Why was Toyota's Camry less affected by sulfur than the other cars in the CRC LEV-Sulfur fleet test?

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A. First I should point out that the sulfur effect on emissions from the Camry LEV is very large compared to the incremental improvements we obtain during development to meet the certification standard. For example, NOx increased by 49% when going from California fuel (40 PPM) to federal average fuel (330 PPM). So the observed sulfur effects are not inconsequential.

B. This vehicle was developed to meet the California Low Emission Vehicle Regulation using California Phase II Reformulated Gasoline. Toyota did not use gasoline having higher sulfur than California Phase II to develop this car. So, the result that this car was less affected by sulfur than other cars in the CRC program was not a result of a development effort. It could have been any of the cars in the test program. The fact that the emissions of <u>all</u> vehicles in the CRC LEV fleet test were increased significantly by sulfur is much more important.

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C. Toyota does not know a certain answer to the question because we have not adopted any specific sulfur-tolerant technologies. Furthermore, we do not have any detailed information about the emission control systems of other vehicles. However, considering that fuel sulfur's behavior on catalysts is well-known and with our special knowledge of the Camry LEV system, I will give you our thoughts as to the reason for the test results:

Camry LEV System
The Camry LEV emissions control system uses two catalysts:

1. Close coupled (CC), (or Start) Catalyst (S/C) with Pt/Pd/Rh,

2. Under-body (UB) or Under-floor (UF) main catalyst with Pt/Rh,

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It also uses two O_2 sensors as shown in Figure 1 and Figure 2.

Figure 1 : Emission Control System of LEV L-4 Engine

Figure 2 : Description of Camry Systems (Tier 1, TLEV, LEV)

Assumed Mechanism Why Toyota's Camry was Less Affected by Sulfur than Any Other Cars

Sulfur compounds bond to the catalyst and deteriorate its conversion efficiency. Figure 3 shows assumed mechanism why the sulfur lowers catalyst activity. Sulfur in fuel is oxidized into SO_2 in combustion process and the SO_2 goes into the catalysts. Some of the SO_2 bonds to the noble metal particles and makes them unavailable to absorb emissions, in this way interfering with the catalyst function. Some of the other sulfur interacts with the cerium (Ce) and lowers its capability of oxygen storage.

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Sulfur compounds also deposit on the alumina in the catalyst support. This reduces the size of the pores and reduces the surface area in contact with the exhaust gas.

Thus, sulfur (SO_2) lowers the catalyst conversion rate by physical and chemical adsorption and causes emissions increase.

The only known ways to eliminate the sulfur adsorbed on the catalyst are (1) high enough temperature to increase the energy of molecular motion, and (2) deoxidizing the SO_2 by supplying reducing compounds (HC, CO).

Sulfur Tolerance of the System

Next I will comment on two possibilities that could minimize sulfur effect:

1. Quick Desorption of Sulfur Adsorbed on the Catalyst during Warm-up Period

2. Sulfur-Tolerant Catalyst

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Quick Desorption of Sulfur Adsorbed on the Catalyst during Warm-up Period: In general, sulfur adsorbed on the catalyst is removed in the following conditions:

- The catalyst temperature is higher than about 650 C
- and operation is at fuel-rich A/F

SAE 910844 (by GM) states that with high A/F ratio, the sulfur stored in catalyst does not separate from catalyst even if the catalyst temperature becomes high. However, GM also shows that with low A/F (fuel rich), if the catalyst temperature becomes high, the sulfur stored in catalyst separates from catalyst.

SAE 922179 (by Toyota) reports results where first, fuel sulfur was 30 ppm, then 300 ppm and then 30 ppm again in that order. When 30 ppm fuel was used after 300 ppm sulfur test, catalyst conversion efficiency did not return to the initial 30 ppm sulfur level. However, if the catalyst temperature was raised sufficiently after the 300 ppm sulfur test, the conversion efficiency with 30 ppm sulfur was returned to the initial 30 ppm sulfur level.

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In the case of the Camry, CO at 10.3K miles ("as-received" catalyst) was the highest of the six models in the CRC LEV test fleet. This indicates that Camry may operate at lower A/F ratio (richer) than other systems.

Also, as Figure 2 shows, a small volume, close-coupled catalyst is used in the Camry to improve warm-up performance and reduce cold HC. So that catalyst temperature may be higher than that of other systems. So the two conditions for desorption of sulfur may be satisfied.

Sulfur Tolerant Catalyst
We have no information relating to sulfur-tolerant catalysts. In the case of the Camry, the catalyst is the general 3-way type that uses Pt, Pd and Rh as shown previously.

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Conclusion

We have no details of other companies' LEV systems or tuning. And we do not know other companies policies on driveability, reliability etc, and other vehicles' technologies. So the causes why Camry was relatively less affected described above are only assumptions. But facts which are clear from the result of this test are:

- Emissions dramatically increased as fuel sulfur increased in all systems tested.

- The Camry was relatively less affected than the other vehicles. However, even in the case of the Camry, the emission increase was a significant per cent of the standard.

- The above means that the effects of fuel sulfur are not small. Less sulfur always reduces emission, and contributes to air quality improvement.

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As for the result of the test using California Phase II gasoline, the Geo was the lowest in NMHC emission, the Sentra was the lowest in NOx emission, and the Escort was the lowest in CO emission. These results are a consequence of the emissions control system on each vehicle. The LEV system on the Camry reflects Toyota's best effort at the time. Toyota will continue system improvement considering future tighter emission standards, driveability, new technology development, and feedback from consumers in the market.

However, based on the results of R & D recently reported, lower emission vehicles are more affected by fuel sulfur. It is unthinkable to be contrary. Thus, Toyota expects reduction of fuel sulfur will be more and more important to improve air quality in the US

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Considering the future, in order to comply with tighter emission standards by 3 way catalyst, the key is to maximize catalyst performance by reducing the effect of sulfur, and control A/F more precisely. Therefore fuel sulfur and volatility will be more and more important. The need for extended catalyst useful life and improved fuel economy will accelerate. That means reduction of the fuel enrichment that is universally used to protect catalyst is required. So catalyst temperature can not be raised any more. From this point of view, fuel sulfur reduction will be essential.

But none of the above should be the focus of today's issue because sulfur causes a substantial increase of emissions from nearly every vehicle on the road today!

Sulfur will increase emissions of nearly every car on the road for the next five years (and ten years, etc).

Even 100 PPM sulfur in gasoline increases the NOx from our Camry by more than 20%.

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Sulfur in fuel is incompatible with American's demand for clean air. Each year, Americans purchase 15 million of the cleanest, lowest emissions vehicles available anywhere in the world. Americans deserve low sulfur fuel for these cars.

In Japan and California, fuel sulfur is already controlled to be less than 30 ppm market average. The cost and technology to control sulfur to be less than 30 ppm is already commercialized. In Europe, controlling to 30-50 ppm in 2005 is being discussed. Fuel sulfur reduction is worldwide trend. Toyota urges EPA to reduce sulfur nationwide because that is an effective way to improve air quality.

The new lean burn gasoline engines require "lean-NOx" catalysts. These are even more sensitive to sulfur than our current three-way cats. Low sulfur gasoline is a necessary prerequisite to introduction of these low fuel consuming, low CO_2 emissions vehicles to the US.

Figure 1

Emission Control System of LEV L-4 Engine

Precise Air Fuel Ratio Control

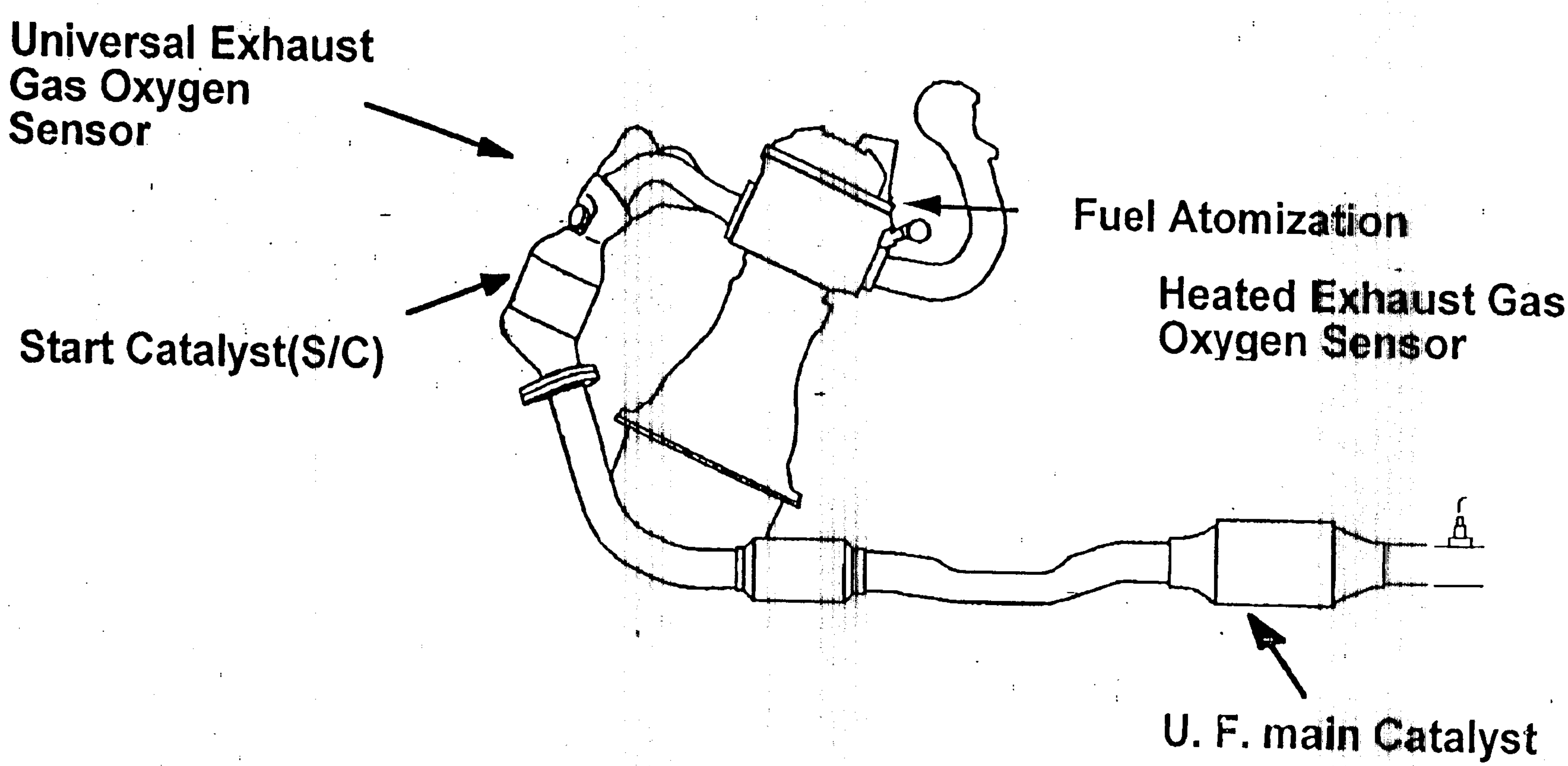


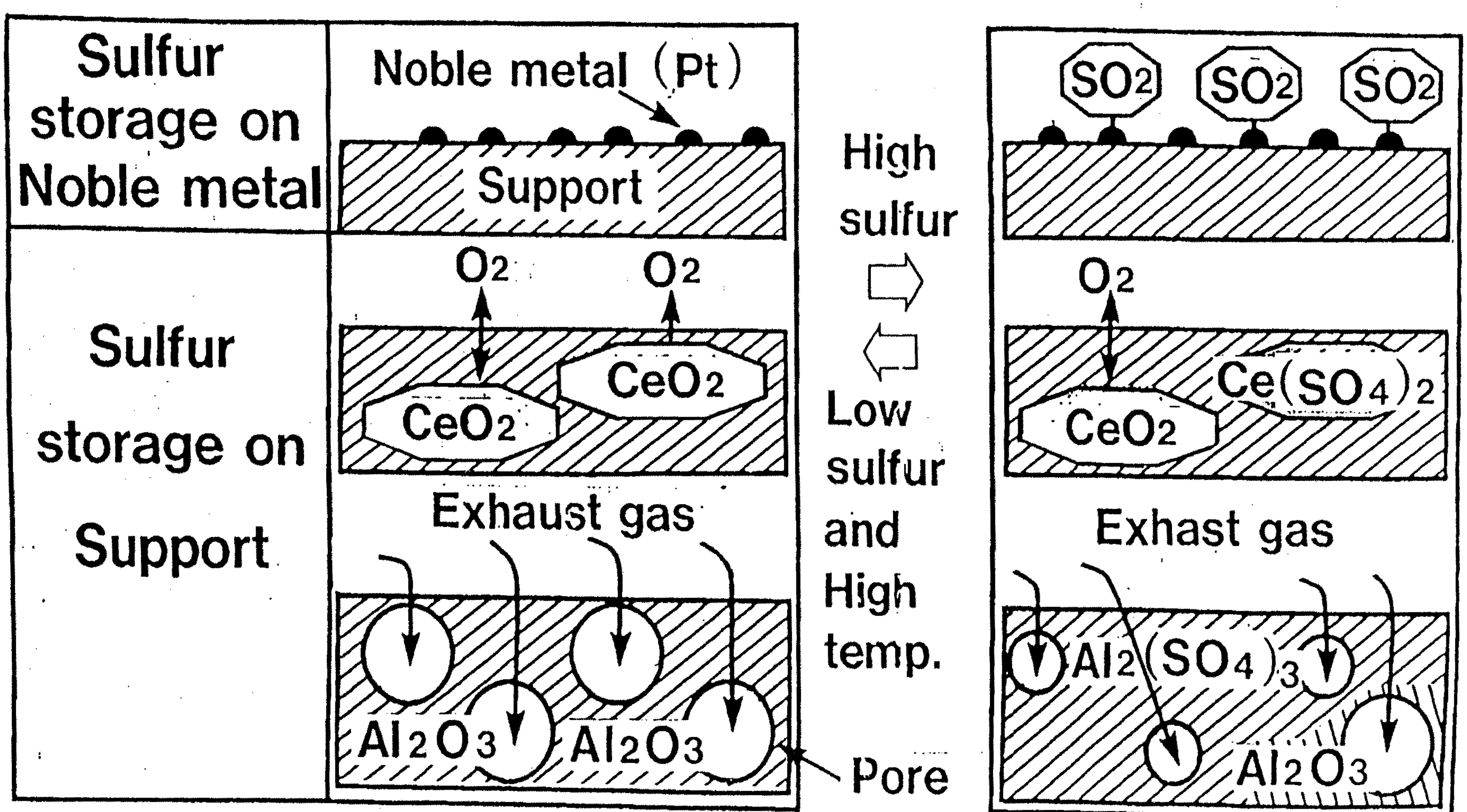
Figure 2

Description of Camry Systems (Tier 1, TLEV, LEV)

MY	Displ. (L)	Cyl.	Catalyst Location & Volume	Exhaust Control	Fuel Management
97 (CA) (LEV proto.)	2.2	L4	CC(0.7L - Pt/Rh/Pd) + UB(1.3L - Pt/Rh)	2 O_2 sensors EGR	MPFI Air assist Individual Inj.
94 (CA) (TLEV)	2.2	L4	CC(1.3L - Pt/Rh) + UB(0.5L - Pt/Rh)	2 O_2 sensors EGR	MPFI Air assist Individual Inj.
92(CA) (Tier 1)	2.2	L4	CC(1.3L - Pt/Rh) + UB(0.5L - Pt/Rh)	2 O_2 sensors EGR	MPFI Individual Inj.

Figure 3

ASSUMED MECHANISM OF CATALYST ACTIVITY DECREASING BY SULFUR



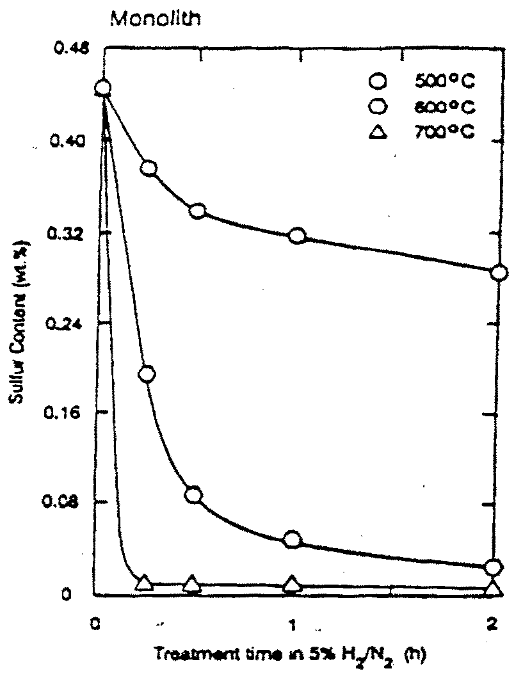


Fig. 9. Sulfur content in the monolith three-way catalyst exposed for 5 h to a simulated exhaust stream containing 20 ppm SO_2, followed by treatment in 5% H_2/N_2 for a variety of temperatures and times.

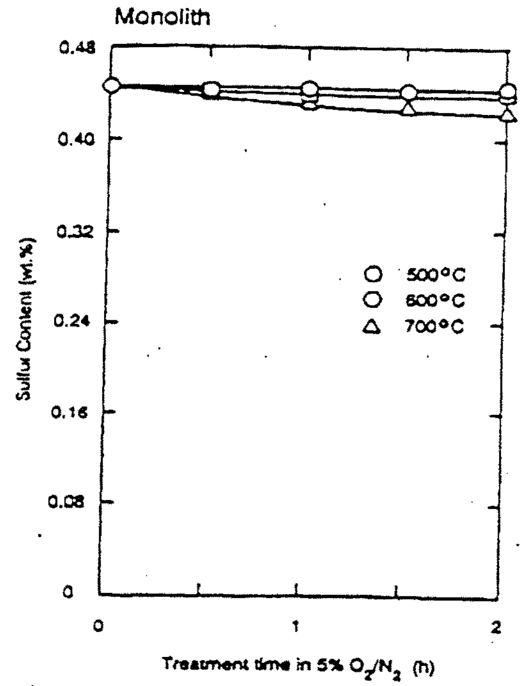


Fig. 8. Sulfur content in the monolith three-way catalyst exposed for 5 h to a simulated exhaust stream containing 20 ppm SO_2, followed by treatment in 5% O_2/N_2 for a variety of temperatures and times.

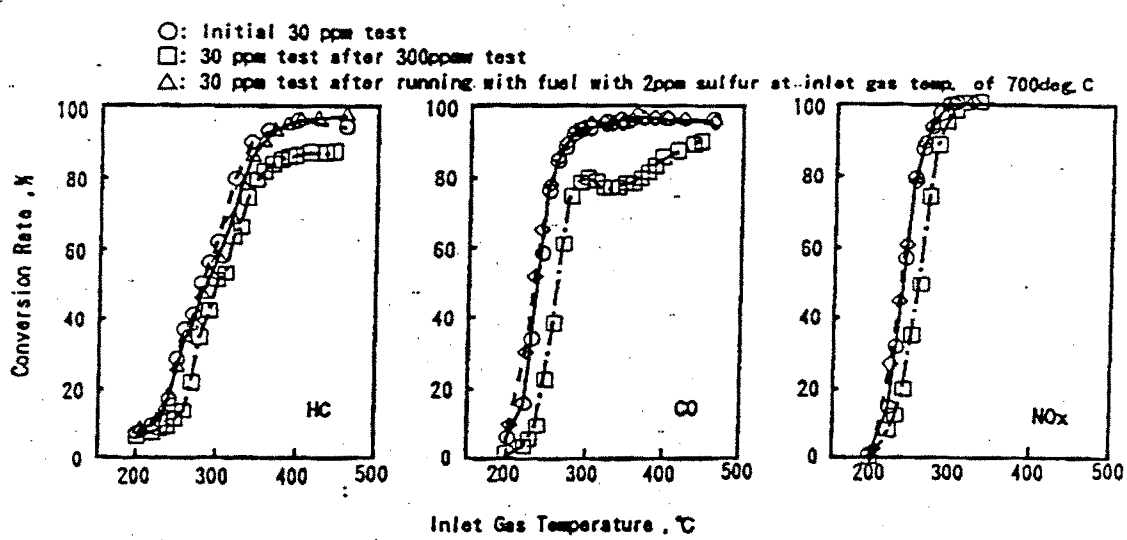


Fig. 13 Conversion Rate reconery after 2ppm Sulfur at Inlet Gas Temp. of 700deg. C

Fig.5

Effect of Fuel Sulfur on Lean NOx Catalyst