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Dynamic Behavior of Three-Way Catalysts

Three-way catalysts (TWC's) are employed in the exhaust treatment for gasoline-fueled vehicles to achieve simultaneous control of CO, hydrocarbons (HC's) and NO emissions. A typical TWC contains precious metals (Pt, Pd, or Rh) and metal oxides which are beneficial for stability of the catalyst support (γ-alumina) or enhancement of the catalyst activity under dynamic operating conditions. The active components are dispersed on the surface of alumina pellets or of an alumina washcoat on a monolith ceramic substrate.

When the TWC is used in vehicles with closed-loop control of the air/fuel (A/F) ratio near the stoichiometric point for the control of the exhaust emissions, its performance has been found, in general, to be better than predicted from steady-state catalyst efficiency (*1–10*). This improved performance relates to several characteristic processes occuring under dynamic operating conditions, including oxygen storage (*1a, 7*), water-gas shift (WGS) reaction (*3, 9*), and "HC retention" on the catalyst (*6*).

The catalyst capacity to store oxygen arises from a surface redox process whereby excess O_2 present during a lean A/F excursion is stored as adsorbed or combined oxygen available for the removal of excess CO and HC in the exhaust gas during a subsequent rich excursion. Similarly, the catalyst's ability to remove NO in a lean excursion would be improved by virtue of the catalyst being in a reduced state after a prior rich excursion, as the catalyst would itself become oxidized by reducing NO to N_2 as well as promote the NO reduction by the CO and H_2 present in the exhaust gas. An increase in the catalyst's activity for WGS reaction would enhance CO conversion, whereas retention of HC on the catalyst during a rich excursion would improve the overall HC conversion as such HC would be readily oxidized in a subsequent lean excursion.

Thus, a quantitative knowledge of a TWC's dynamic behavior is essential to the evaluation of its potential for simultaneous control of the three exhaust pollutants. We note here salient observations from a study of the dynamic behavior of a monolith TWC with the ultimate goal to obtain quantitative descriptions of the transient reactions involved.

Published studies on TWC dynamic behavior have been made mostly with pelleted TWC in absence of SO_2, a catalyst poison present in automotive exhaust gas. A few studies were made, however, of the effect of sulfur poisoning on the WGS and steam-reforming reactions over laboratory-prepared TWC (*11*) and on the oxygen storage capacity of aged monolithic TWC (*12*). The results discussed below were obtained with an engine dynamometer-aged monolith TWC in the presence of SO_2 at a concentration (20 ppm) normally found in the engine exhaust gas. Cyclic injection of stoichiometric oxidizing and reducing pulses was employed to simulate vehicle A/F modulation near the stoichiometric point in the time domain of 1 s. Premixed gases of O_2, CO, H_2, C_3H_6, and C_3H_8 in UHP helium (Matheson) were used for the oxidizing and respective reducing pulses injected into a carrier stream of UHP helium. The conversion of each reactant in the injected pulses was determined by means of a data acquisition system connected to a mass spectrometer. Details of the experimental apparatus and procedure were as described elsewhere (*12*). Table 1 shows the analysis of the aged TWC used in this work.

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TABLE 1

Analysis of Aged TWC

Component	wt (%)	μmol/g
Pt	0.17	8.7
Rh	0.014	1.4
Ni	1.5	260
Ce	1.0	71
Pb	0.03	1.4

Note. Catalyst support: 46 square channels/cm^2; washcoat: γ-alumina (10 wt%); bulk density: 0.7 g/cm^3; aging treatment: 19,200 km on engine dynamometer.

Oxygen storage. As expected, the extent of the catalyst redox reaction and hence of the dynamic oxygen storage will depend on the nature of the reducing gas. Table 2 shows that the dynamic oxygen storage capacity of the catalyst decreases with the three reducing gases in this order: $H_2 > CO > C_3H_6$. However, in terms of gross conversions, the catalyst efficiency for the three reductants would be as follows: $C_3H_6 > H_2 > CO$. A similar order of catalyst efficiency has been reported with a feed gas containing all the three reactants over a Rh TWC (*3*).

TABLE 2

Effect of Reducing Gas on Oxygen Storage[a]

Temp. (°C)	Reducing gas	Conc. (%)	Conv. (%)	O_2 storage[b] cm^3/100 cm^3 cat.
450	CO	2.0	11	0.66
	H_2	2.0	16	0.95
	C_3H_6	0.21	36	0.58
500	CO	2.0	15	0.90
	H_2	2.0	23	1.33
	C_3H_6	0.21	41	0.65
550	CO	2.0	20	1.15
	H_2	2.0	43	2.48
	C_3H_6	0.21	52	0.78

[a] Oxidizing gas—1% O_2; pulse volume—3 cm^3; space velocity—40,000 h^{-1}.

[b] Excludes O_2 for oxidation of carbon deposit in C_3H_6 runs.

Our previous study (*12*) shows that the NiO in an aged TWC contributes little to catalyst oxygen storage; a similar observation has been reported by other investigators (*9*). Since the oxidation of the catalyst surface is relatively fast (*7*, *13*), and since oxygen adsorbed on or combined with precious metals can be readily removed by CO, the increased oxygen storage obtained with H_2 reflects a greater reduction of the ceria than obtainable by CO. The extent of the Ce^{4+} to Ce^{3+} reduction by H_2 remains small—about 7% at 550°C.

For a first-order approximation, we estimated the extent of the precious metals partaking in the oxygen exchange process by noting that the Ce^{4+} to Ce^{3+} reduction by CO would be negligible at 450°C (*12*). On the assumption that one Pt or Rh atom would either adsorb or combine with one oxygen atom, we found that about 9% of the Pt + Rh in the catalyst took part in the redox reaction process. This serves also as an approximate measure of the dispersion of the precious metals in the aged catalyst.

Though the dynamic oxygen storage measured with CO alone is appreciable, the contribution of catalyst oxygen storage capacity to the enhanced CO conversion under dynamic conditions would depend on the reaction rate for the reduction of oxidized sites by CO in competition with the H_2 and HC present in the exhaust gas. While a knowledge of the reaction kinetics is necessary to determine this contribution quantitatively, the catalyst efficiency order noted above suggests that catalyst oxygen storage may not play an important role for the observed enhancement of CO conversion under dynamic conditions.

Water-gas shift reaction. Although Pt, Rh, and Ni are known to promote the WGS reaction (*1b*, *3*), their shift activity has been shown to be affected by sulfur poisoning (*4*, *11*, *14*). As shown in Table 3, under transient conditions simulating A/F modulation during automotive exhaust treatment, a significant enhancement of CO conversion takes place due to WGS reaction. At 550°C

TABLE 3

CO Conversion In Presence of H_2O[a]

Temp. (°C)	Pulse vol. (cm^3)	CO conversion (%) 0% H_2O	CO conversion (%) 2.5% H_2O	{Column 4 / Column 3}
450	3.0	11.2	18.4	1.6
	6.2	5.7	12.4	2.2
500	3.0	15.2	30.2	2.0
	6.2	10.1	23.8	2.4
550	3.0	19.7	50.5	2.6
	6.2	11.9	42.8	3.6

[a] Oxidizing pulse—1% O_2; reducing pulse—2% CO; space velocity—20,000 h^{-1}.

the CO conversion from WGS reaction is about two to three times that from reduction of catalyst sites in absence of competition from H_2 and HC. Thus, WGS reaction would be an important factor for the enhanced CO conversion under dynamic conditions, especially at elevated temperatures.

The transient nature of this shift activity was confirmed by extending the duration of the reducing pulse after an oxidizing pulse during a cyclic pulse injection experiment in presence of water vapor. The H_2 production from the shift reaction was then found to decay gradually to zero. The final decay of the shift activity took a period well over 10 min after an initial sharp H_2 peak for a period of a few seconds. We speculate that two types of active sites would be involved. The TWC under study contains Ni particles of micrometer size and, presumably, the slowly decaying sites are associated with this base metal component.

We have also determined the shift CO conversion in presence of H_2 at a CO/H_2 ratio (3/1) typical for the automotive exhaust and found a significant H_2 inhibition effect. Qualitatively, this observation is consistent with published studies on the WGS reaction indicating the reaction rate to be inversely proportional to H_2 concentration (*15*). However, the H_2 inhibition effect reported in a published work is for steady-state conditions in the absence of SO_2. The inhibition effect observed in our study under dynamic conditions and in the presence of SO_2 may reflect also catalyst poisoning due to sulfur compounds (e.g., H_2S) formed in a reducing atmosphere.

Carbon deposition. The conversion of C_3H_6 shown in Table 2 included the conversion of the HC to a carbon deposit that was detected as CO_2 formed during the oxidizing pulse. This carbon deposit presumably results from cracking of the HC adsorbed on the catalyst, as has been reported in the literature for adsorbed HC on precious metals at elevated temperatures (*16, 17*). Due to limitations of the analytical instrument, we were unable to determine the H_2O formed from any H_2 retained in the carbon deposit. We have, however, determined HC conversions for both C_3H_6 and C_3H_8, in the presence as well as in the absence of water vapor.

As expected from the coking propensity of the olefins, C_3H_6 forms more carbon deposit than C_3H_8 (Table 4). The carbon deposition found in our study is in qualitative agreement with the "HC retention" reported by Kaneko *et al.* (*6*). These investigators found comparable HC retention for both C_3H_6 and C_3H_8 pulses over a Rh TWC and in the absence of SO_2. For the TWC of our study in the presence of SO_2, water vapor greatly reduced the carbon deposition

TABLE 4

Reaction of C_3H_6/C_3H_8 over Oxidized TWC[a]

Temp. (°C)	HC gas	O_2 storage[b]	Conv. (%)	Carbon deposit[c]	CO formed[c]
450	C_3H_6	0.75	59	0.54	0.71
	C_3H_8	0.78	30	0.07	0.50
500	C_3H_6	0.84	66	0.56	0.54
550	C_3H_6	0.99	84	0.48	0.57
	C_3H_8	0.99	59	0.06	0.61
		In presence of 2.5% H_2O			
450	C_3H_6	0.80	74	0.34	0.78
	C_3H_8	0.54	52	0.02	0.64
500	C_3H_6	0.96	93	0.2	0.63
	C_3H_8	0.59	82	0.0	0.6

[a] Pulses (3 cm^3) of 0.5% O_2 and 0.11% HC; space velocity—40,000 h^{-1}/dry, 80,000 h^{-1}/wet.

[b] In cm^3/100 cm^3 catalyst.

[c] As fraction of C3 reacted + carbon deposit and of C3 reacted only, respectively.

from C_3H_6 and no carbon deposit was detected when the olefin was replaced by C_3H_8, indicating that water vapor may inhibit the coking process as well as initiate the steam-reforming reaction. The gross reaction rate in presence of water was high so that the HC conversion was evaluated at an increased space velocity.

As indicated in Table 4, over 50% of the HC reacted with the preoxidized catalyst was found as CO. A study of the material balance for each run showed that an appreciable amount of H_2 in the consumed HC remained unreacted. This unreacted H_2 was confirmed by monitoring the peak for mass 2 during the reducing pulse. Although the conversion of C_3H_6 is greater than that of C_3H_8 under comparable conditions, the dynamic oxygen storage obtained with both HC's in the absence of water vapor remains essentially the same. However, in the presence of water vapor, C_3H_6 effects a greater reduction of the oxidized catalyst sites than C_3H_8. The underlying reason for this apparent difference in the reduction of the catalyst sites is not well understood.

In conclusion, we note that the dynamic behavior of TWC for automotive exhaust treatment involves coupled complex process kinetics. A quantitative description of the TWC dynamic performance requires a comprehensive evaluation of the kinetic parameters involved in the oxygen storage process, the transient WGS activity, and the HC coking and steam-reforming reactions. Such an approach was taken in an expanded experimental study of the transient reaction kinetics. The insights gained in the above observations were incorporated in a dual site kinetic model which yielded good correlation of the experimental data.

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