

## Lowering Sulfur Content in Fuels

Since automobile catalysts were first introduced in the U.S.A. and Japan in 1975, the negative effects from impurities in the fuel on catalyst performance have been recognised. Lead, added as an octane booster, or sulfur (S), a constituent of crude oil, are the major impurities.

Lead poisons the catalyst, reacting with the active noble metal sites. This reduces catalyst (and O<sub>2</sub> sensor) performance. Unleaded fuel was therefore made available when catalysts were introduced.

Sulfur also poisons the catalyst, and severe worldwide vehicle emissions legislation is forcing lower S limits in gasoline and diesel fuel (see Table).

**Gasoline:** When gasoline is combusted SO<sub>2</sub> is formed in the exhaust. In vehicles with some early Pt-containing catalysts the SO<sub>2</sub> was oxidised to SO<sub>3</sub> which was converted to sulfuric acid on contact with water. Sulfur became a bigger issue when Pt-Rh three-way catalysts (TWCs) were introduced. On running slightly lean (for improved fuel economy) the S oxides (SO<sub>x</sub>) formed were stored as sulfate on the TWCs. On rich operation (more fuel to accelerate) this sulfate was converted to H<sub>2</sub>S and emitted in a pungent burst from the tailpipe. The H<sub>2</sub>S/sulfate problem has been reduced by improved engine calibration, catalyst design and lowered S levels in the fuel. Indeed, tests on conventional catalyst-equipped gasoline engines have shown that if S levels are lowered from 600 to 300 ppm, emissions of hydrocarbon, carbon monoxide and nitrogen oxides (NO<sub>x</sub>) are reduced by 10–50%, depending on the vehicle.

Gasoline engines (such as direct injection) are in development for *improved fuel economy and lower CO<sub>2</sub>*

*emissions.* Such engines will operate at much leaner air:fuel ratios than at present. But under lean operation the O<sub>2</sub> does not allow NO<sub>x</sub> to be reduced over the TWC, so special catalyst technology, a ‘NO<sub>x</sub>-trap’, will be needed. The trap will store NO<sub>x</sub> as a nitrate salt on a chemical trap (a Ba salt added to the TWC formulation). When the trap is full the engine will briefly switch to rich operation, releasing NO<sub>x</sub> which will be reduced to N<sub>2</sub> by the catalyst (1). Any SO<sub>x</sub> present will compete for NO<sub>x</sub>-trap storage sites, lowering the storage capacity; so, *longer*, rich operation will be needed to remove the SO<sub>x</sub>, compromising fuel economy. S-free fuel is therefore needed by these advanced engines.

**Diesel:** If a diesel vehicle carries a catalyst (Pt) lowering the S content in the fuel will improve catalyst efficiency as SO<sub>x</sub> adsorbs onto active sites lowering oxidation performance.

The main diesel emission problem is particulate matter (PM) (legislated). Sulfate (SO<sub>2</sub> oxidised on Pt) coalesces with water on the PM, increasing its measured mass. PM is removed from the exhaust by a *particulate filter*, which needs frequent cleaning by fast, high-temperature combustion with the O<sub>2</sub> present in the lean mixture. In this reaction S is oxidised to sulfate, again coalescing on the PM.

If the Pt catalyst and filter are part of a CRT<sup>TM</sup> then trapped PM continuously reacts with NO<sub>2</sub> (from NO oxidised over the Pt catalyst before the filter). SO<sub>2</sub> competes with NO for the catalyst sites, so lowering the amount of NO<sub>2</sub> formed.

NO<sub>x</sub> in diesel engine exhaust is controlled at present by the engine. *NO<sub>x</sub>-traps* may find use in the future. Again S would be an issue.

Clearly, fuel S reduction with advanced catalysts and engines, will result in cleaner exhaust gas.

### Reference

- 1 M. V. Twigg, *Platinum Metals Rev.*, 2003, 47, (1), 15

A. J. J. WILKINS

Tony Wilkins is a former Technology Development Manager in Johnson Matthey's Catalytic Systems Division. His long experience of the autocatalyst industry give him a breadth of insight into the changing technology and its complexities.

Year	Gasoline	Diesel	Comments
2000	150 (50 <sup>*</sup> )	350 (50 <sup>*</sup> )	–
2005	50 (10 <sup>*</sup> )	50 (10 <sup>*</sup> )	U.K. now
2009	10	10	Germany now

<sup>\*</sup> with fiscal incentives; <sup>+</sup> to be available