5). One explanation for the above-mentioned results is that the position of sulfur vacancies along the edge can be quite different on M-edge and S-edge. Indeed, previous STM study by Tuxen et al. [62] has provided such atomic image that sulfur vacancies can only be formed on the corner sites of S-edge whereas they can be created on all the M-edge. Indeed, the energy required to remove S atoms from the different positions of S-edge could be quite different [61]. The H₂ treatment may only remove these S atoms with lower sulfur bonding energy, i.e. the S atoms located at corner sites. An alternative proposal is related to the S-H groups on S-edge. The existence of S-H groups on MoS₂ phase has been evidenced by IR [63] and STM [18]. It was also proposed that H adsorbs more strongly on S-edge than M-edge [60,64,65]. Furthermore, the S-H group was found to have a strong stabilization effect on S-edge [64]. This strong stabilization effect may account for that the 20-h H₂ treatment cannot further remove sulfur from S-edge compared with the 2-h one.

Another result revealed by the H_2 treatment experiment is that there are at least two types of sites on the M-edge distinguishable by their sulfur coverage after sulfidation. Indeed, according to Ref. [28], the v(CO) bands located at ~2110 cm⁻¹ and ~2098 cm⁻¹ are assigned to CO adsorption on M-edge with different sulfur coverage. Moreover, only the sulfur coverage of the former M-edge can be further reduced upon H_2 treatment and thus the v(CO) band is shifted from 2110 cm⁻¹ to 2107 cm⁻¹ (Fig. 5). Meanwhile, a careful analysis of the IR/CO spectra obtained on sulfided Mo(CA/ Mo = 2)/Al₂O₃ catalyst indicates that besides the main CO adsorption band on S-edge (band at ~2065 cm⁻¹), there are two others v(CO) shoulders located at ~2045 cm⁻¹ and ~2020 cm⁻¹ (More details in Supplementary Materials). These v(CO) shoulder bands were discussed in Ref. [28] and assigned to CO adsorption on Sedge sites with different sulfur coverage. In our work, all these shoulder bands are taken into consideration when calculating the v(CO) band area for CO adsorption on M-edge and S-edge.

4.2.2. The reactivity of M-edge and S-edge in HDS reaction

The IR/CO characterization of sulfided $Mo(CA/Mo = x)/Al_2O_3$ (Fig. 2) demonstrates that MoS₂ morphology is changed as a function of the amount of added citric acid. This result is very interesting since it allows one for the first time to compare the reactivity on M-edge and S-edge of real MoS₂/Al₂O₃ catalyst. Accordingly, by calculating the TOFs of M-edge and S-edge, we find that the S-edge has a higher intrinsic activity than M-edge in thiophene HDS reaction. It should be noted that the determination of TOFs on M-edge and S-edge by IR/CO characterization is rather delicate, since it strongly depends on the molar adsorption coefficient of CO adsorption on M-edge (ε_{M-edge}) and S-edge (ε_{S-edge}). Accordingly, the error in determining the TOF_{M-edge} and TOF_{S-edge} was analyzed (Details are provided in Supplementary Material). It was calculated that the RSD (Relative Standard Deviation) in determining TOF_{M-edge} is 17%, whereas the RSD for TOF_{S-edge} is 27%. Based on the error analysis and the TOF values, it is relevant to conclude that the S-edge has a higher intrinsic activity than M-edge in thiophene HDS reaction (TOF_{S-edge} > TOF_{M-edge}).

In fact, the conclusion that S-edge is intrinsically more active than M-edge can be tentatively correlated with the results of thiophene adsorption. Indeed, subsequent CO adsorption followed by IR spectroscopy reveals that the electron back-donation from the adsorption sites to the adsorbed thiophene molecules is much stronger on S-edge than M-edge (Fig. 6). Such electron back-donation should play a role in the activity of the edge sites since it may result in a distortion of the thiophene ring [43], which can strongly activate the adsorbed thiophene toward the following reactions.

Furthermore, the conclusion that S-edge is intrinsically more active than M-edge is also in good agreement with the results in literature. By calculating the reaction barrier of the elemental reactions in thiophene HDS process, Moses et al. [66] proposed that S–C scission is easier to proceed on S-edge. Following this proposition, one may expect a higher intrinsic activity on S-edge by considering that the S–C scission is the rate limiting step in HDS reaction, which is in accordance with the kinetic study of Hensen et al. [67] on carbon-supported Mo catalysts. Thus, our work allows not only to show that S-edge is intrinsically more active than M-edge in HDS reaction but also to link this activity with the activation of thiophene through its adsorption for subsequent S–C bond cleavage.

It is also interesting to stress that although sulfur vacancies are found to be more easily created upon H_2 treatment on M-edge than S-edge, this does not conflict with the conclusion that S-edge is intrinsically more active than M-edge. Taking into account previous discussion on edge activity, although the proposed HDS mechanisms [68] require the participation of coordinatively unsaturated sites (CUS), it appears that CUS formation is not the kinetic relevant step of thiophene HDS scheme.

4.3. On MoS₂ morphology and slab length

According to the TEM analysis, addition of citric acid decreases the average slab length of the Mo catalyst. Considering that each slab presents 6 corners, it would induce an increase of the corner/ edge ratio that could be tentatively linked with the observed change of IR band ratio upon citric acid addition. Indeed, attributions of the two bands at 2110 and 2070 cm⁻¹ to respectively edge and corner sites have been proposed by Muller et al. by comparison with CO adsorption on metal particles [25]. However, we discard such assignment because of the following reasons: (i) As far as we know, no DFT (density functional theory) simulation was done to valid corner and edge assignment. By contrast, the S-edge and M-edge assignment consists well with DFT simulations [26,27]. (ii) The corner and edge assignment is contradicted with the IR experimental observation that an increase of CO band 2070/2110 intensity ratio is observed with increasing Mo loading which will increase the slab length and thus lead to a decrease of corner/edge ratio [38].

The increased dispersion of Mo upon addition of citric acid allows to explain that the total edge site concentration increases as revealed by IR spectroscopy. Indeed, for a given slab length, the change of morphology from triangle like to hexagonal shape would induce a decrease of edge concentration, taking into account that the length observed by TEM is the edge length of the triangle but the wide length of the hexagon.

5. Conclusions

With low-temperature CO adsorption followed by IR spectroscopy (IR/CO) characterization, it is found that the addition of citric acid during preparation of MoS_2/Al_2O_3 promotes the growth of Sedge at the expense of M-edge on MoS_2 slab. By varying the amount of citric acid addition it is demonstrated that the morphology of MoS_2 slab on Al_2O_3 can be progressively modified from a slightly truncated triangle with predominantly M-edge to a hexagon with both M-edge and S-edge. To our knowledge, this is the first experimental study about such MoS_2 morphology change on industrial-type MoS_2/Al_2O_3 catalyst. Moreover, it reveals, again for the first time, an important effect of chelating agent on the morphology of MoS_2 slabs, which provides new insight into the role of chelating agents in HDS catalysts.

Another important conclusion is that M-edge and S-edge demonstrate different reactivity in HDS reaction. It is found that sulfur vacancy creation occurs more easily on M-edge whereas at room temperature thiophene tends to adsorb more strongly on S-edge. Furthermore, the adsorption of thiophene on S-edge involves significant electron back-donation from S-edge sites to thiophene molecules, implying that S-edge is probably more efficient to activate the adsorbed thiophene toward subsequent reactions. Accordingly, parallel between IR/CO study and HDS tests reveals that Sedge has a higher intrinsic activity than M-edge in thiophene HDS reaction.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.10.005.

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