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Coating SiO₂ Support with TiO₂ or ZrO₂ and Effects on Structure and CO Oxidation Performance of Pt Catalysts

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Abstract: In this work, we studied how TiO₂ and ZrO₂ coatings enhance the CO oxidation performance of SiO₂-supported Pt catalysts under conditions relevant to automotive emissions control. SiO₂ was coated with metal oxides TiO₂ or ZrO₂ by sol-gel method and the subsequent Pt loading was done by incipient wetness method. The prepared catalysts Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂ were compared with Pt/SiO₂ and Pt/Al₂O₃ in fresh, sulfated, and hydrothermally aged states. The structure of the catalysts was characterized with BET, XRD, TEM, EDS, EXAFS, XANES, TPD and TPR to help interpret the CO oxidation performance. Higher dispersion, stability, and oxidation state of Pt were achieved on TiO₂-SiO₂ and ZrO₂-SiO₂ supports due to stronger metal-support interaction leading to superior CO oxidation performance compared to Pt/SiO₂ and Pt/Al₂O₃. TiO₂ and ZrO₂ coatings introduced surface acidity but negligible basicity, which is a likely reason for the weak and low adsorption of SO₂. The results suggest that the sol-gel coating of SiO₂ with metal oxides could be an attractive strategy for designing automotive oxidation catalysts with enhanced performance such as low-temperature activity, sulfur tolerance, and hydrothermal stability.

Keywords: platinum; SiO₂; TiO₂; ZrO₂; surface coating; sulfur tolerance; hydrothermal stability; CO oxidation; diesel oxidation catalysts

1. Introduction

Diesel oxidation catalysts (DOCs) have been extensively studied due to their various roles in the emission control systems of diesel engine vehicles. For example, DOCs such as Pt/Al₂O₃ catalyze the oxidation of carbon monoxide (CO), nitric oxide (NO), unburned hydrocarbons (HC) and the soluble organic fraction (SOF) of particulates [1–11]. Despite the successful commercial implementation of DOCs, however, performance loss due to hydrothermal aging is still an important challenge [4,5]. Indeed, DOCs are often exposed to temperatures above 800 °C created to regenerate downstream diesel particulate filters (DPFs) and/or desulfate NO_x control devices. Sulfur poisoning of DOCs themselves is another significant technical barrier [2,3].

Alumina is a most widely used support for DOCs due to good thermal stability and interaction with Pt-group metals. Its high reactivity with SO_x, however, can lead to the formation of Al₂(SO₄)₃ with resultant performance degradation [2]. Non-basic metal oxides including Ta₂O₅, Nb₂O₅, WO₃, SnO₂, V₂O₅, TiO₂, SiO₂ have been studied as supports for Pt to mitigate the adsorption of acidic sulfur oxides (SO_x) [9,10]. Kröcher *et al.* investigated the adsorption and desorption of SO_x on commercial DOCs [2]. Their work showed that catalysts with higher SiO₂ content required lower desulfation temperatures as SiO₂ formed few sulfates. Based on these results, the authors suggested the use of metal-oxides less sensitive to SO₂ than Al₂O₃ to mitigate sulfur poisoning.

While high surface area SiO₂ is relatively inert toward SO_x, SiO₂-supported catalysts suffer from sintering of Pt particles due to the weak interaction between Pt and SiO₂. It was recently shown that the dispersion and stability of SiO₂-supported Pt can be greatly enhanced by incorporating a layer of TiO₂, ZrO₂, CeO₂ or V₂O₅ [12–15]. Interaction between Pt and the supports was enhanced by the formation of Pt-O-M (M: Ti, Zr, Ce, V) linkages which keep Pt particles from coarsening at elevated temperatures. These oxide-coated catalysts showed excellent performance in the oxidation of carbon monoxide, methane and propane.

Building upon the knowledge gained in the previous research [12–15], the aim of this study was to further understand the effects of metal-oxide coatings (TiO₂, ZrO₂) on the structure and catalytic performance of Pt/SiO₂. In particular, the sulfur tolerance aspect of these metal-oxide-coated Pt/SiO₂ catalysts has not been addressed in the previous work. This paper presents data obtained from detailed characterization of catalysts and explains how metal-oxide coatings improve the CO oxidation performance of Pt/SiO₂ in fresh, sulfated, and hydrothermally aged states, even outperforming the widely used Pt/Al₂O₃.

2. Results and Discussion

2.1. Catalyst Morphology and Pt Dispersion

Table 1 lists the composition and BET surface area of supports and Pt catalysts (refer to Section 3 for the synthesis procedure). The surface area of Al_2O_3 and SiO_2 was, respectively, 160 and 195 m^2/g before the Pt impregnation and reduced to 142 and 176 m^2/g after. The TiO_2 -coated Pt catalyst had a surface area of 193 m^2/g which is almost identical to that of SiO_2 , indicating that a thin layer of TiO_2 was formed on SiO_2 surfaces. By contrast, the ZrO_2 -coated Pt catalyst possessed a significantly lower surface area of 118 m^2/g . This substantial reduction could be explained by a higher loading obtained with ZrO_2 (*ca.* 27–28 wt% of Zr) than with TiO_2 (*ca.* 6–7 wt% of Ti). In addition to coating SiO_2 surfaces, some ZrO_2 was present as stand-alone ZrO_2 particles as confirmed by the X-ray diffraction (XRD) patterns of the fresh catalysts (see the peaks at 2θ of 28.2°, 30.2°, 31.4°, 35.2°, 50.2° and 60.0° in Figure 1). These ZrO_2 particles are likely to have blocked some of SiO_2 micropores thereby reducing BET surface area. The target Pt loading was 1 wt% and actual values determined by ICP and EDS are summarized in Table 1.

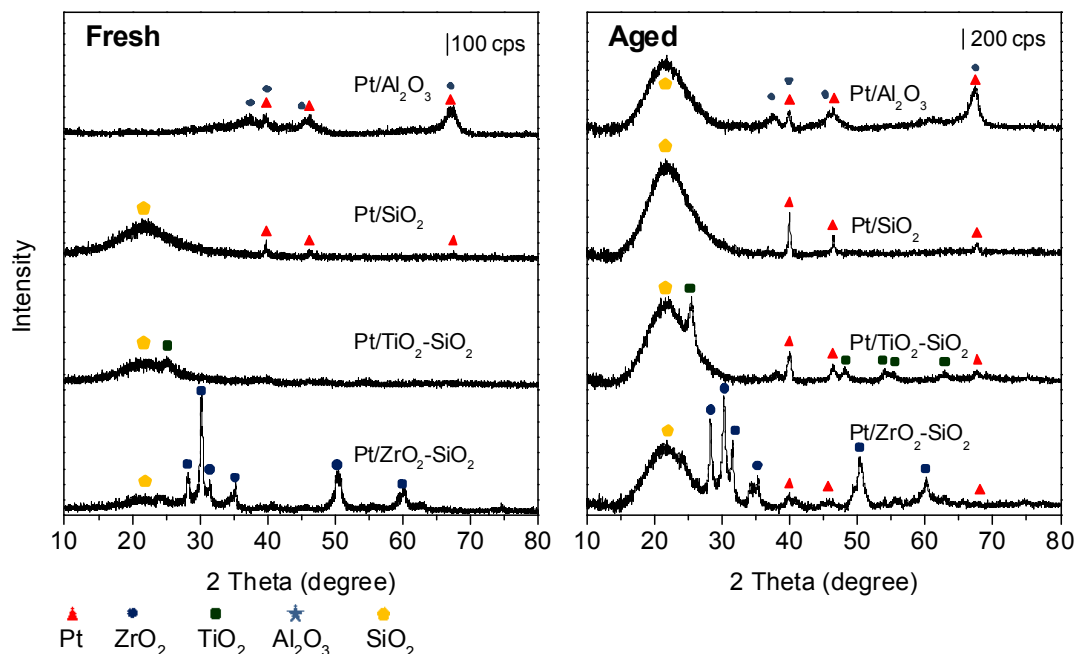
Table 1. Composition and BET surface area of the supports and Pt catalysts.

Samples	Composition (wt%)			S_{BET} (m^2/g)
	Pt	Ti	Zr	
	ICP/EDS	ICP/EDS	ICP/EDS	
Al_2O_3	-	-	-	160
SiO_2	-	-	-	195
Pt/ Al_2O_3	0.60/0.83	-	-	142
Pt/ SiO_2	0.83/1.12	-	-	176
Pt/ TiO_2 - SiO_2	0.94/0.99	5.85/7.02	-	193
Pt/ ZrO_2 - SiO_2	0.88/0.59	-	27.3/28.3	118

X-ray diffraction patterns were recorded for each of the samples to investigate both the phases present and their crystallinity (Figure 1). The diffraction peaks of Pt particles appear at 2θ of 39°, 46°, and 67°, while those of Al_2O_3 are found at 2θ of 32°, 37°, 39°, 45°, 61° and 66° [14]. Our Pt/ Al_2O_3 sample showed diffraction peaks corresponding to Al_2O_3 ; the peaks near 2θ of 39° are too small to distinguish between Al_2O_3 and Pt. Pt/ SiO_2 exhibited peaks attributable to Pt particles in addition to a broad peak at 2θ of 22° corresponding to amorphous SiO_2 structure. Pt/ TiO_2 - SiO_2 did not present any diffraction peaks relative to Pt particles; a small peak at 2θ of 25° corresponds to an anatase-type TiO_2 . Pt/ ZrO_2 - SiO_2 did not exhibit any Pt-attributable peak either. The absence of Pt peaks on Pt/ TiO_2 - SiO_2 and Pt/ ZrO_2 - SiO_2 in fresh state suggests that incorporating TiO_2 and ZrO_2 on SiO_2 considerably improved Pt dispersion likely due to a stronger Pt and support interaction.

Transmission electron microscopy (TEM) images in Figure 2 show clear differences in the size of Pt particles among samples. Large Pt particles of 20 nm were observed on Pt/ SiO_2 with an average particle size of *ca.* 4 nm. In contrast, uniform and fine dispersion of Pt was achieved on TiO_2 - and ZrO_2 -coated SiO_2 with an average particle size of less than 3 nm. This value is comparable to that obtained on Al_2O_3 (< 3 nm). Coating SiO_2 with TiO_2 and ZrO_2 , therefore, appears to be an effective way to enhance the interaction between Pt and supports.

Figure 1. XRD patterns of Pt/ Al_2O_3 , Pt/ SiO_2 , Pt/ TiO_2 - SiO_2 , and Pt/ ZrO_2 - SiO_2 in fresh and hydrothermally aged state. The large SiO_2 peaks observed on all the hydrothermally aged catalysts were due to the quartz powder physically mixed with the catalysts for the reactor evaluation.



The micro-structural properties determined using extended X-ray absorption fine structure (EXAFS), which reflects the averaged environment around a selected atomic species, confirm the XRD and TEM observations on Pt dispersion and provide more detailed information. The EXAFS data were analyzed using IFEFFIT software package [16] and fitted to the EXAFS theoretical calculations [17]. The EXAFS results are summarized in Table 2. An atom of Pt in a closest packing structure has 12 neighboring Pt atoms as the first nearest neighbors, whereas an atom of Pt in small particles has a smaller Pt coordination number (CN) [18,19]. The reduction in average CN occurs because the surface-to-volume ratio increases as particle size decreases and particles on the surface have lower CNs.

Figure 2. TEM images of fresh Pt catalysts supported on Pt/ Al_2O_3 , Pt/ SiO_2 , Pt/ TiO_2 - SiO_2 or Pt/ ZrO_2 - SiO_2 ; a few representative Pt particles are marked with circles in the images.

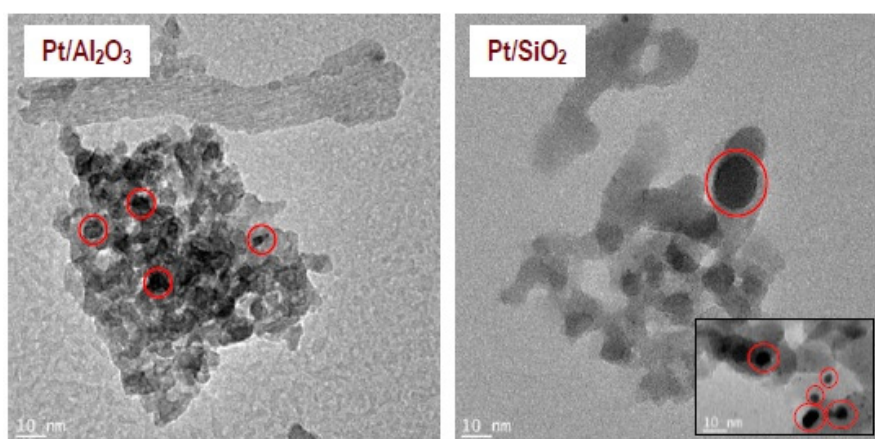
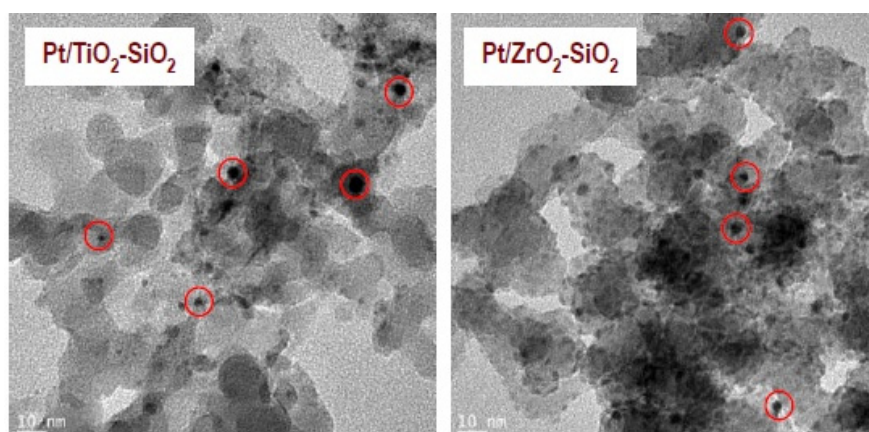


Figure 2. Cont.



For a given catalyst sample, there was a difference in the CN of Pt-Pt atomic pairs between reductive and oxidative gas environments: the CNs for all the samples were higher in H₂ flowing condition than O₂ flowing condition. This indicates that re-dispersion of Pt particles occurred in O₂ flow. It has been reported that Pt particles sintered at high temperature in H₂ flow can be re-dispersed by O₂ treatment above 400 °C [20–24]. In the H₂ flowing condition, the CN of the Pt-Pt atomic pairs of Pt/Al₂O₃ was 10.4 at around $R = 2.7 \text{ \AA}$ and that of Pt/SiO₂ was 10.5. This similarity between Pt/Al₂O₃ and Pt/SiO₂ appears to contradict the TEM results (Figure 2) which evidenced the presence of larger particles on SiO₂. The apparent discrepancy could be explained by the fact that EXAFS is a bulk, average technique while TEM can discern large particles (e.g., 20 nm Pt/SiO₂) present on samples with small average particle sizes (e.g., 4 nm particles for Pt/SiO₂ support). On the other hand, the CNs of the Pt-Pt atomic pairs were 5.2 and 5.1 on TiO₂-SiO₂ and ZrO₂-SiO₂, respectively. This CN of *ca.* 5 suggests an average particle size of about 1 nm [19]. This value agrees well with the TEM data further confirming that TiO₂ and ZrO₂ coatings enhanced Pt dispersion on SiO₂. The Pt-Pt distance for Pt/Al₂O₃, Pt/SiO₂, Pt/TiO₂-SiO₂, and Pt/ZrO₂-SiO₂ were 2.743, 2.743, 2.651 and 2.604, respectively. In a previous study, indeed, the distance of Pt-Pt atomic pairs was shown to decrease from 2.75 to 2.60 Å with decreasing Pt particle size [25]. The shortened distance between Pt and Pt atoms further corroborates the improved Pt dispersion.

Table 2. EXAFS results ^a.

Catalyst	Condition ^b	Atomic pair	CN	R (Å)	σ^2 (Å ²)
Pt/Al ₂ O ₃	H ₂	Pt-Pt	10.4(4) ^c	2.743(5)	0.011(1)
	O ₂	Pt-Pt	9.2(4)	2.758(3)	0.010(1)
Pt/SiO ₂	H ₂	Pt-Pt	10.5(2)	2.743(1)	0.012(1)
	O ₂	Pt-Pt	8.2(2)	2.758(2)	0.010(1)
Pt/TiO ₂ -SiO ₂	H ₂	Pt-Pt	5.2(2)	2.651(3)	0.014(1)
	O ₂	Pt-O	3.7(1)	2.001(3)	0.003(1)
Pt/ZrO ₂ -SiO ₂	H ₂	Pt-Pt	5.1(1)	2.604(2)	0.012(1)
	O ₂	Pt-O	3.1(1)	2.024(2)	0.004(1)

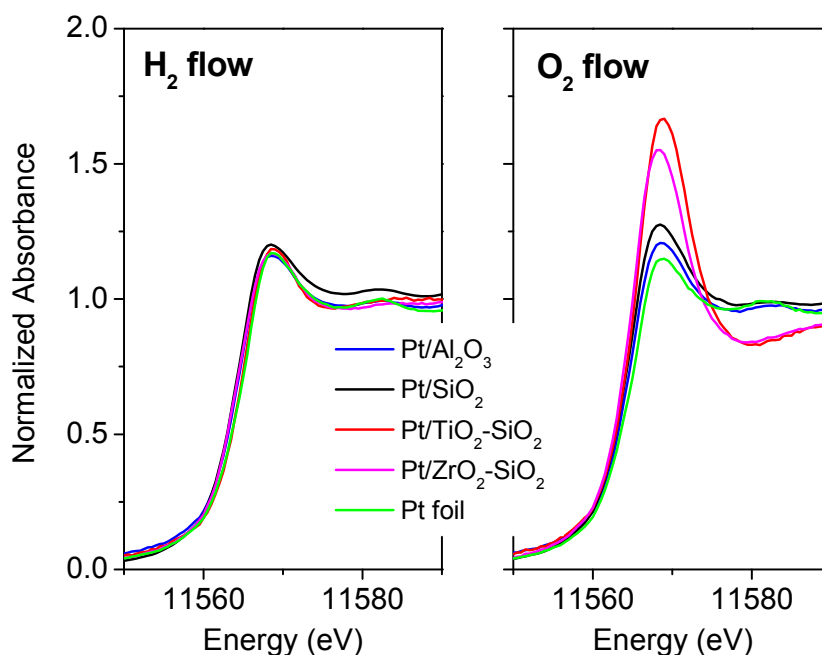
^a Determined from the fitted EXAFS spectra of the Pt catalysts at Pt L_{III}-edge; $S_0^2 = 0.86$, k^3 weighted; CN: coordination number; R: bond length; σ^2 : Debye–Waller factor. ^b Measured at 400 °C. ^c The calculated limits of accuracy in the last reported digit.

In O_2 flow, EXAFS demonstrated that O atoms existed at 2.0 Å from a Pt atom whereas the Pt atoms at 2.7 Å nearly disappeared on Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂. This finding indicates that most of the Pt particles were oxidized in the O_2 flowing condition at 400 °C. In fact, it has been known that small Pt particles tend to be easily oxidized [26,27]. The presence of the Pt-O atomic pairs on Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂ could also be due in part to the formation of Pt-O-M (M: Ti, Zr) bonds at the interface between Pt particles and TiO₂ and ZrO₂, which stabilized small Pt particles [14–17,28,29]. Compared to the data obtained in H_2 flow, those collected in O_2 flow provide information on the chemical state and dispersion of Pt particles more relevant to interpreting CO oxidation performance.

2.2. Redox Properties of Supported Pt

The Pt L_{III}-edge X-ray absorption near edge structure (XANES) spectra obtained in H_2 and O_2 flows are shown in Figure 3. The peaks near 11567 eV in the XANES spectra, namely white lines, are mainly the result of electron transition from 2p_{2/3}-band to 5d-band in the X-ray absorption process [30,31]. The peak intensity of the white lines is proportional to the 5d-band vacancy. Furthermore, it can also depend on the size and morphology of Pt particles. There were significant differences in the XANES spectra depending on the flowing gas type. The XANES spectra obtained in H_2 flow were practically identical for all catalysts and the reference Pt foil. This similarity means that the contribution of particle size and morphology to the white line intensity is negligible in a reductive gas environment. By contrast, the XANES spectra obtained in O_2 flow varied considerably with the type of catalyst support. While the white-line intensity for Pt/Al₂O₃ and Pt/SiO₂ increased slightly, that of Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂ increased dramatically when exposed to the O_2 flow. These results indicate that the Pt atoms dispersed on the TiO₂- and ZrO₂-coated SiO₂ had a greater affinity towards oxygen leading to higher oxidation states of Pt.

Figure 3. Pt L_{III}-edge XANES spectra obtained at 400 °C for Pt/Al₂O₃, Pt/SiO₂, Pt/TiO₂-SiO₂, Pt/ZrO₂-SiO₂, and Pt foil in H_2 and O_2 flow.



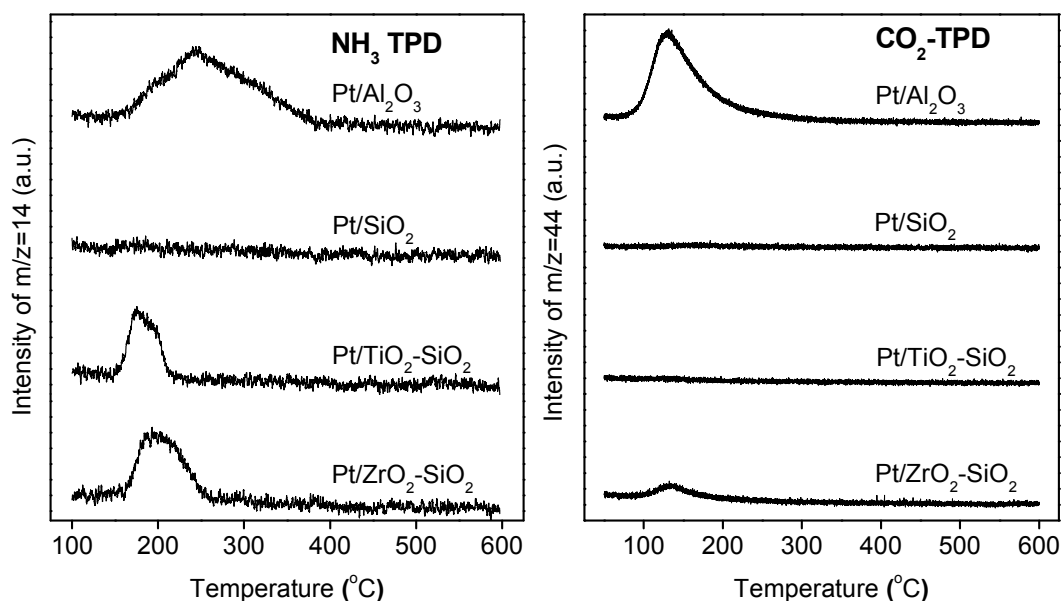
2.3. Surface Acidity, Basicity and Sulfur Tolerance

It has been reported that high acidity and low basicity induce high sulfur tolerance of catalytic materials [2,9,10,32,33]. The acidic and basic properties of the Pt catalysts studied here were assessed using the temperature programmed desorption (TPD) of NH_3 and CO_2 , respectively. The TPD profiles varied significantly for the different catalyst supports as shown in Figure 4. The area under the TPD curve is directly proportional to the amount of NH_3 or CO_2 desorbed from the surface, and therefore provides a relative measure of the number of surface acidic or basic sites. In addition, the temperatures of the desorption peak maxima (T_m) provide information about the relative strength of the acidic or basic sites.

For NH_3 , $\text{Pt}/\text{Al}_2\text{O}_3$ had both the largest desorption peak and highest T_m around 250 °C, while Pt/SiO_2 exhibited negligible NH_3 desorption. Coating SiO_2 with TiO_2 generated surface acidity as manifested by a desorption peak near 190 °C. ZrO_2 coating also led to surface acidity with an NH_3 desorption peak (150–250 °C) slightly larger than that of the TiO_2 -coated catalyst. The amount and strength of surface acidic sites estimated from NH_3 -TPD were in the order of $\text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{ZrO}_2\text{-SiO}_2 > \text{Pt}/\text{TiO}_2\text{-SiO}_2 > \text{Pt}/\text{SiO}_2$. These results are in line with an earlier report that $\text{TiO}_2\text{-SiO}_2$ and $\text{ZrO}_2\text{-SiO}_2$ mixed oxides possess strong acidity, while the individual oxides TiO_2 and ZrO_2 show relatively weak acidity [34].

The profiles of CO_2 -TPD showed that $\text{Pt}/\text{Al}_2\text{O}_3$ had significant basicity as well with a peak at 150 °C. On the other hand, Pt/SiO_2 had no desorption confirming its inertness in terms of surface basicity. Contrary to the surface acidity, coating with TiO_2 or ZrO_2 did not generate a significant amount of surface basicity as confirmed by near zero CO_2 desorption from $\text{Pt}/\text{TiO}_2\text{-SiO}_2$ and a minor desorption from $\text{Pt}/\text{ZrO}_2\text{-SiO}_2$ at around 150 °C. The relative amounts of NH_3 and CO_2 desorbed are summarized in Table 3.

Figure 4. NH_3 and CO_2 TPD profiles for $\text{Pt}/\text{Al}_2\text{O}_3$, Pt/SiO_2 , $\text{Pt}/\text{TiO}_2\text{-SiO}_2$, and $\text{Pt}/\text{ZrO}_2\text{-SiO}_2$ catalysts.

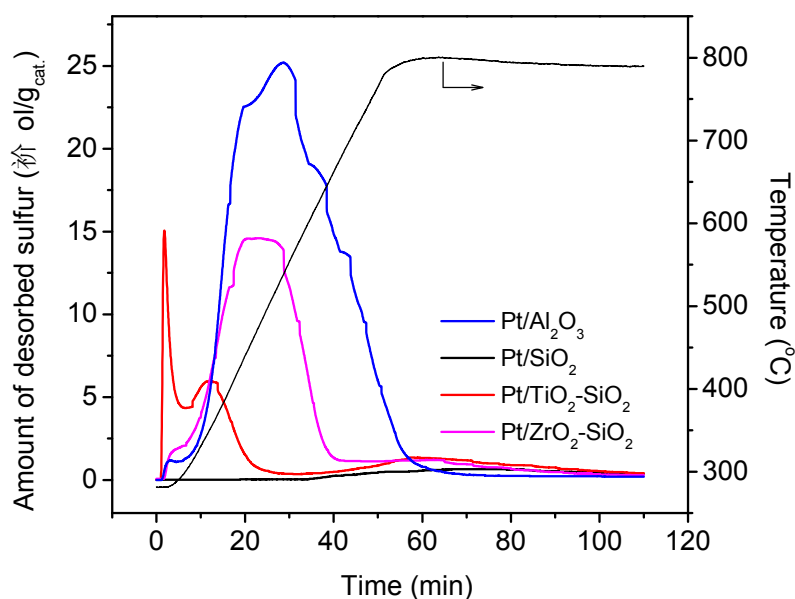


Our data in Table 3 suggest that Pt/SiO₂ should be the least reactive toward SO₂ adsorption due to its inertness followed by Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂. To confirm this conjecture, we performed H₂ temperature-programmed reduction (TPR) of the sulfated catalysts. The TPR-desulfation data are compiled in Figure 5 and Table 3. As expected, Pt/Al₂O₃ adsorbed the most sulfur species, which were also more stable (higher release temperature), while sulfur adsorption/desorption was negligible on Pt/SiO₂. Relatively small amount of sulfur species of weak adsorption strength were present on Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂ catalysts.

Table 3. Acidic and basic sites of Pt catalysts and amount of desorbed sulfur during temperature-programmed reduction (TPR).

Catalyst	Relative amount of acidic sites	Relative amount of basic sites	Amount of desorbed sulfur (μmol/g _{cat})
Pt/Al ₂ O ₃	1	1	726
Pt/SiO ₂	0	0	37
Pt/TiO ₂ -SiO ₂	0.35	0	171
Pt/ZrO ₂ -SiO ₂	0.63	0.08	368

Figure 5. Sulfur release profiles during H₂-TPR of the sulfated Pt/Al₂O₃, Pt/SiO₂, Pt/TiO₂-SiO₂, and Pt/ZrO₂-SiO₂.



2.4. Hydrothermal Stability of Pt Particles

XRD peaks attributable to Pt particles ($2\theta = 39^\circ$, 46° , and 67°) were observed on all the catalysts after a 2-h hydrothermal aging at 800 °C preceded by a TPR desulfation to 800 °C (Figure 1). The significant growth of Pt peaks (XRD) compared to the fresh state indicates significant sintering of Pt particles. The average Pt particle sizes were estimated from diffraction peaks using the Scherrer equation: Pt/Al₂O₃ 18.4 nm, Pt/SiO₂ 44.4 nm, Pt/TiO₂-SiO₂ 13.6 nm, and Pt/ZrO₂-SiO₂ 12.3 nm.

Relative changes in peak intensity (*i.e.*, extent of Pt particle growth) were, however, dependent on the support type. Pt/SiO₂ exhibited the highest/sharpest diffraction peaks, indicating significant sintering of Pt particles. Pt/ZrO₂-SiO₂ was the most resistant to Pt sintering as evident from the smallest diffraction peaks. This observation is consistent with a previous study which reported that ZrO₂-coating enhances the stability of Pt/SiO₂ at high temperatures under an oxidizing environment [14]. Our results also show that Pt dispersion was maintained on ZrO₂-SiO₂ even during sulfation and high-temperature desulfation in reducing conditions.

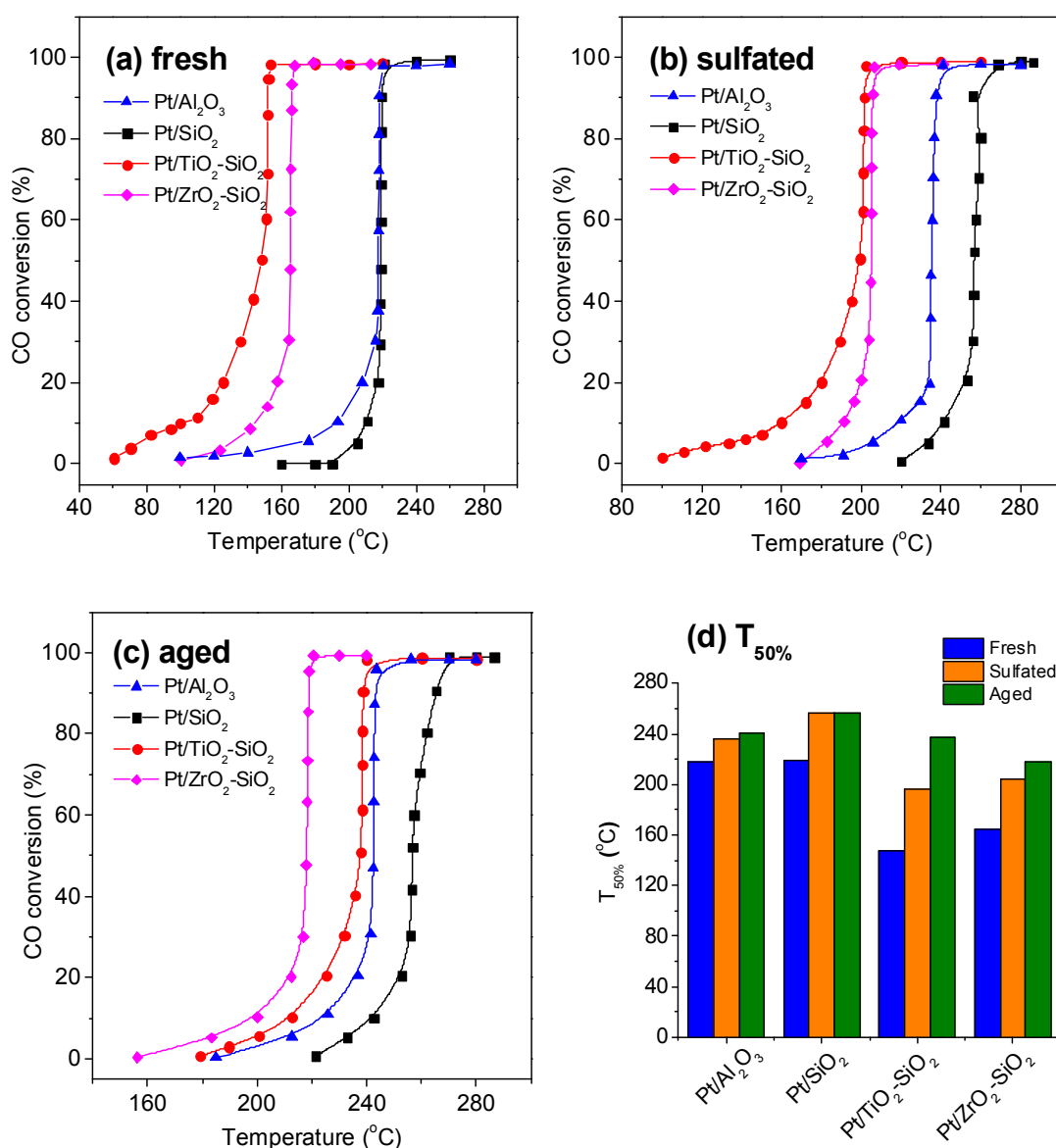
2.5. Catalytic Performance in CO Oxidation

Figure 6 shows the catalytic CO oxidation performance of the four Pt catalysts in fresh, sulfated, and hydrothermally aged states. In addition to the temperature-conversion profiles (Figure 6a–c), the $T_{50\%}$ value (“light-off temperature”, defined as the temperature at which 50% conversion of CO is achieved) for each catalyst at different states is summarized using a bar graph in Figure 6d. It is to note that there were some differences in Pt loading (0.6–0.94% by ICP, Table 1) among the catalysts. However, those differences were not significant enough to affect the overall interpretation of the light-off curves. That is, the order of the light-off temperatures remains the same whether or not the CO conversion activity is normalized by Pt loading (results not shown). As expected based on the characterization data, the catalytic activity was sensitive to the type of support and catalyst state. The Pt catalysts supported on TiO₂- and ZrO₂-coated SiO₂ had a higher catalytic activity than Pt/SiO₂ and Pt/Al₂O₃ regardless of treatment type. The $T_{50\%}$ was 148 °C on Pt/TiO₂-SiO₂ and 165 °C on Pt/ZrO₂-SiO₂ in the fresh state (Figure 6a). Pt/Al₂O₃ and Pt/SiO₂ both had a $T_{50\%}$ of around 218 °C. However, it should be noted that the fresh Pt/Al₂O₃ was intrinsically more active than Pt/SiO₂: the former achieved higher CO conversion at temperatures below $T_{50\%}$ where the apparent catalytic activity was less affected by heat and mass transfer limitations. The superior activity of TiO₂- and ZrO₂-coated catalysts agrees well with their higher Pt dispersion. It has been reported that the CO oxidation proceeds via a Langmuir-Hinshelwood mechanism involving reaction between CO and dissociated-O₂ adsorbed on Pt surfaces [31,35], and that high oxygen coverage of Pt surfaces is favorable for CO oxidation whereas high CO coverage limits catalytic performance (“self-poisoning”) [36]. Strong interaction between Pt and metal oxide (TiO₂ and ZrO₂) have been shown to suppress the adsorption of CO [37,38]. Moreover, our XANES results suggest that the interaction between Pt and O was enhanced by TiO₂ and ZrO₂ coatings as deduced from the increased Pt oxidation state. The weakly adsorbed CO and high O coverage on Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂ could have contributed to the superior catalytic performance compared to Pt/Al₂O₃ which also had relatively good Pt dispersion.

The CO oxidation activity of all the catalysts was significantly decreased by sulfation (Figure 6b,d). For instance, the $T_{50\%}$ of Pt/SiO₂ and Pt/Al₂O₃ increased to 260 and 240 °C, respectively. Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂ also lost performance with a $T_{50\%}$ of roughly 200 °C. Nonetheless, the performance advantage of Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂ was still maintained after the sulfation, which can be explained in part by their weak interaction with SO₂ (Table 3, Figure 5). Pt/TiO₂-SiO₂ had the lowest $T_{50\%}$ in both fresh and sulfated states. Another remarkable observation on Pt/TiO₂-SiO₂ is its very low initiation temperature as shown in Figure 6a–c. For example, the catalyst achieved 10% conversion below 100 °C in the fresh state. It is also worth mentioning that Pt/SiO₂ suffered a significant activity

loss even though it adsorbed negligible amount of SO_2 . This loss might be due to Pt sintering during sulfation. It has been reported that SO_2 can facilitate Pt sintering at relatively low temperatures [39]; it is likely that SO_2 -induced Pt sintering was most pronounced on Pt/SiO_2 because of the weak metal-support interaction.

Figure 6. Catalytic performance of $\text{Pt}/\text{Al}_2\text{O}_3$, Pt/SiO_2 , $\text{Pt}/\text{TiO}_2\text{-SiO}_2$, and $\text{Pt}/\text{ZrO}_2\text{-SiO}_2$ in the oxidation of carbon monoxide with a total flow rate of 200 ml/min (1% CO , 4% O_2 , 5% H_2O , Ar balance); (a) fresh catalysts; (b) sulfated catalysts; (c) hydrothermal aged catalysts and (d) light-off temperatures ($T_{50\%}$).



The catalytic performance further degraded after hydrothermal aging (Figure 6c). Again, $\text{Pt}/\text{TiO}_2\text{-SiO}_2$ and $\text{Pt}/\text{ZrO}_2\text{-SiO}_2$ outperformed the other catalysts. Unlike the fresh and sulfated states, the $T_{50\%}$ of $\text{Pt}/\text{ZrO}_2\text{-SiO}_2$ was lower than that of $\text{Pt}/\text{TiO}_2\text{-SiO}_2$. This trend is in good agreement with the XRD data (Figure 1) which highlight the superior stability of Pt particles on $\text{ZrO}_2\text{-SiO}_2$. Little activity

change was observed on Pt/SiO₂ after the hydrothermal aging step; it is likely that an extensive Pt sintering had already occurred during the sulfation step as described above.

3. Experimental Section

3.1. Preparation of Pt Catalysts

Amorphous fumed silica (Strem Chemicals, 0.012 µm) was used as a support for the preparation of Pt catalysts. Titanium and zirconium oxides were coated on the SiO₂ surface following the procedure described in previous papers [12–15]. SiO₂ was first dehydrated with anhydrous ethanol (90% ethanol with 5% isopropyl alcohol and 5% methyl alcohol as denaturants, Aldrich) and reacted at 80 °C for 3 h with titanium(IV) *n*-butoxide (98+%, Alfa Aesar) or zirconium(IV) *n*-propoxide (70% w/w in *n*-propanol, Alfa Aesar) dissolved in ethanol. TiO₂ or ZrO₂-coated SiO₂ were obtained by removing the non-reacted precursors through washing with ethanol followed by drying at 100 °C and calcining at 500 °C for 2 h. Tetraamineplatinum(II) nitrate (50.0+%, Pt basis, Aldrich) was impregnated on TiO₂-SiO₂ and ZrO₂-SiO₂ supports by incipient wetness method to 1 wt% Pt loading. After the impregnation, the catalysts were dried at 100 °C in air and treated with hydrogen peroxide (35% w/w aqueous solution, Alfa Aesar) at 60 °C. The Pt catalysts treated with hydrogen peroxide were dried at 100 °C and reduced in a flow of 10% H₂ in Ar at 500 °C for 2 h. The prepared catalysts were named as Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂. For comparison, Pt catalysts supported on uncoated SiO₂ (Pt/SiO₂) and Al₂O₃ (Pt/Al₂O₃; acidic alumina, pore size 58 Å~150 mesh, Aldrich) were also prepared by incipient wetness method.

3.2. Characterization

The content of Ti, Zr, and Pt of the prepared catalysts was determined using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Optima 4300 DV, Perkin-Elmer, Waltham, MA, USA) and an Energy Dispersive X-ray Spectroscopy (EDS) system (EX-200, Horiba, Kyoto, Japan) attached to a scanning electron microscope (S-4700, Hitachi, Tokyo, Japan). The X-ray diffraction patterns of catalysts were recorded on a powder X-ray diffractometer (X'Pert PRO, PANalytical, Almelo, The Netherlands) operated at 45 kV and 40 mA using CuKα radiation ($K_{\alpha} = 0.154178$ nm). A transmission electron microscope (LIBRA-120, Carl Zeiss, Oberkochen, Germany) equipped with a LaB₆ filament was employed to examine the dispersion of Pt particles. The acceleration voltage was 120 kV. TEM samples were prepared by dropping ethanol suspension of Pt catalysts on a copper grid. The particle size of Pt was estimated from the digitized TEM photos using image analysis software (Scion Image, Scion Corporation, Frederick, MD, USA). The surface area of catalysts was determined using an automatic volumetric adsorption apparatus (Gemini 275, Micromeritics, Norcross, GA, USA). Surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation.

Temperature-programmed desorption experiments were carried out using a flow reactor system. For each TPD experiment, 0.1 g of catalyst was placed in a U-shaped quartz tube (8 mm I.D.) and pretreated at 600 °C for 0.5 h in an Ar flow. After cooling to 100 °C, the catalyst was exposed to a flow of 0.1% NH₃ in Ar for 1 h, then to an Ar flow for a 0.5-h purge. Subsequently, desorption was programmed at 10 °C/min to 600 °C in an Ar flow. The total flow rate was 200 mL/min (STP) for all

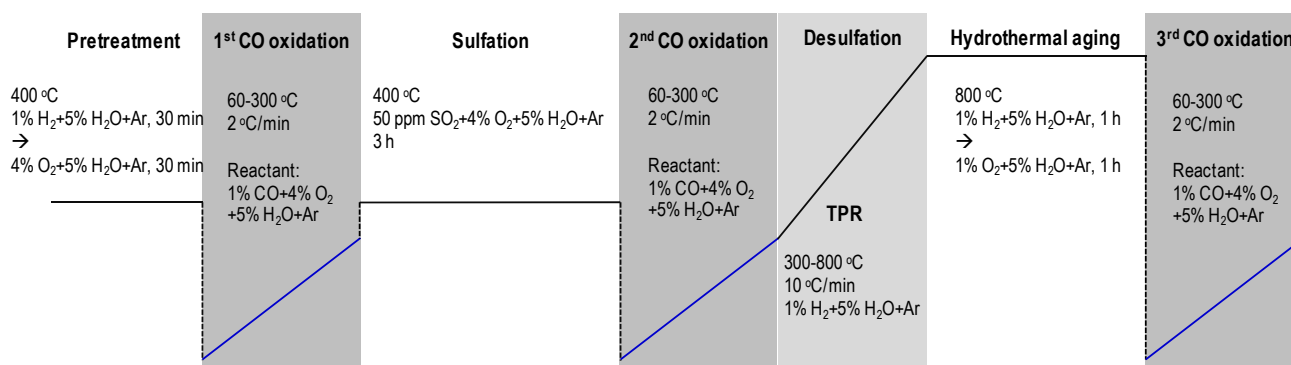
the steps. The procedure for the CO₂ TPD experiments was identical except that the adsorption was done in a flow of 10% CO₂ in Ar at 50 °C followed by a 1-h purge. Gas composition was continuously analyzed by a quadrupole mass spectrometer (RGA100, SRS, Sunnyvale, CA, USA). The *m/z* ratios monitored were 14 for NH₃, 18 for H₂O, 40 for Ar and 44 for CO₂.

The *in-situ* X-ray absorption spectra (EXAFS and XANES) were recorded at the 9 BM of the Advanced Photon Source. X-ray spectra were monochromated by a double crystal monochromator composed of Si(111) and Si(222) crystals. The X-ray absorption of platinum atoms was measured at the Pt L_{III}-edge (11,564 eV). The measurements were done in a flow of 3.5% H₂ in He (100 mL/min, STP) and a flow of 5% O₂ in He (100 mL/min, STP) at 400 °C to study changes in chemical states in reductive or oxidative environment. The X-ray absorption data were processed using an IFFEFIT program based on the FEFF8 theoretical model. A *S*₀² value of 0.86 was used for a curve fitting of EXAFS spectra. The *k*³-weighted data were fitted in the *R* range of 1.5–3.3 Å.

3.3. Evaluation of Catalytic CO Oxidation Performance

The catalytic performance of the prepared Pt catalysts was compared for CO oxidation under atmospheric pressure. A flow reactor equipped with a quadrupole mass spectrometer (RGA100, SRS, Sunnyvale, USA) and a fluorescent SO₂ analyzer (100 A UV fluorescence SO₂ analyzer, Teledyne API, San Diego, CA, USA) was employed. As previously described in [40], there was a reactor loaded with an oxidation catalyst downstream of the main reactor to oxidize H₂S to SO₂ because the sulfur analyzer detected only SO₂. For each reactor run, a physical mixture of 0.1 g of Pt catalyst and 0.3 g quartz powder was positioned between plugs of quartz wool in a U-shaped quartz tube. Prior to experiments, the catalysts were pretreated in an Ar flow at 400 °C for 1 h. The reaction gas consisting of 1% CO, 4% O₂, and 5% H₂O in Ar balance was fed into the reactor at a total flow rate of 200 mL/min (STP). The performance was evaluated by continuously increasing the reaction temperature from 60 to 300 °C at 2 °C/min. The effluent gas composition was analyzed with the mass spectrometer. The monitored *m/z* ratios were 17 for H₂O, 28 for CO, 40 for Ar and 44 for CO₂. To obtain CO values, the contribution from CO₂ fragmentation (*m/z* 28) was taken into account.

Figure 7. Sequence of reactor evaluation of catalysts including sulfation, desulfation, and hydrothermal aging steps.



Three consecutive CO oxidation runs were performed for each catalyst as shown in Figure 7. After the first run, the catalysts were sulfated at 400 °C for 3 h in a flow of 50 ppm of SO₂, 4% O₂, 5% H₂O,

and Ar balance, and evaluated again for CO oxidation. Subsequently, the catalysts were desulfated by temperature-programmed reduction to 800 °C at 10 °C/min in a H₂ flow with effluent-gas sulfur analysis. Then, the desulfated catalysts were hydrothermally aged at 800 °C for 2 h. Finally, the hydrothermally aged catalysts were evaluated in CO oxidation.

4. Conclusions

We investigated the impact of TiO₂ and ZrO₂ coatings on the performance of SiO₂-supported Pt catalysts. Key findings in the present study were:

- Coating SiO₂ with TiO₂ or ZrO₂ via sol-gel method before Pt impregnation led to enhanced dispersion and hydrothermal stability of Pt due to stronger interaction between Pt and supports;
- TiO₂ and ZrO₂ coatings increased the oxidation state of Pt in O₂ environment;
- TiO₂ and ZrO₂ coatings generated acidity but negligible basicity on the catalyst surface, which explains relatively low and weak sulfur uptake on Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂;
- Pt/TiO₂-SiO₂ and Pt/ZrO₂-SiO₂ exhibited better CO oxidation performance than Pt/SiO₂ and Pt/Al₂O₃ in fresh, sulfated, and hydrothermally aged states due to the favorable properties brought by metal-oxide coating as described above;
- Results suggest that the sol-gel coating of SiO₂ with metal oxides can be an attractive strategy for designing automotive oxidation catalysts with enhanced performance such as low-temperature activity, sulfur tolerance, and hydrothermal stability;
- Further research is necessary to further our understanding of the structure and chemistry of TiO₂ and ZrO₂ coatings; a follow-up study of Pt/TiO₂ and Pt/ZrO₂ will be particularly helpful. Furthermore, as Pd is another widely used metal component of state-of-the-art DOCs, it would be appropriate to study Pd catalysts to determine if oxide coating has similarly beneficial impact on catalyst performance.

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Declaration

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Conflict of Interest

The authors declare no conflict of interest.

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