

Novel electropositively promoted monometallic (Pt-only) catalytic converters for automotive pollution control

I. V. Yentekakis*, M. Konsolakis, I. A. Rapakousios, and V. Matsouka

Laboratory of Physical Chemistry and Chemical Processes, Department of Sciences, Technical University of Crete, 73100 Chania, Crete, Greece

Novel, Pt-only, electropositively promoted by Na, monolithic catalytic converters are developed and tested under simulated exhaust conditions within 150–500 °C. The effects of CeO₂ and La₂O₃ additives on the novel TWC washcoat are also studied. The performance of these simple in constitution, with one precious metal TWCs, was found to be well compared to that of a commercial bimetallic (Pt/Rh)-TWC.

KEY WORDS: TWC; Pt; simulated exhaust conditions; Na-promotion.

1. Introduction

In the last years air pollution generated from vehicles is a major environmental problem [1]. Currently, three-way catalytic converters (TWCs) employ a well established technology for automotive emissions control, capable to reduce NO_x and simultaneously oxidize CO and unburned hydrocarbons. Commercial TWCs use formulations based variously on Pt, Pd and Rh [1]. Among these noble metals, regarding NO_x reduction, Pt and Pd exhibit poor activity and selectivity towards N₂, whereas Rh is the key component in TWCs for this process due to its high activity for the dissociative chemisorption of NO [2]. However, the scarcity of Rh makes its use highly undesirable. In effect, much attention has been recently dedicated to discover means for enhancing the de-NO_x properties of the other two noble metals, Pt and Pd, objected to reduce or avoid the use of Rh. We have recently shown that electropositive promoters, e.g. alkalis, can drastically enhance both the de-NO_x activity and N₂-selectivity of both Pt and Pd. Hydrocarbons and CO oxidation reactions were also significantly enhanced by the same way [3–6].

Guided by these encouraging results we developed monolithic Pt-only catalytic converters promoted by Na. The performance of these novel TWCs under simulated exhaust conditions in a wide temperature range (150–500 °C) is studied here, in comparison to that of a commercial bimetallic (Pt/Rh)-TWC. The effects of varying Na-promoter loading, as well as the washcoat enrichment by structure stabilizers/promoters, ceria and lanthana, are also investigated.

2. Experimental methods

The washcoat of the novel catalytic converters, which consisted of only one noble metal (Pt) as the active material, γ -Al₂O₃ as the main supporting material enriched with CeO₂ and La₂O₃ structure stabilizers/promoters, and, Na as the surface promoter of the active phase, was prepared as follows: The CeO₂ and La₂O₃ enriched γ -Al₂O₃ support (Aldrich, 155 m²/g) was impregnated in an aqueous solution of dinitrodiamine-Pt and NaNO₃ with appropriate Pt and Na concentrations in order to yield a low of 0.5 wt % Pt loading and the desirable loading of Na promoter. The suspension was initially dried at 80 °C, then at 110 °C overnight and finally calcined at 600 °C for 2 h. The produced powder was mixed with a small amount of water and ball milled for 3 h, until a viscous slurry was formed. The amounts of ceria and lanthana in the γ -Al₂O₃ washcoat were typically 6 wt% and 2 wt%, respectively; the percentage units are normalized on the basis of 100 g washcoat (washcoat weight normalized percentage). A sample with 20 wt% of CeO₂ was also produced in order to investigate the effect of CeO₂ content. For comparison, one more sample prepared by the sol-gel instead of the wet impregnation method, was also produced.

The washcoat slurries were deposited on cylindrical cordierite honeycomb monoliths (400 cells/in²) according to the following procedure: monoliths were immersed in the stirring slurry for 30 s. The washcoated monoliths were withdrawn and the excess of slurry was removed by blowing air. Subsequently, the loaded specimens were dried at 110 °C for 2 h and calcined at 600 °C for 2 h. This procedure was repeated until the desired percentage of washcoat weight was obtained (20 ± 0.5 wt% of the total monolith weight). The washcoated monolithic samples were then heated in He flow (400 °C /1 h/100 cm³ min⁻¹) and finally reduced in H₂ flow (400 °C /1 h/100 cm³ min⁻¹). All the TWCs

* To whom correspondence should be addressed.
E-mail: yyentek@science.tuc.gr

produced and tested in the present study are listed in Table 1; the constitutions in the table are expressed by two different ways for better comparison: as percentages in 100 g of washcoat weight (washcoat normalized percentage) and, as percentages in 100 g of TWC weight i.e., washcoat + cordierite substrate (TWC normalized percentage). A commercial bimetallic (Pt/Rh)-TWC was also tested. Its constitution (see Table 1) was evaluated by ED-XRF analysis.

The feed composition employed during catalytic test experiments that simulate automotive exhaust emissions was: 0.1% NO, 0.7% CO, 0.1067% C₃H₆ and 0.78% O₂, balance He at 1 bar. The total gas flow rate was 3200 cm³(STP)/min, which corresponds to a Gas Hourly Space Velocity (GHSV) of 50500 h⁻¹ regarding to the TWC specimen volume (3.8 cm³). All TWC samples arranged in the quartz tubular reactor for testing had the same weight of 2 g (± 0.1 g). Note that the total noble metal (Pt + Rh) loading of the commercial TWC is 4.5-fold higher in comparison to the Pt loading contained in same weight of the novel Pt-only TWCs (see Table 1). Before acquisition of the *light-off* curves the TWCs specimens were operated in reaction conditions for 24 h at 700 °C and then at 550 °C for 5 days; sparse test experiments during this second period did not show any loss in the catalytic properties (activity/selectivity) of the specimens.

The influence of the existence of H₂O and CO₂ in the gas stream was also examined for one representative TWC sample, in order to record possible effects of these molecules, since they are present in real exhaust gases. In these experiments the feed composition was enriched with 10% H₂O and 10% CO₂, (i.e., 0.1% NO, 0.7% CO, 0.1067% C₃H₆, 0.78% O₂, 10% H₂O, 10% CO₂, balance He at 1 bar).

3. Results and discussion

3.1. CO and C₃H₆ oxidations

Figures 1a and 1b depict the CO and propene conversions, respectively, versus temperature for the seven TWCs listed in Table 1; six of these TWCs are prepared with different Na-promoter loading and/or different loadings of ceria and lanthana, while the seventh concerns the commercial TWC. Focusing first on the behavior of the TWC in which the washcoat contains only Pt dispersed on non-enriched γ -Al₂O₃ (i.e., no Na promoter or CeO₂ and La₂O₃, catalyst C0-0-0), it is obvious that it never achieves 100% conversion of CO or propene, even at high temperatures (up to 500 °C). However, when the washcoat is enriched with 6 wt% CeO₂ and 2 wt% La₂O₃ (catalyst C0-6-2), the monolith achieves ~100% conversion of CO and propene for temperatures >~380 °C and offers CO and propene *light-off* temperatures (i.e., temperature for 50% conversion of CO or propene) at 350 °C and 370 °C

Table 1
The monolithic TWCs and their constitutions normalized on the basis of both 100 g of washcoat and 100 g of TWC (washcoat + cordierite substrate)

TWC code	Washcoat normalized percentage				TWC (washcoat + cordierite substrate) normalized percentage			
	Noble metal content (wt%)	Na content (wt%)	CeO ₂ content (wt%)	La ₂ O ₃ content (wt%)	Noble metal content (wt%)	Na content (wt%)	CeO ₂ content (wt%)	La ₂ O ₃ content (wt%)
C0-0-0	0.5	0	0	0	0.1	0	0	0
C0-6-2	0.5	0	6	2	0.1	0	1.2	0.4
C5-6-2	0.5	5	6	2	0.1	1	1.2	0.4
C10-6-2	0.5	10	6	2	0.1	2	1.2	0.4
C10-6-2sg	0.5	10	6	2	0.1	2	1.2	0.4
C10-20-2	0.5	10	20	2	0.1	2	4.0	0.4
Commercial	-	-	-	-	0.37Pt + 0.08Rh	0	8.0	0.9

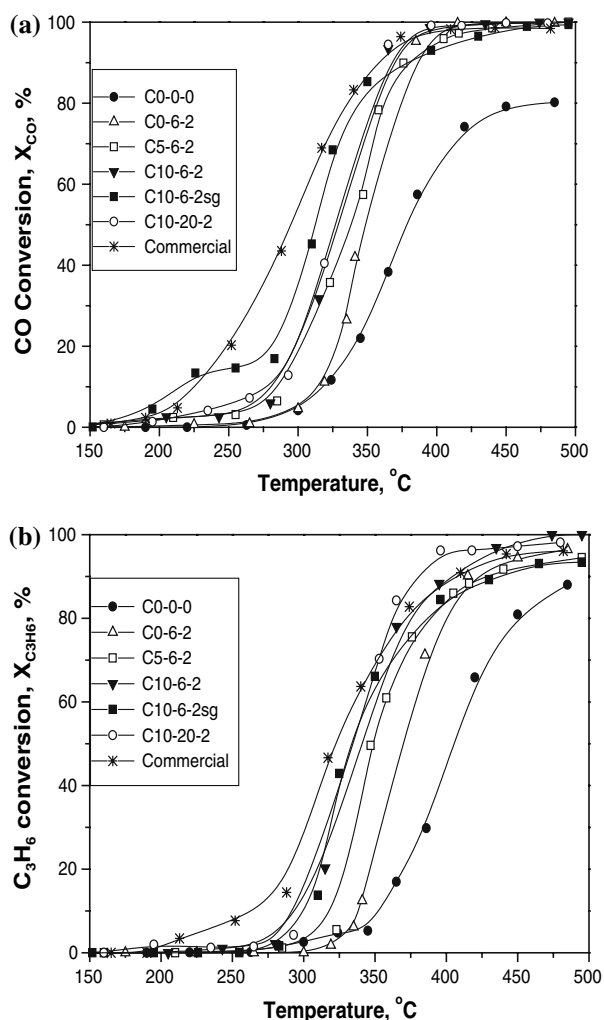


Figure 1. CO (a) and C_3H_6 (b) conversion profiles versus temperature for the TWC samples listed in Table 1.

respectively, which are $\sim 30^\circ C$ less than the corresponding *light-off* temperatures obtained with the C0-0-0 TWC. This shows the, well known from the literature, support-mediated promotional effects on the CO and H/C oxidation reactions, caused by the use of CeO_2 and La_2O_3 in commercial TWCs.

Interestingly, as our data shows, these support-mediated promotional effects obtained via ceria and lanthana, can be further improved by the addition of a surface promoter; in the present case sodium. This is clearly indicated from the CO and C_3H_6 conversion profiles of catalysts C5-6-2 and C10-6-2 with 5 and 10 wt% Na, respectively (figure 1). The best CO and C_3H_6 conversion performances were achieved by the C10-6-2 and C10-20-2 TWCs. Although, the C10-20-2 sample with 20 wt% CeO_2 exhibits slightly better X_{CO} and $X_{C_3H_6}$ *light-off* profiles than that of C10-6-2 sample with 6 wt% CeO_2 , both offer CO and C_3H_6 *light-off* temperatures of about $20^\circ C$ lower than the Na-free catalyst C-0-6-2, thus approaching even better the conversion performance of the commercial TWC sample;

the latter, however, is significantly (4.5-fold) more heavily loaded with noble metals, in comparison to the Pt-only TWCs produced here.

The data in figure 1 also show that the C10-6-2sg catalyst prepared by the sol-gel method has even better CO, but not propene, conversion performance i.e. $\sim 20^\circ C$ lower CO *light-off* temperature, in comparison to the corresponding performance of the similar constitution C10-6-2 catalyst prepared by the wet impregnation method.

3.2. NO reduction

The data for total NO conversion versus temperature is displayed in figure 2a. Figure 2b shows the corresponding NO conversion to N_2O . It is obvious that enrichment of the TWC-washcoat with ceria and lanthana significantly promotes the total NO conversion (see C0-6-2 in comparison to C0-0-0, figure 2a), but it has insignificant effect on the N_2O/N_2 product distribution (figure 2b).

Sodium addition in the TWC-washcoat further enhances the total NO conversion; the superior behavior is obtained by C10-6-2 sample, the total NO conversion

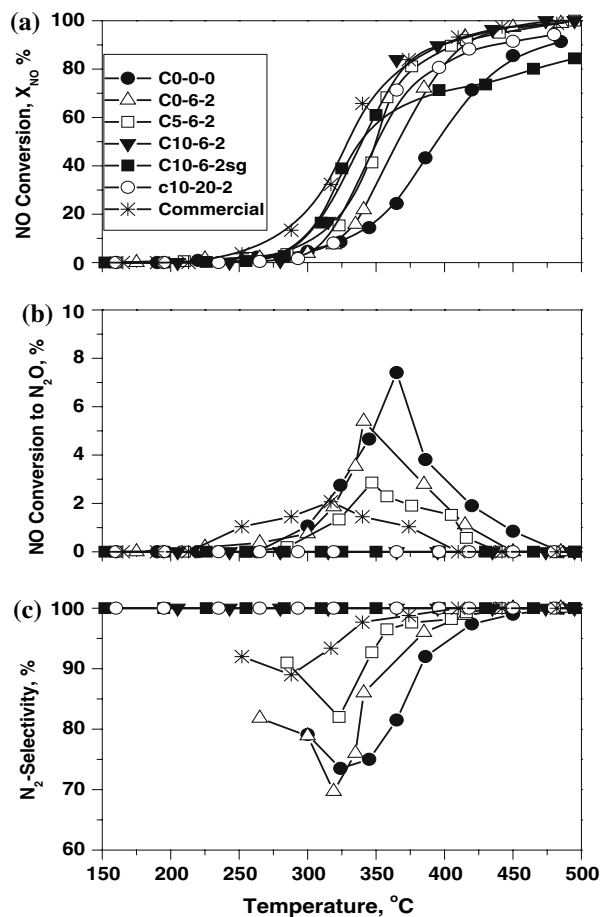


Figure 2. The total NO conversion (a), NO conversion to N_2O (b) and the corresponding N_2 -selectivity (c) as a function of temperature for the TWC samples listed in Table 1.

profile of which, is similar to that of the commercial TWC. More interestingly, Na addition causes substantial beneficial effect on the distribution of N-containing products; the production of N_2O is significantly decreased (figure 2b). Practically, all samples with 10 wt% Na promoter convert NO exclusively to N_2 , a behavior which is favorable compared to that obtained by the commercial TWC sample; the latter converts a notable portion of NO to the undesirable N_2O at temperatures between 200–420 °C. This effect of Na on the N-containing product distribution results to the achievement of highly selective TWCs, with $\sim 100\%$ selectivity towards N_2 instead of N_2O , as clearly shown in figure 2c, which depicts the selectivity behavior of all the TWCs tested in the present study; the commercial TWC was found not to be completely selective at temperatures between 200–400 °C.

Figure 3 depicts the influence of 10% H_2O and 10% CO_2 in the feed stream for C10-20-2 novel TWC sample. Obviously, X_{CO} profile practically remains unaffected, while slightly better and slightly worse performances are recorded for X_{NO} and $X_{C_3H_6}$, respectively, when these molecules are present in the gas stream. In both cases, i.e. with or without H_2O and CO_2 , the selectivity towards N_2 remains unchanged at 100% in the whole temperature range.

The main experimental observations of this study can be remarked as follows:

(i) Ceria and lanthana enrichment of the $\gamma-Al_2O_3$ support in monometallic (Pt)-TWC washcoat significantly improves its catalytic activity for all NO reduction and CO and hydrocarbon oxidation reactions, but has negligible effect on the selectivity towards N_2 . A shift of about ~ 30 °C to lower temperatures on the X_{CO} , $X_{C_3H_6}$ and X_{NO} profiles

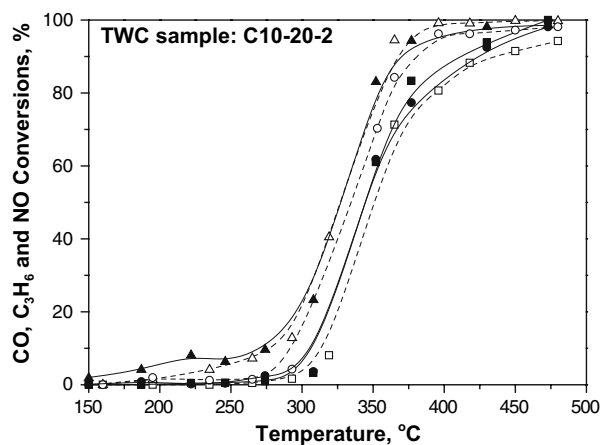


Figure 3. CO (triangles), C_3H_6 (cycles) and NO (squares) light-off performances of C10-20-2 TWC sample operated without (dashed line, open symbols) or with 10% H_2O and 10% CO_2 (solid line and symbols) in the feed gas composition. Other conditions: 0.1% NO, 0.7% CO, 0.1067% C_3H_6 , 0.78% O_2 , balance He at 1 bar.

has been obtained by the washcoats enriched with CeO_2 and La_2O_3 in comparison to the non-enriched C0-0-0 washcoat. Such support-mediated promotional effects of basic oxides in the three-way catalytic chemistry are well known in the literature and attributed mainly to the oxygen storage/release capacity due to CeO_2 [7]. The new and interesting observation of the present study is that Na addition in the above ceria and lanthana enriched washcoats provides TWCs with further improved catalytic activity for all reactions related to the CO, hydrocarbon and NO control, and more interestingly, offers TWCs exclusively selective towards N_2 for the NO reduction process; this indicates a synergy of the two methods of promotion in TWC catalytic chemistry. A sodium content of 10 wt% in the washcoat optimizes its catalytic performance under simulated exhaust conditions.

- (ii) 10% H_2O and 10% CO_2 enrichment of the simulated exhaust gas mixture is not found to cause any notable influence in the catalytic performance (conversion/selectivity) of our electropositively promoted by Na TWCs.
- (iii) Although washcoat prepared by the sol-gel method provides better CO oxidation performance, its de- NO_x efficiency is remarkably worse than that of the similar constitution washcoat prepared by the wet impregnation method. Therefore, impregnation can be considered as a simple, economic and efficient method for the production of the novel monometallic TWCs.

The origin of the promotional effects of Na on TWC catalytic chemistry is not the object of the present study; the way of action of Na modifier has been extensively investigated in previous detailed kinetics and spectroscopic studies where the origins of the promoting phenomena have been well rationalized [3–6]. The main object of this paper is to record the performance of these materials in more realistic conditions and in the form that they are used in practical applications. Although, the novel TWCs were operated for several days (> 5) in reaction conditions without to show any loss in their catalytic performance, it must be emphasized that long term durability and thermal stability tests are necessary in order to verify their fitness and merits for practical applications. Work on this line is currently in progress.

4. Conclusions

Combination of (i) support-mediated promotional effects by ceria and lanthana enrichment of $\gamma-Al_2O_3$ washcoat for monometallic Pt-only TWCs, with (ii) surface-induced promotional effects by Na, provides novel TWC formulations that can effectively remove all the main pollutants (NO, CO and HCs) from automotive emissions. Their conversion performance, even with

4.5-fold lower noble metal loading, is closely compared to that of the commercial TWC, while their N₂-selectivity is much superior (~100% in the whole temperature range of 150–500 °C).

Besides of the good activity/selectivity performance of the novel TWC formulations under TWC catalytic chemistry they are related with much lower cost (usage of only one noble metal at much lower loading, without the need of Rh). Furthermore, due to their simple constitution they can be more economically recycled, while the conventional wet impregnation method remains an efficient method for their production.

Acknowledgments

Financial support of this research by the Greek General Secretary of Research and Technology and the

European Union under the PENED programs (PENED-2003, Grand No: 03ED606) is gratefully acknowledged.

References

- [1] J. Kašpar, P. Fornasiero and N. Hickey, *Catal. Today* 77 (2003) 419.
- [2] M. Shelef and G.W. Graham, *Catal. Rev.-Sci. Eng* 36 (1994) 433.
- [3] I.V. Yentekakis, R.M. Lambert, M.S. Tikhov, M. Konsolakis and V. Kioussis, *J. Catal* 176 (1998) 82.
- [4] I.V. Yentekakis, M. Konsolakis, R.M. Lambert, N. Macleod and L. Nalbandian, *Appl. Catal. B* 22 (1999) 123.
- [5] M. Konsolakis and I.V. Yentekakis, *Appl. Catal. B* 29 (2001) 103.
- [6] M. Konsolakis, N. Macleod, J. Isaac, I.V. Yentekakis R.M. Lambert, *J. Catal* 193 (2000) 330.
- [7] J. Kašpar, P. Fornasiero and M. Graziani, *Catal. Today* 50 (1999) 285.