

## Measurement of the ceria surface area of a three-way commercial catalyst after laboratory and engine bench aging.

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### ABSTRACT

The ceria surface area of a commercial Pt-Rh three-way catalyst was determined after laboratory hydrothermal aging at 1173-1373 K and after 200 h on engine bench. It was measured by X-ray diffraction (XRD) line broadening analysis and by a method based on the exploitation of the hydrogen temperature programmed reduction (TPR) profiles. In this case, the hydrogen uptakes below about 900 K include the ceria surface reduction and that of the oxidized noble metals. They are analyzed and discussed, assuming two possibilities for the metals oxidation state.

Compared to the fresh catalyst, the TPR profiles are deeply modified by the aging treatments. The ceria seems to sinter more than alumina, particularly between 1173 K and 1273 K. After aging at 1273-1373 K, the calculated ceria surface area is only 15-10 m<sup>2</sup>g<sup>-1</sup> washcoat, which represents 20% of the BET area, instead of 40% initially. A stabilization treatment at 823 K under reactants leads to an additional ceria sintering, even for the more aged system. Finally, the measurements on the engine bench aged catalysts seem to indicate a better resistance of ceria to sintering in working conditions. The presence of a pollutant layer, containing phosphorus, zinc and calcium, did not modify the accessible ceria surface area measured by TPR.

## 1. INTRODUCTION

Determining the surface area of ceria in three-way catalysts is an important problem for the characterization of these systems. Indeed, cerium oxide is a key component which enhances the global activity, particularly through the oxygen storage capacity (OSC), essential characteristic for regulating the oxidative power of the catalyst in a real catalytic converter [1-3]. Moreover, it has been proposed on model systems that the ceria support may become itself the active phase [4-7]. Accordingly, there is a great practical interest to find methods which are easily usable and allow a correct estimation of this parameter for fresh as well as for aged catalysts. In preceding papers, we have described a methodology to measure the exposed surface area in model metal/ceria-alumina catalysts [8-10]. It is based on the use of temperature programmed reduction (TPR) with hydrogen. It was shown that the reduction peaks for T lower than about 900-950 K, could be attributed to the reduction of both the oxidized precious metals and the superficial ceria layer. It has been established that 3.9  $\mu\text{mol H}_2$  are necessary to reduce 1  $\text{m}^2$  of  $\text{CeO}_2$  [9].

The objective of this study is to extend this methodology to the case of a commercial three-way catalyst deposited on a ceramic monolith and to follow the evolution of the ceria surface area at different stages of its life-time, including long time engine-bench testing. In this case, it is important to examine the impact of poisons on TPR curves.

## 2. EXPERIMENTAL

All characterizations were carried out on the same commercial catalyst (COM1). The active phase was constituted of 0.152 wt.% Pt and 0.031 wt.% Rh, the corresponding Pt/Rh weight ratio being 5/1 with a 32 g  $\text{ft}^{-3}$  loading. The ceramic was constituted of cordierite which contained iron as impurity. The hydrothermal laboratory aging (LA) consisted in treating the fresh catalyst during 5h at 1173, 1273 or 1373 K under a 6  $\text{l.h}^{-1}$  nitrogen flow containing 10%  $\text{H}_2\text{O}$  introduced with an automated syringe. These four catalysts were stabilized (St), i.e. treated 1h at 823 K under stoichiometric reactants synthetic mixture ( $\text{CO}$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ). Moreover, the catalyst was studied after aging on engine bench (EB) during 200 h, with a air/fuel equivalence ratio oscillating around stoichiometry ( $\lambda \approx 1$ ). Table 1 gives the results of the chemical analysis performed on the initial (fresh) monolith system. The figures remained nearly the same (within  $\pm 10\%$ ) after laboratory or engine-bench aging.

We used X-ray diffraction technique to determine the  $\text{CeO}_2$  crystallite sizes from the line broadening and the hydrogen TPR to calculate the ceria surface area according to a method developed on model catalysts [9,10]. In the case of TPR, the samples were ground before characterization. 250 mg were necessary for each run. They were treated 1h at 673 K under air, and then 1h30 at 773 K under argon flow before the TPR run. The heating ramp was 20  $\text{K min}^{-1}$  up to

about 1073 K, temperature which was kept constant during 45 min. All the values will be given per gram of actual washcoat (WC)

Some XPS and SEM-EDX analysis were also realized on the engine bench aged catalysts in order to measure the surface composition of the catalytic washcoat which was modified by the poisons layer deposit.

Table 1  
Chemical analysis of catalyst COM1 (wt. % basis).

Washcoat	Pt	Rh	Ba	Ce	Cl	Fe	La	S
30.75	0.152	0.031	0.66	6.3	0.145	0.45	0.3	0.15

## 2. RESULTS

### 2.1. Ceria mean particle size from X ray diffraction

Each catalyst was studied by XRD. To improve the intensity of the diffraction lines, the washcoat was scraped off the cordierite before analysis. The XRD spectra show the presence of alumina, ceria and some residual cordierite. The precious metals are never detected, as metal or oxide. For the fresh catalysts, the lines are broad meaning poorly crystallized phases. The resolution is greatly improved after aging. No other phase like cerium aluminate or other transformation product were evidenced on the XRD spectra.

The calculation of the particle size of ceria was done on the broadening of the line at  $2\theta = 56.37^\circ$  which is the best resolved and does not interfere with alumina. The results are given in Table 2.

Table 2  
Ceria particle size determined from XRD diagram (line  $2\theta = 56.37^\circ$ ).

Catalyst	particle size of CeO <sub>2</sub> (nm)		S <sub>CeO<sub>2</sub>-XRD</sub> (m <sup>2</sup> g <sup>-1</sup> )*	
	before stabilization	after stabilization	before stabilization	after stabilization
Fresh	8.5	10.3	25	21
LA1173	11.8	13.9	18	15
LA1273	17.8	18.1	12	12
LA1373	22.2	24.4	10	9

\* S = [ 6,000 / (7.15 \* Diameter in nm) ] \* ceria percentage in the washcoat

In the fresh state, the ceria is rather well dispersed with a mean size of around 8 nm. During the aging up to 1373 K, this size increases from 8.5 to 22.2 nm, which evidences an important sintering of the ceria particles. This evolution is identical for the stabilized catalysts, with however slightly higher sizes. The corresponding surface areas per gram of washcoat are also given in Table 2. They were calculated by assuming spherical particles and a theoretical density of  $7.15 \text{ g.cm}^{-3}$  for ceria.

## 2.2. Selective measurement of the ceria surface area by TPR

### *Catalysts before stabilization*

Figure 1 shows the TPR profiles of the catalyst as received and after laboratory aging at 1173, 1273 and 1373 K. The main features correspond to those observed on model catalysts [10]. In the fresh state, there is a well-resolved peak at 570 K, ascribable to the reduction of the oxidized precious metals and the ceria surface. After aging, the curve becomes flattened with much lower  $\text{H}_2$  uptakes. When the aging temperature is increased from 1173 to 1373 K, the intensity of the first peak is reduced to nearly zero, whilst two other curve inflexions or small peaks become more distinct at around 800 and 970-1000 K.

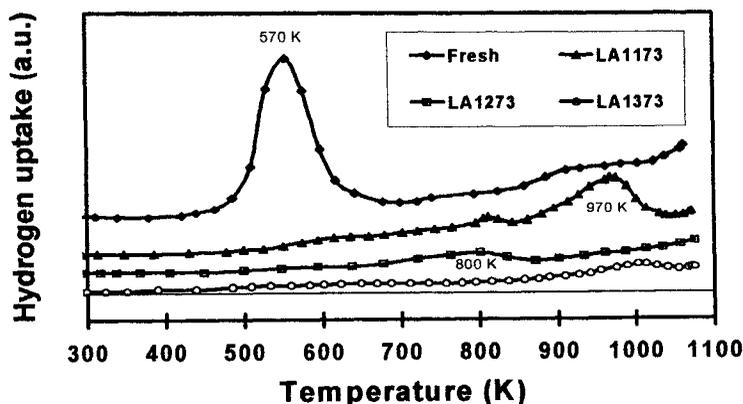


Figure 1.  $\text{H}_2$  TPR of the catalysts before stabilization. Heating rate :  $20 \text{ K min}^{-1}$

Although the separation between surface and bulk reduction is not always straightforward, the hydrogen consumption quantities were determined for temperatures lower than 900-950 K. They are given in Table 3. From them, it is possible to calculate the ceria surface areas of each catalyst, provided that some hypothesis are done on the mean oxidation state of the precious metal before starting the TPR experiment. In this study, the calculations were made with two different hypothesis : hypothesis 1) the metals are under the  $\text{Rh}^{3+}$  and  $\text{Pt}^{2+}$  states, hypothesis which was found valid for the fresh systems [9] and hypothesis 2)

rhodium is in a 3<sup>+</sup> state whereas platinum is in a metallic state with a very small O/Pt ratio and set to 0 in the present study [10]. This second hypothesis has been supported by a separate TPR measurement performed on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst hydrothermally aged at 1323 K. Compared to the alumina support aged in the same conditions, no additional hydrogen consumption was detected during the TPR. The experimental hydrogen uptakes for the low temperature peaks and the calculated ceria surface areas are given in Table 3 with the BET areas.

Table 3

Ceria surface areas, per gram of washcoat, measured by the TPR method.

Catalyst	S <sub>BET</sub> m <sup>2</sup> g <sup>-1</sup>	H <sub>2</sub> exp. → $\approx$ 900 K $\mu$ mol g <sup>-1</sup>	S <sub>CeO<sub>2</sub></sub> (hypo 1) <sup>a</sup> m <sup>2</sup> g <sup>-1</sup>	S <sub>CeO<sub>2</sub></sub> (hypo 2) <sup>b</sup> m <sup>2</sup> g <sup>-1</sup>	Reduction extent <sup>c</sup> (%)
Fresh	167	309	69	75.5	128
LA1173	101	163	30	38	121
LA1273	77	75	7.5	15	44
LA1373	54	55	2.4	10	41
Fresh St.	139	251	54	61	126
LA1173 St.	96	124	20	28	74
LA1273 St.	72	74	7.2	15	48
LA1373 St.	41	49	1	8.5	29

<sup>a</sup>hypothesis 1 : O/Pt = 1 and O/Rh = 1.5

<sup>b</sup>hypothesis 2 : O/Pt = 0 and O/Rh = 1.5

<sup>c</sup>see text

The difference between hypothesis 1 and 2 is about 6-8 m<sup>2</sup>g<sup>-1</sup> and corresponds to the hydrogen quantity needed to reduce Pt<sup>2+</sup> into Pt<sup>0</sup>. For the fresh catalyst, hypothesis 1 is the most appropriate and leads to a ceria surface area of 69 m<sup>2</sup>g<sup>-1</sup>. For the aged catalysts, the relative uncertainty between the values of S<sub>CeO<sub>2</sub></sub> obtained with the two hypothesis is acceptable for LA1173, but not after aging at 1273 and 1373 K. As said above, hypothesis 2 seems the most reasonable, and the calculated values of the ceria surface areas are 15 and 10 m<sup>2</sup>g<sup>-1</sup> after aging at 1273 and 1373 K. They are effectively in better agreement with the XRD results, than with hypothesis 1.

To have more informations on the evolution of the support after the aging treatments, it is possible to follow an other parameter which is the reduction percentage of the catalyst at the end of the TPR. It corresponds to the ratio between the experimental hydrogen consumption during the whole TPR, including the 45 min step at 1073 K, and the maximum theoretical H<sub>2</sub> consumption necessary for the reductions (CeO<sub>2</sub> → Ce<sub>2</sub>O<sub>3</sub>; PtO → Pt<sup>0</sup>; Rh<sub>2</sub>O<sub>3</sub> → Rh<sup>0</sup>). For fresh and LA1173, this percentage is higher than 100% (128 and 121%) and close to that of the washcoat without precious metals (131%). It

decreases to 44 and 41 %, for LA1273 and LA1373 respectively. We can deduce that : i) in the initial solid and after mild aging (1173 K), some reducible species other than precious metals and ceria are present in the system, and ii) the main modification of the catalyst during the aging treatments occurs between 1173 and 1273 K. In this respect, LA1173 can be considered as a weakly aged catalyst.

To explain the reduction extent higher than 100%, several hypothesis were considered but were not verified. The reduction of the iron oxide present in the cordierite was not observed during a separate TPR. The presence of barium sulfate was also evidenced by XPS. In the TPR conditions,  $\text{BaSO}_4$  begins to be reduced at about 1000 K. However, the hypothesis of its reduction in the catalysts was not kept, since the reduction percentage of a platinum catalyst supported on a ceria-alumina modified with  $\text{BaSO}_4$  was a little lower than that performed in absence of barium sulfate. The assumption of the hydrogenation of some carbonates species, as surface lanthanum carbonates, was also rejected, since, as evidenced by mass-spectrometry, there is no relationship between the excess reduction percentage and the formation in the gas phase at very low concentration of  $\text{CH}_4$ , or even  $\text{CO}$  and  $\text{CO}_2$ . The question is still under study.

#### *Catalysts after stabilization*

Figure 2 exhibits the TPR profiles of the previous catalysts, after 1 h at 823 K under the reactants, and Table 3 presents the results. For the fresh catalyst after stabilization, the initial low temperature peak is split into two peaks of lower intensity. For the aged catalysts, the stabilization leads also to profiles with a lower intensity during the whole TPR. Accordingly, the hydrogen uptakes are lower than those of the initial systems. If one supposes that the metals after reoxidation at 673 K have the same mean oxidation state before and after stabilization, which means no change in their size and their state during the stabilization, the calculated ceria surface areas are lower after stabilization (Table 3). Thus, the stabilization results in an additional ceria surface loss.

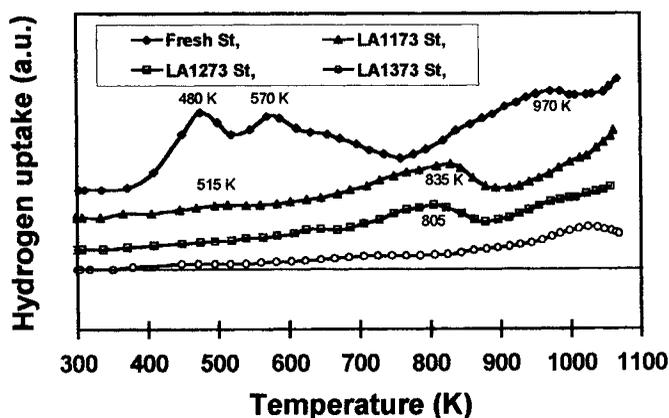


Figure 2.  $\text{H}_2$  TPR of the catalysts after stabilization. Heating rate  $20 \text{ K min}^{-1}$ . (hydrogen uptake scale about two times higher than in Fig.1)

### 2.3. Study of the catalyst after 200 h aging on an engine-bench.

One of the difficulties to study this catalyst is the possible influence of the poisons deposited on the active phases during the test and originated from the gasoline or motor oil components such as Si, Ca, P, Zn, S ... [11,12]. In particular, the TPR study may become totally erroneous if additional reducible compounds are present. To take into account this influence and to evidence an eventual aging gradient along the axis of the monolith, three samples were selected after the test, at the inlet, in the middle and at the outlet of the monolith.

The analysis and distribution of the poisons were done by SEM coupled with an EDX analysis. A macroporous layer of pollutants was evidenced on the surface. The analysis was done on the elements of the support (Al, Ba and Ce) as well as the poisons usually found after such a treatment, i.e. P, Ca and Zn [11]. Sulfur was searched for but was not detected. In the front side of the converter, the poisons were the only elements detected, with almost 50% Zn, 40% P and 10% Ca. It means that the poison layer is thicker than that analysed by EDX, i.e. about 1 $\mu$ m. The Zn concentration decreased quickly in a few millimeters axially and then was not detected (<1%), whilst P and Ca were always found in high proportion. However their concentration decreased also continuously along the axis of the converter, from 20 to 7% for Ca, and from 40 to 30% for phosphorus. It results that, after an engine bench test, the washcoat is covered by a thick layer of poisons which becomes progressively thinner when arriving to the outlet.

These results are in agreement with those obtained by XPS on the superficial composition of the three selected samples. As shown in Table 4, Zn is detected only at the inlet, phosphorus is evenly distributed along the whole length, and the calcium content decreases between the inlet and the outlet. Conversely, the washcoat constituents concentrations increase continuously along the axis.

Table 4  
Surface composition (atomic percentage) of the washcoat after an engine bench aging, as determined by XPS.

Analysed zone	Al	Ce	Ba	O	C	Ca	P	Zn
Inlet	7.6	1.6	1.3	54.3	9.0	8.3	12.8	5.2
Middle	11.6	2.5	2.1	50.2	12.1	7.8	13.8	0
Outlet	14.2	3.1	2.2	54.2	8.1	5.5	12.8	0

A TPR study was performed on the same samples, but after grinding. As shown on Figure 3, there is no significant difference between the three samples, indicating that the poisons are not reduced in the TPR conditions. The TPR profile was attenuated compared to the fresh catalyst, but less than the aged and stabilized solids. Table 5 gives the quantitative results obtained, as above, from the hydrogen uptakes up to  $\approx$ 900 K.

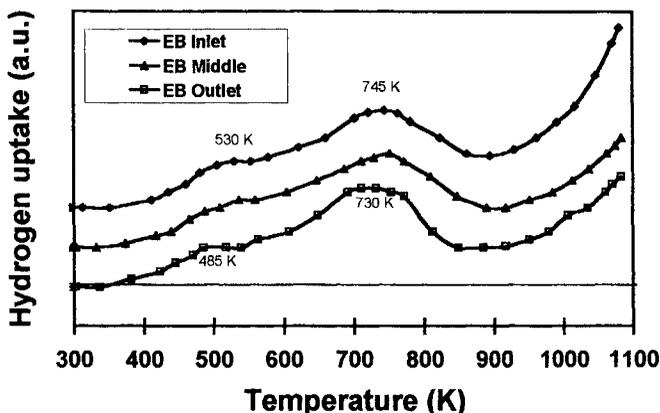


Figure 3. H<sub>2</sub> TPR of engine bench aged catalysts. Heating rate : 20 K min<sup>-1</sup>. (hydrogen uptake scale about four times higher than in Fig.1)

Table 5

Ceria surface areas measured by the TPR method.

Catalyst	S <sub>BET</sub> m <sup>2</sup> g <sup>-1</sup>	H <sub>2</sub> exp. →≈900 K μmol g <sup>-1</sup>	S <sub>CeO<sub>2</sub></sub> (hypo 1) <sup>a</sup> m <sup>2</sup> g <sup>-1</sup>	S <sub>CeO<sub>2</sub></sub> (hypo 2) <sup>b</sup> m <sup>2</sup> g <sup>-1</sup>	Reduction extent <sup>c</sup> (%)
EB Inlet	66	101	16	22	52
EB Middle	66	104	17	23	43
EB Outlet	60	103	16	23	43

<sup>a</sup>hypothesis 1 : O/Pt = 1 and O/Rh = 1.5

<sup>b</sup>hypothesis 2 : O/Pt = 0 and O/Rh = 1.5

<sup>c</sup>see text

It appears that the engine bench aging effects are comparable to those obtained in laboratory at 1273 K for the BET area, but seem less severe for S<sub>CeO<sub>2</sub></sub>. Moreover, there is no significant difference in S<sub>BET</sub> and S<sub>CeO<sub>2</sub></sub> from the inlet to the outlet of the converter which confirms the absence of negative effect of the pollutants layer on the measurement of the ceria surface area.

### 3. DISCUSSION

The ceria surface area of a commercial three-way catalyst has been measured by XRD and by TPR at different stages of its evolution. The reliability of the results has to be discussed. It can be recalled that S<sub>CeO<sub>2</sub>-XRD</sub> corresponds to the sum of the surfaces of each crystallite, whereas TPR measures the area accessible to hydrogen. For the fresh and LA1173 catalysts, S<sub>CeO<sub>2</sub>-TPR</sub> is higher

than  $S_{\text{CeO}_2\text{-XRD}}$ . It is likely that a noticeable proportion of the ceria in the initial solid is poorly crystallized. During the aging, ceria becomes more and more crystallized, and bigger  $\text{CeO}_2$  particles are formed which can be composed of several crystallites. In these conditions,  $S_{\text{CeO}_2\text{-XRD}}$  becomes closer to the actual ceria surface and may even become higher than  $S_{\text{CeO}_2\text{-TPR}}$  which measures only the external surface of these big particles.

In other respects,  $S_{\text{CeO}_2\text{-TPR}}$  depends on the hypothesis made on the mean oxidation state of the precious metals. We saw that hypothesis 1 can be valid for fresh catalysts and also after aging at 1173 K. For higher aging temperatures, the mean oxidation state of platinum tends towards zero when supported on alumina. The same hypothesis is also probable for ceria-alumina. The relative good agreement between the values of  $S_{\text{CeO}_2\text{-TPR}}$  and  $S_{\text{CeO}_2\text{-XRD}}$  supports this assumption. A decrease in the reducibility of the rhodium ions in interaction with alumina is also quite possible but difficult to be quantified in the case of a ceria-alumina support. Accordingly, a summary of the most probable data is presented in Table 6. For engine bench aging, hypothesis 2 was chosen, considering that, in this case, the reduction extent is closer to that of the most aged systems.

Table 6

Summary of the results obtained by TPR and XRD on the catalyst after various aging treatments.

$S_{\text{CeO}_2}$ $\text{m}^2\text{g}^{-1}$	Catalyst									
	Fresh		LA1173		LA1273		LA1373		EB	
	St.	St.	St.	St.	St.	St.	Inlet	Outlet		
TPR	69 <sup>a</sup>	54 <sup>a</sup>	30 <sup>a</sup>	20 <sup>a</sup>	15 <sup>b</sup>	15 <sup>b</sup>	10 <sup>b</sup>	8.5 <sup>b</sup>	22 <sup>b</sup>	23 <sup>b</sup>
XRD	25	21	18	15	12	12	10	9		

<sup>a</sup>hypothesis 1 : O/Pt = 1 and O/Rh = 1.5

<sup>b</sup>hypothesis 2 : O/Pt = 0 and O/Rh = 1.5

Finally, to describe the evolution of the ceria surface areas, if both methods are necessary, the TPR method seems more reliable for fresh and weakly aged catalysts. After aging at 1273-1373 K, the ceria surface area is only 15-10  $\text{m}^2\text{g}^{-1}$  instead of 69  $\text{m}^2\text{g}^{-1}$  initially, which represents 20% of the BET area instead of 40% initially. It results that ceria sinters more than alumina in the washcoat.

Even if the engine bench test was considered as not very severe, with a catalyst temperature of about 1130 K, the BET areas and the reduction extents taken as a criterion of the aging, seem to indicate that the EB catalyst was submitted locally to temperatures at least higher than 1273 K. Indeed, the BET surface area was found lower than for the catalyst aged at 1273 K, 66-60 instead of 77-72  $\text{m}^2\text{g}^{-1}$ . However the calculated ceria surface remained rather high, 22-23  $\text{m}^2\text{g}^{-1}$  for the upstream and the downstream face. Since we observed that stabilization under reactants leads to lower ceria surface areas, this less severe

ceria sintering during the engine bench test cannot be attributed to the redox processes occurring during the three-way catalysis. According to previous results on the thermal stability of pure ceria [13], it could be tentatively interpreted as due to the stabilizing effect at high temperature of CO<sub>2</sub> present at around 10 vol.% in the exhaust gases. Indeed, it could preserve the ceria specific area by forming stable carbonate species on the ceria.

#### 4. CONCLUSION

It is shown that the TPR method developed in the case of ceria-alumina supported Pt-Rh model catalysts can be used to estimate the ceria surface area of commercial three-way monolithic catalysts. Upon hydrothermal aging, a strong decrease of the ceria surface area was evidenced, the main modification of the catalyst being observed between 1173 and 1273 K. As shown by the  $S_{\text{BET}}$  and  $S_{\text{CeO}_2\text{-TPR}}$  values, a stabilization treatment at 823 K under reactants leads to an additional sintering, even for the more aged system. That shows that redox conditions are able to modify the catalyst surface state even at temperatures much lower than during aging.

Engine bench test was found equivalent to an hydrothermal aging at 1273 K, with however a better resistance of ceria to sintering. The surface of these engine bench aged samples is covered by a more or less compact layer of pollutants. Its thickness decreases from the inlet to the outlet of the converter. However, the presence of these poisons does not modify the accessible ceria surface area measured by the TPR method.

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