

## Mechanism of Carbon Deposit/Removal in Methane Dry Reforming on Supported Metal Catalysts

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The greater resistance to coke deposition for Pt/ZrO<sub>2</sub> compared to Pt/Al<sub>2</sub>O<sub>3</sub> in the CH<sub>4</sub>/CO<sub>2</sub> reaction has been attributed to the higher reactivity of coke with CO<sub>2</sub> on Pt/ZrO<sub>2</sub> [1]. Hence, in this communication, the reaction of coke derived from methane (CH<sub>x</sub>: which is an intermediate in the reforming reaction and also a source of coke deposition) with CO<sub>2</sub> was studied on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub> at 1070 K. The reactivity of coke itself on Pt, as measured by its reaction with H<sub>2</sub>, was higher on Pt/Al<sub>2</sub>O<sub>3</sub> than on Pt/ZrO<sub>2</sub>. However, the reactivity of coke toward CO<sub>2</sub> was lower. Hence, the difference between the two catalysts cannot be attributed to the difference in the reactivity of coke itself. Next, the ability of the active site to activate CO<sub>2</sub> (probably oxygen defect sites on the support), as shown by CO evolution measurement in CO<sub>2</sub> stream, was higher on Pt/ZrO<sub>2</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub>. Therefore, the high reactivity of coke toward CO<sub>2</sub> on Pt/ZrO<sub>2</sub> is attributed not to the intrinsic reactivity of coke itself but to the high activity of CO<sub>2</sub> at oxygen defect sites of ZrO<sub>2</sub> that are in the vicinity of Pt particles.

### 1. INTRODUCTION

Pt/ZrO<sub>2</sub> has been found to be a stable catalyst for CH<sub>4</sub>/CO<sub>2</sub> reforming reaction in a wide range of temperatures, while Pt/Al<sub>2</sub>O<sub>3</sub> deactivates at these same conditions [2]. The cause of catalytic deactivation for Pt/Al<sub>2</sub>O<sub>3</sub> is attributed to coke deposition on catalytic reactive site at temperatures lower than 1070 K [1,3]. In an earlier work, we have proposed the deactivation mechanism for Pt/Al<sub>2</sub>O<sub>3</sub> at 1070 K [1]. A part of coke derived from methane (CH<sub>x</sub>: 0 ≤ x ≤ 3) remains on Pt/Al<sub>2</sub>O<sub>3</sub> without being oxidized by CO<sub>2</sub> and gradually covers the Pt particles. After a while, only the Pt-Al<sub>2</sub>O<sub>3</sub> interface remains as the active site. The coke deposition is brought about by an imbalance between coke (CH<sub>x</sub>) formation on Pt particles and oxidation of the coke by activated CO<sub>2</sub>. On the other hand, over Pt/ZrO<sub>2</sub>, coke deposition is minimal. Therefore, the catalyst maintains stable activity for a longer time. A combination of three processes can be used to explain why coke deposited from methane is oxidized by CO<sub>2</sub> more rapidly on Pt/ZrO<sub>2</sub>: (i) coke on Pt that is supported on ZrO<sub>2</sub> is more reactive toward CO<sub>2</sub> than on Pt supported on Al<sub>2</sub>O<sub>3</sub>; (ii) CH<sub>4</sub> decomposition is slower on Pt/ZrO<sub>2</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub>; (iii) coke which may cover active sites is hardly formed on ZrO<sub>2</sub>.

In this communication, we investigate (i); i.e., why coke on Pt supported on  $ZrO_2$  is more reactive toward  $CO_2$  than on Pt supported on  $Al_2O_3$  at 1070 K. The reactants are coke derived from methane ( $CH_x$ ) and  $CO_2$ . Studying the reactivity of each species helps in the understanding of the difference in reactivity of coke toward  $CO_2$ . Temperature programmed hydrogenation (TPH) is performed to investigate the reactivity of coke itself on  $Pt/Al_2O_3$  and  $Pt/ZrO_2$  after exposure to  $CH_4/CO_2$  (in the  $CH_4/CO_2$  reforming reaction) or  $CH_4/He$  (which produces  $CH_x$ ). The results are compared with the results of temperature programmed reaction (TPRn) of coke with  $CO_2$  (reproduced from [1]). Further, the reactivity of  $CO_2$  on  $Pt/Al_2O_3$  and  $Pt/ZrO_2$  is compared by following the amount of CO evolved when  $CO_2$  flows on over the catalysts.

## 2. EXPERIMENTAL

$Pt/ZrO_2$  and  $Pt/Al_2O_3$  were prepared by the wet impregnation technique. For this purpose, a solution of  $H_2PtCl_6 \cdot 6H_2O$  in water,  $ZrO_2$  (RC-100, Gimex, Japan), and  $Al_2O_3$  (000-3AQ, AKZO, The Netherlands) were used. The catalysts were dried overnight at 395 K in static air and calcined for 15 h at 925 K (heating rate  $3 K min^{-1}$ ) in flowing air ( $30 ml min^{-1}$ ).

TPH and TPRn with  $CO_2$  were performed in an Altamira AMI-2000 apparatus. 0.1 g of catalyst was loaded into a tubular quartz reactor and a thermocouple was placed at the top of the catalyst bed to measure the temperature of the catalyst. After the catalyst was reduced *in situ* with  $H_2$  for 1 h at 1120 K, the temperature was lowered to 1070 K in He stream and feed gas mixture ( $CH_4/He$  (1/1) or  $CH_4/CO_2$  (1/1) with a total flow of  $28 ml min^{-1}$ ) was fed to the reactor for required time. Then, the catalyst was kept in He for 30 min at the reaction temperature and then cooled to 340 K. For the TPH experiment, the sample was then exposed to a flow of  $H_2/He$  (10/90 with a total flow of  $30 ml min^{-1}$ ) at 340 K and subsequently heated up to 1273 K (heating rate  $10 K min^{-1}$ ).  $CH_4$  ( $m/e=16$ ),  $H_2O$  ( $m/e=18$ ),  $CO$  ( $m/e=28$ ) and  $CO_2$  ( $m/e=44$ ) signals were measured with a mass spectrometer. For TPRn with  $CO_2$ ,  $H_2/He$  in the above experiment was replaced with  $CO_2/He$  (10/90 with a total flow of  $30 ml min^{-1}$ ). The final dwell time at 1273 K was 10 min.

In order to perform CO evolution measurements during  $CO_2$  flow, 0.2 g of a catalyst ( $Pt/ZrO_2$  or  $Pt/Al_2O_3$ ) was used. After reduction, the catalyst temperature was adjusted to 1070 K in He. The catalyst was purged by He for 1h to remove residue  $H_2$  and  $CO_2/He$  (1/3 with a total flow of  $40 ml min^{-1}$ ) were fed to the reactor for 30 min (1st run). In subsequent experiments, the catalyst was again treated in  $H_2$  followed by He at the reaction temperature of the 1st run (1070 K) and  $CO_2/He$  was again fed to the reactor for 30 min at the temperature (2nd run). The amount of CO evolved was analyzed by a gas chromatograph (Aera M200) equipped with a 2m-MS-5A column and a TCD.

## 3. RESULTS AND DISCUSSION

### 3.1. Temperature programmed hydrogenation (TPH)

TPH profiles ( $m/e=16, 18, 28,$  and  $44$ ) for  $Pt/Al_2O_3$  and  $Pt/ZrO_2$  after exposure to  $CH_4/He$  for 10 min are shown in Fig. 1. First, we will discuss the contribution of O ( $m/e=16$ ) fragmentation from  $H_2O$  ( $m/e=18$ ),  $CO$  ( $m/e=28$ ), and  $CO_2$  ( $m/e=44$ ) to  $CH_4$  ( $m/e=16$ ). The peak intensities for  $H_2O$  on these catalysts decreased with temperature, and those for  $CO$  and  $CO_2$  were small compared to those for  $m/e=16$ , indicating that the contribution was quite small.

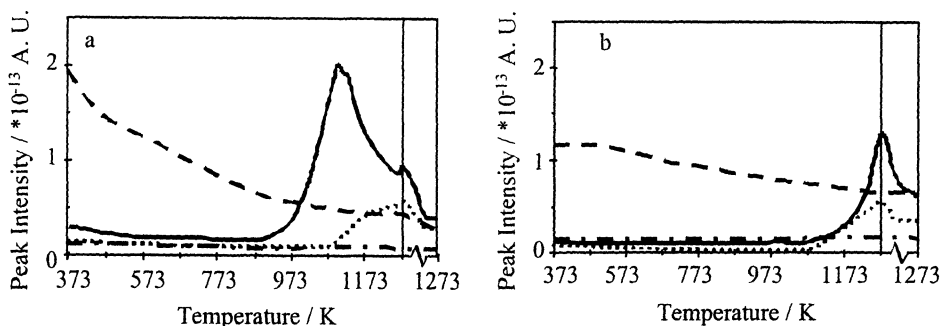


Fig. 1. Temperature programmed hydrogenation (TPH) profiles of  $m/e =$  (—) 16, (---) 18, (·····) 28, and (- · -) 44 for (a) Pt/Al<sub>2</sub>O<sub>3</sub> and (b) Pt/ZrO<sub>2</sub> after exposure to CH<sub>4</sub>/He at 1070 K for 10 min.

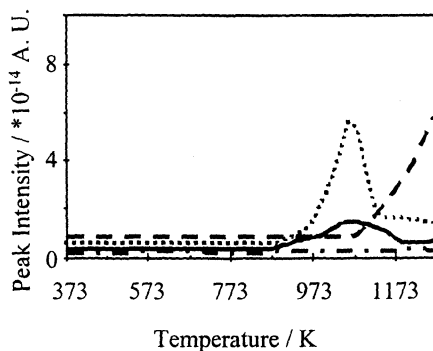


Fig. 2. Temperature programmed hydrogenation (TPH) profiles of  $m/e=16$  for Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> after exposure to CH<sub>4</sub>/CO<sub>2</sub> at 1070 K for 1 or 12 h. (—); Pt/Al<sub>2</sub>O<sub>3</sub> coked for 1 h, (·····); Pt/Al<sub>2</sub>O<sub>3</sub> coked for 12 h, (- · -); Pt/ZrO<sub>2</sub> coked for 12 h, (---); Al<sub>2</sub>O<sub>3</sub> coked for 12 h.

Peaks for CH<sub>4</sub> were observed above 873 K for Pt/Al<sub>2</sub>O<sub>3</sub>, while a sole peak was visible above 1073 K for Pt/ZrO<sub>2</sub>. The results indicate that some of the coke on Pt/Al<sub>2</sub>O<sub>3</sub> is more reactive with H<sub>2</sub> than that on Pt/ZrO<sub>2</sub>. For both catalysts, the peak intensities for CH<sub>4</sub> at 1273 K (after temperature was kept for 10 min) were higher than background level. Hence, some of coke seemed not to be removed from catalysts by the reaction with H<sub>2</sub> below 1273 K. On the other hand, the amount and peak temperature (above 1073 K) for CO formation were almost the same for both catalysts. Coke may have reacted with oxygen (lattice oxygen and/or hydroxyl) on the support to give CO above 1070 K.

It is necessary to confirm that coke deposited after catalyst was exposed to CH<sub>4</sub>/He reflects the nature of the coke in the CH<sub>4</sub>/CO<sub>2</sub> reaction. Thus, TPH is performed on Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> after these catalysts are exposure to CH<sub>4</sub>/CO<sub>2</sub> for 1 or 12 h. The CH<sub>4</sub> evolution profiles are shown in Fig. 2. No peak was visible on Pt/ZrO<sub>2</sub> even after reaction for 12 h, in accordance with the result of temperature programmed oxidation [1], which showed that no coke was deposited on Pt/ZrO<sub>2</sub> at the same reaction condition. On the other hand, for

Pt/Al<sub>2</sub>O<sub>3</sub>, the peak intensities at 1273 K were higher than background level, implying some of the coke was not activated by H<sub>2</sub> below 1273 K. Further, a single peak was observed on Pt/Al<sub>2</sub>O<sub>3</sub> above 873 K with different exposure times (Fig. 2), and the peak temperature was identical with the temperature of the peak for the catalyst after exposure to CH<sub>4</sub>/He for 10 min (Fig. 1a). The results indicate that the nature of the coke formed on Pt/Al<sub>2</sub>O<sub>3</sub> at these conditions (CH<sub>4</sub>/CO<sub>2</sub> and CH<sub>4</sub>/He) is almost the same, and we assume this observation is applicable to the coke on Pt/ZrO<sub>2</sub> as well. Fig. 2 shows that CH<sub>4</sub> is produced above 1073 K for Al<sub>2</sub>O<sub>3</sub> after exposure to CH<sub>4</sub>/CO<sub>2</sub> for 12 h, and the temperature is higher than that of Pt/Al<sub>2</sub>O<sub>3</sub> (873 K), indicating that the coke on Pt can be hydrogenated more easily than that on Al<sub>2</sub>O<sub>3</sub>. Therefore, most of the peak (CH<sub>4</sub>) observed on Pt/Al<sub>2</sub>O<sub>3</sub> after exposure to CH<sub>4</sub>/He (Fig. 1) and CH<sub>4</sub>/CO<sub>2</sub> (Fig. 2) would be attributed to coke on Pt. On the other hand, coke on Pt/ZrO<sub>2</sub> is attributed to coke on Pt, as confirmed in reference [1].

### 3.2. Temperature programmed reaction (TPRn) with CO<sub>2</sub>

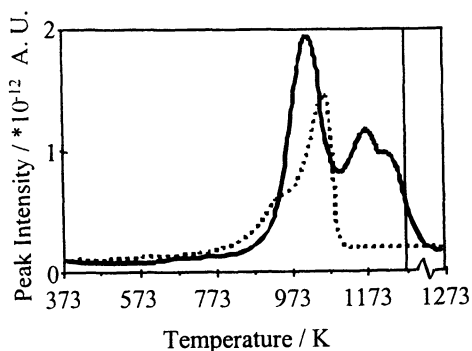


Fig. 3. Temperature programmed reaction (TPRn) with CO<sub>2</sub> profiles of  $m/e=28$  for (—) Pt/Al<sub>2</sub>O<sub>3</sub> and for (·····) Pt/ZrO<sub>2</sub> after exposure to CH<sub>4</sub>/He at 1070 K for 10 min.

Figure 3 shows the TPRn profiles with CO<sub>2</sub> for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub> after exposure to CH<sub>4</sub>/He for 10 min. These results are reproduced from an earlier work [1]. During the experiments, coke was converted to CO (in all experiments the contribution of the CO<sub>2</sub> fragment to CO ( $m/e=28$ ) has been subtracted). Our results indicate that CO is not evolved during experiments with the freshly reduced catalysts (not shown). This rules out the possibility of any significant contribution of the CO<sub>2</sub> dissociation (CO<sub>2</sub> → CO + O) during TPRn with CO<sub>2</sub>. For Pt/Al<sub>2</sub>O<sub>3</sub>, peaks were observed below and above reaction temperature (1070 K), and these were assigned to coke on Pt and on Al<sub>2</sub>O<sub>3</sub>, respectively. On the other hand, for Pt/ZrO<sub>2</sub>, two peaks were observed below reaction temperature and these were assigned to coke on Pt. Varying the exposure time to CH<sub>4</sub>/He on Pt/ZrO<sub>2</sub>, we see that only the coke corresponding to lower temperature peak forms on Pt/ZrO<sub>2</sub> in the CH<sub>4</sub>/CO<sub>2</sub> reaction. Therefore, we have concluded that coke on Pt is more reactive toward CO<sub>2</sub> on Pt/ZrO<sub>2</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub>.

### 3.3. Comparison of the reactivity of coke (on Pt) with H<sub>2</sub> and CO<sub>2</sub> for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub> catalysts

The results of TPH have been used to investigate the nature and reactivity of carbon species on the catalysts. The peak temperature is related to the composition of deposited coke [4-6]. Erdöhelyi *et al.* [6] distinguished three forms of carbon on supported Rh catalysts: (i) the highly reactive carbidic form, which can be hydrogenated even below 350-400 K, (ii) a less reactive amorphous layer,  $T_p=235-495$  K, and (iii) the relatively inactive graphitic form, which reacts with hydrogen only above 650 K. In our experiments, the coke on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub> were activated by H<sub>2</sub> (to produce CH<sub>4</sub>) above 873 and 1073 K, respectively (Fig. 1). From above consideration, the forms of coke on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub> would be graphitic. Further, coke reactivity with H<sub>2</sub> was higher on Pt/Al<sub>2</sub>O<sub>3</sub> than on Pt/ZrO<sub>2</sub> (Fig. 1), indicating that the reactivity of coke itself would be better on Pt/Al<sub>2</sub>O<sub>3</sub> than on Pt/ZrO<sub>2</sub>. The difference in coke reactivity between Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub> could be attributed to the difference of coke crystallinity because in both cases graphitic coke was formed. The crystallinity of the coke is higher on Pt/ZrO<sub>2</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub>.

We discuss here the factors that affect the peak temperature during TPH and TPRn with CO<sub>2</sub> in order to discuss the reactivity of coke toward CO<sub>2</sub>. During TPH, coke activation would mainly depend on the reactivity of coke itself [6]. On the other hand, during TPRn with CO<sub>2</sub>, it could depend on the nature of coke itself and/or the nature of activated CO<sub>2</sub>. CO<sub>2</sub> activation (CO<sub>2</sub> → CO + O) would be catalyzed on the active site which is associated with the oxide support, i.e., the presence of oxygen lattice defects on the support [10]. Our results (Fig. 1 and 3) show the reactivity of coke with H<sub>2</sub> was lower on Pt/ZrO<sub>2</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub>. In contrast, the reactivity of coke on Pt/ZrO<sub>2</sub> (corresponding to lower temperature peak, which was related to catalyst stability) toward CO<sub>2</sub> (Fig. 3) was higher than on Pt/Al<sub>2</sub>O<sub>3</sub>. The reactivity of coke with H<sub>2</sub> would be mainly affected by the nature of coke itself, while the reactivity of coke toward CO<sub>2</sub> (for Pt/ZrO<sub>2</sub>, lower temperature peak in Fig. 3) would be strongly affected by the reactivity of CO<sub>2</sub> on these catalysts. During the CH<sub>4</sub>/CO<sub>2</sub> reaction, coke would be removed by the reaction with CO<sub>2</sub>. This process would depend strongly on the ability to activate CO<sub>2</sub>, i.e., on the nature of the support.

### 3.4. Activation of CO<sub>2</sub> by oxygen defects on the support

In earlier studies, CO<sub>2</sub> activation has been related to carbonate formation on supports [2,3,8,9]. We study here the CO<sub>2</sub> activation (CO<sub>2</sub> → CO + O) on the oxygen defect sites. CO evolution is measured as a function of time in CO<sub>2</sub> flow tests on these catalysts at 1070 K, and the results are shown in Fig. 4. CO<sub>2</sub> flowing over reduced catalysts yielded only CO (CO<sub>2</sub> → CO + O) in the gas phase, and the CO yield decreased with time on stream. These results are in accordance with those in earlier CO<sub>2</sub> pulsing tests at 875 K on Pt/ZrO<sub>2</sub> and IR spectroscopic measurements at 775 K [9]. The decrease of CO yield with time of exposure is explained by blocking of the sites that decompose CO<sub>2</sub> to adsorbed oxygen (O) and CO. However, the results of EXAFS for Pt/ZrO<sub>2</sub> have not given evidence for the presence of adsorbed oxygen on Pt or (surface) oxides of Pt-O, so it is not likely that oxygen is located on Pt. The results are also supported by XANES [9,10]. Thus, we have concluded that oxygen is consumed at the metal-support interface. In addition, earlier work has shown that CO<sub>2</sub> pretreatment increases CH<sub>4</sub> conversion (when CH<sub>4</sub> is pulsed on Pt/ZrO<sub>2</sub>) compared with H<sub>2</sub> pretreatment [9]. It is likely that adsorbed oxygen left on the catalyst reacts with coke derived from methane under CH<sub>4</sub>/CO<sub>2</sub> reaction conditions. The initial CO yield (rate of active oxygen production) and total amount of CO<sub>2</sub> converted (number of CO<sub>2</sub> activation sites) were higher

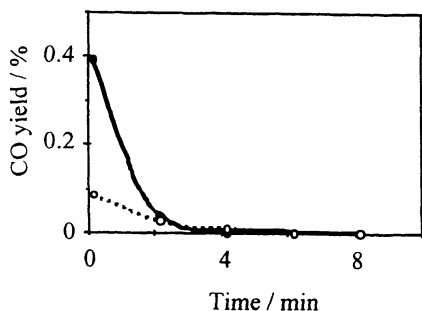


Fig. 4. CO evolution for (○) Pt/Al<sub>2</sub>O<sub>3</sub> and (●) Pt/ZrO<sub>2</sub> (reduced at 1120 K) during CO<sub>2</sub> exposure at 1070 K (1st run).

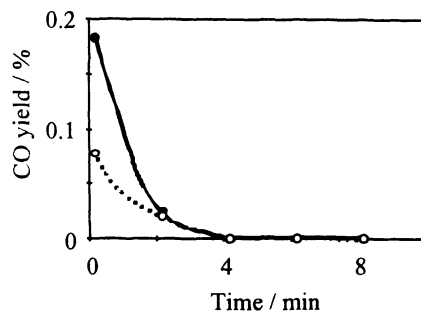


Fig. 5. CO evolution for (○) Pt/Al<sub>2</sub>O<sub>3</sub> and (●) Pt/ZrO<sub>2</sub> (reduced at 1070 K) during CO<sub>2</sub> exposure at 1070 K after 1st run (2nd run).

on Pt/ZrO<sub>2</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub>, indicating that the ability to produce active oxygen was higher on Pt/ZrO<sub>2</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub> at these conditions. Since the formation of oxygen defect sites may depend on reduction temperature, the catalysts were reduced with H<sub>2</sub> again after the 1st run, purged with He, and subsequently exposed to CO<sub>2</sub> (2nd run) at the same reaction temperature as in the 1st run (1070 K) (Fig. 5). At the same conditions as the 1st run (H<sub>2</sub> reduction at 1120 K, He purge, and subsequent CO<sub>2</sub> flow at 1070 K), we obtained similar CO yields after this 2nd run as for the 1st run. Thus the decrease in CO yield during our experiments for the 2nd run compared to the 1st run are due to a decrease in the sites accepting O from CO<sub>2</sub>. Since the reduction temperature of the 2nd run is the same as that for the CH<sub>4</sub>/CO<sub>2</sub> reaction, the CO yield during the 2nd run (Fig. 5) would be more related to a practical condition than that during the 1st run (Fig. 4). Pt/ZrO<sub>2</sub> showed higher initial CO yield and total number of CO<sub>2</sub> converted than Pt/Al<sub>2</sub>O<sub>3</sub> during the 2nd run, indicating that the CO<sub>2</sub> activation was more rapid on Pt/ZrO<sub>2</sub> than on Pt/Al<sub>2</sub>O<sub>3</sub> for the CH<sub>4</sub>/CO<sub>2</sub> reaction. The difference between the catalysts can be attributed to the reducibility of Zr<sup>4+</sup> (to Zr<sup>n+</sup>) producing oxygen defect site. Under CH<sub>4</sub>/CO<sub>2</sub> reaction conditions, coke would react with the active oxygen (produced on the oxygen defect site) to produce CO, and the oxygen defect site would be replenished by CO<sub>2</sub> (cycled).

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