Current and future US Tier 2 vehicles program and catalytic emission control technologies to meet the future Tier 2 standards

Moon Hyeon Kim[†]

Department of Environmental Engineering, Daegu University, 15 Naeri, Jillyang, Gyeongsan 712-714, Korea (Received 3 March 2006 • accepted 18 July 2006)

Abstract—The Tier 2 vehicles program, defining a variety of emission standards, concepts and provisions, of the EPA in the United States has been phased in for all light-duty vehicles (LDVs), light-duty trucks (LDTs) and medium-duty passenger vehicles (MDPVs) from model year 2004, and this program will be continued until 2009, depending on the vehicle categories. Ultimately, not only should manufacturers of LDVs, LDTs and MDPVs and their importers in the United States meet the new Tier 2 standards, but all exporters outside the United States, such as Korean car makers, must also certify their vehicles by using this standard program. The principal rule for successfully applying this program to all the LDVs, LDTs and MDPVs is the use of the same Tier 2 standards if these vehicles are included in the same weight rating category, irrespective of fuel and engine types being used. This review provides an indepth discussion of key issues and provisions related to Tier 2 vehicles with engine measure strategies for automotive engineers and related academic researchers who are particularly interested in investigating how manufacturers will develop, certify, produce, and market their Tier 2 vehicles. A detailed mechanism for the phase-in of the Tier 2 standards to different vehicle weight categories will be discussed in this review, and the major difference between the US Tier 2 standards during the phase-in years and the EURO ones will be substantially compared. Great roles in meeting the future Tier 2 vehicle applications will be extensively discussed.

Key words: Tier 2 Standards, Average Fleet NO_x Standards, Vehicle Categories, Catalytic Emission Control Technologies, EURO Standards

INTRODUCTION

Significant improvement in ambient air quality in the United States (US) and European Union (EU) has been achieved by successively tightening stringent emission standards for nitrogen oxides (NO_x), unburned and partially burned hydrocarbons (HCs), carbon monoxide (CO) and particulate matter (PM) from gasoline and diesel engine-equipped automobiles, particularly passenger cars and lightduty vehicles [1]. In spite of such a considerable ambient air quality improvement due to reductions in engine-out emissions of these air pollutants, the Tier 2/Gasoline Sulfur program and the Auto-Oil I/II program were documented by the respective US Environmental Protection Agency (EPA) and European Commission in the late 1990s to apply them to the automotive and refinery industries because of the need for substantial reductions in the levels of unhealthy road transport pollution to which millions of people are exposed [1-5]. To maximize effectiveness in an effort to reduce the emissions from new vehicles, these programs are using a multifaceted approach combining advanced engine and fuel injection technology, advanced emission control technology, and an improvement in automotive fuel quality such as low sulfur fuel and narrow fuel density range. The advanced emission control technology consisting mainly of catalyst-based control strategies plays a central role in diesel and gasoline vehicles meeting future emission standards.

Very stringent US emission standards, which are generally known as the Tier 2 standards and were finally established by the EPA on

21 December 1999 for cars, light trucks and large passenger vehicles, are focused on simultaneously reducing the engine-out emissions of NO_x, non-methane organic gases (NMOG) consisting primarily of HCs and contributing to ambient volatile organic compounds (VOC), CO, formaldehyde (HCHO), and PM [6]. The phasein implementation of the new automotive exhaust standards to those vehicles is of particular interest in achieving large NO_x and PM reductions. Under the Tier 2 standards program, the same emission standards apply to the same vehicle weight categories; thus, cars, light trucks, minivans, and sport utility vehicles (SUVs) have the same emission limit value if they are included in the same categories, regardless of fuel being used. Thus the Tier 2 program includes all passenger vehicles expected to be on the road in the foreseeable future. In the present paper, details of the new Tier 2 standards for gasoline- and diesel-powered passenger vehicles and light-duty trucks (LDTs) at the US Tier 2/Gasoline Sulfur program have been extensively reviewed with a substantial statement on future EU emission standards, commonly dubbed as EUROs I, II, III, etc., for passenger cars and light commercial vehicles equipped with gasoline and diesel engines. However, the US Tier standards for heavy-duty trucks and buses are not covered in this paper. The operating principles of a variety of catalyst-based emission control technologies have been also covered with their requirements and limitations as ultimate solutions to the Tier 2 vehicles.

1. Recent Tendency in US and EU Automotive Emission Regulations

The new Tier 2 program requiring much tighter tailpipe and evaporative emissions controls in new passenger cars and LDTs was legally initiated from model year (MY) 2004 [6], and the Tier 2 standards

^{*}To whom correspondence should be addressed. E-mail: moonkim@daegu.ac.kr

M. H. Kim

will be fully phased in by MY 2009, as shown in Table 1. A detailed mechanism for the full phase-in of the Tier 2 standards to different vehicle weight categories will be discussed in Section 4 below. To significantly improve the implementation efficiency of the Tier 2 program and to increase the economic efficiency of the transition and model availability, this federal standard program is strongly aligned with the California Low Emission Vehicle II (CalLEV II) regulations, applicable from MYs 2004 through 2010 and later, which was an update of an original CalLEV I and was approved by the California Office of Administrative Law on October 28, 1999

and filed with the Secretary of State to become effective on 27 November 1999, especially during the interim program [7]. The Tier 2 program basically requires comparable emission limits for passenger cars and LDTs to the CalLEV II standards but does not have the zero emission vehicles (ZEVs) or the partial ZEVs (PZEVs)/ hybrid substitute requirements defined in the CalLEV II program. Consequently, the CalLEV II program plays a role in leading emission regulations for vehicles in the United States as well as in highly industrialized countries, such as EU.

EURO IV standards in EU are used for type approvals of new

Table 1. Implementation plans of new emission standards for new passenger cars, and light- and heavy-duty trucks in the United States and European Union

	Year												
	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
Emission standard California	LEV II^a												
USA	Tier 2^b										Tier 3 ^{c,}	1	Tier 4^d
EU	EURO III ^e	EURO IV ^f			EURO V	5	EURO VI ^d						EURO VII^d
Note. LEV: low emission vel	nicle.												

^aPhase-in until 2010.

^bPhase-in until 2009.

^eInterim step prior to Tier 4 standards.

^dBeing underway to determine limit values for engine-out emissions.

^eFrom 2000 to 2004.

²2006 for Korean (Korean automobile manufacturers association, KAMA) car makers.

^gA preliminary draft proposal for the standards has been produced by the European Commission on July, 2005.

				Limit values for mandatory tailpipe emissions											
Tier	Category	Class	ass Reference weight (kg)	CO (g/km)		HC (g/km)		NO_x (g/km)		HC+NO _x (g/km)		PM (g/km)		PM (#/km)	
			(8)	Gaso- line	Diesel	Gaso- line	Diesel	Gaso- line	Diesel	Gaso- line	Diesel	Gaso- line	Diesel	Gaso- line	Diesel
EURO III	M^a		All	2.30	0.64	0.20	-	0.15	0.50	-	0.56	-	0.05		
	\mathbf{N}_1^b	Ι	RW≤1,305	2.30	0.64	0.20	-	0.15	0.50	-	0.56	-	0.05	-	
		II	1,305 <rw≤1,760< td=""><td>4.17</td><td>0.80</td><td>0.25</td><td>-</td><td>0.18</td><td>0.65</td><td>-</td><td>0.72</td><td>-</td><td>0.07</td><td>-</td><td></td></rw≤1,760<>	4.17	0.80	0.25	-	0.18	0.65	-	0.72	-	0.07	-	
		III	1,760 <rw< td=""><td>5.22</td><td>0.95</td><td>0.29</td><td>-</td><td>0.21</td><td>0.78</td><td>-</td><td>0.86</td><td>-</td><td>0.10</td><td></td><td></td></rw<>	5.22	0.95	0.29	-	0.21	0.78	-	0.86	-	0.10		
EUROIV	M^{a}		All	1.00	0.50	0.10	-	0.08	0.25	-	0.30	-	0.025		
	\mathbf{N}_1^b	Ι	RW≤1,305	1.00	0.50	0.10	-	0.08	0.25	-	0.30	-	0.025		
		II	1,305 <rw≤1,760< td=""><td>1.81</td><td>0.63</td><td>0.13</td><td>-</td><td>0.10</td><td>0.33</td><td>-</td><td>0.39</td><td>-</td><td>0.04</td><td></td><td></td></rw≤1,760<>	1.81	0.63	0.13	-	0.10	0.33	-	0.39	-	0.04		
		III	1,760 <rw< td=""><td>2.27</td><td>0.74</td><td>0.16</td><td>-</td><td>0.11</td><td>0.39</td><td>-</td><td>0.46</td><td>-</td><td>0.06</td><td></td><td></td></rw<>	2.27	0.74	0.16	-	0.11	0.39	-	0.46	-	0.06		
EURO V	\mathbf{M}^{a}		All	1.00	0.50	0.075	-	0.06	0.20	-	0.25	0.005 ^{d,e}	0.005^{d}	\times^{f}	\times ^f
	\mathbf{N}_1^b	Ι	RW≤1,305	1.00	0.50	0.075	-	0.06	0.20	-	0.25	0.005 ^{d,e}	0.005^{d}	\times^{f}	$\times f$
		II	1,305 <rw≤1,760< td=""><td>1.81</td><td>0.63</td><td>0.10</td><td>-</td><td>0.075</td><td>0.26</td><td>-</td><td>0.32</td><td>0.005^{d,e}</td><td>0.005^{d}</td><td>\times^{f}</td><td>\times ^f</td></rw≤1,760<>	1.81	0.63	0.10	-	0.075	0.26	-	0.32	0.005 ^{d,e}	0.005^{d}	\times^{f}	\times ^f
		III	1,760 <rw< td=""><td>2.27</td><td>0.74</td><td>0.12</td><td>-</td><td>0.082</td><td>0.31</td><td>-</td><td>0.38</td><td>0.005^{d,e}</td><td>0.005^{d}</td><td>$\times f$</td><td>$\times f$</td></rw<>	2.27	0.74	0.12	-	0.082	0.31	-	0.38	0.005 ^{d,e}	0.005^{d}	$\times f$	$\times f$

Table 2. Current and future EU standards for passenger cars and light commercial vehicles

^aExcept vehicles the maximum mass of which exceeds 2,500 kg.

^bAnd those Category M vehicles which are specified in note^a.

^eBased on a draft proposal of the European Commission, July 2005 and a final proposal of the EC, December 2005.

^dPM limit values relate to the existing measurement procedure. A revised measurement procedure shall be adopted once the work of the UN/ECE Particulate Measurement Programme (UN/ECE PMP) is complete and the limit values will be adjusted accordingly to reflect the difference in the measurement techniques.

^ePM mass standards apply only to vehicles which use lean burn (LB) direct injection engines.

⁴After the completion of the UN/ECE PMP, a PM number standard will be introduced with the final approval of EURO V standards.

passenger cars and light commercial vehicles under the respective M and N₁ vehicle categories from 1 January, 2005 and continued to certify these vehicles until MY 2007, as seen in Table 1 [2,5,8,9]. In MY 2008, all automotive manufacturers will produce new EU light-duty vehicles (LDVs), such as passenger cars and light commercial vehicles, certified to new EURO V standards, for which a preliminary draft proposal was published by the European Commission in July 2005 to receive comments on all the issues covered by the draft proposal from stakeholders and a final proposal was published in December 2005 [8-10]. New limits for NO_x, CO, HCs and PM emissions from the vehicle categories proposed at the Commission document are listed in Table 2. Different emission limit values have been applied to diesel and gasoline vehicles since the EURO II standards which had been effective from 1 January 1996 to 31 December 1999. Stricter CO standards were proposed for EURO V diesel vehicles as in the case of the EUROs III and IV but less tighter standards will be used to certify NO_x emissions from the vehicles, as seen in Table 2. Although both conventional gasoline engine automobiles and lean-burn (LB) gasoline direct injection ones were exempted from PM emission requirements through the EURO IV stage, the latter EURO V vehicles will be included for PM regulations based on the Commission proposal, and PM number standards will be subsequently introduced for all EURO V diesel and gasoline vehicles (Table 2).

2. Operating Conditions of Automobiles and Their Engineout Emissions

The need to meet the future mileage rate of CO_2 emissions and corporate average fuel economy (CAFE) for LDVs, LDTs and MDPVs boosts extensive R&D activities for advanced diesel and gasoline engines to automotive industries throughout the world. The respective diesel and LB gasoline engine vehicles can offer less CO_2 emissions of ca. 40 and 10% than conventional gasoline ones [11,12]. The exhaust emissions from the diesel engines also contain much smaller amounts of CO and unburned HCs than the stoichiometrically-operated engines, but PM emissions from diesel engines are higher, by one to two orders of magnitude, than that from comparable gasoline engines [13].

Although diesel and LB engine-equipped vehicles possess such advantages in engine-out emissions, they all are strongly required to be in compliance with future stringent emission standards, such as US Tier 2 program and EU EUROS IV and V, to continue and expand sales in US and EU markets. The extent of the emissions of NO_x, HCs, CO and PM from gasoline and diesel vehicles is significantly dependent on their engine operating conditions; therefore, auto manufacturers need to use all possible measures in engine control strategies including advanced electronic engine controls, prior to introducing advanced catalytic emission control technologies for meeting the future engine exhaust standards.

2-1. Gasoline-fueled Engine Vehicles

Conventional gasoline engines are operated within a narrow λ window near the stoichiometric λ of unity, in which λ is defined by the ratio of the actual air-to-fuel ratio (AFR) to the stoichiometric AFR that is equal to 14.7 for the traditional gasoline engines, although modern LB technology engines have been able to achieve significantly leaner λ s [14,15]. The extent of the engine-out emissions of NO_x, HCs and CO from the conventional gasoline engine vehicles depends strongly on λ values, as shown in Fig. 1. Opera-

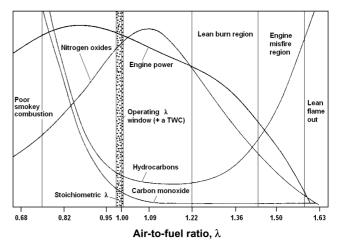


Fig. 1. Engine-out emissions vs. normalized air-to-fuel ratio (λ) for a gasoline-fueled engine [14,16].

tion of the engines at $\lambda < 1$ gives higher engine power output but fuel consumption increases. The HCs and CO emissions are relatively high at such low λ s because of insufficient amounts of oxygen to completely burn them out, and the emissions of NO_x from the gasoline engines represent a bell-shaped behavior around $\lambda = 1.09$. Even under any λ conditions, catalytic abatement technologies need to comply with current legislation limits for engine-out emissions of these pollutants, and much more advanced catalytic control technologies with advanced engines are required to meet the Tier 2 and EURO V standards. Current three-way catalytic converters (TWCs) can effectively remove the pollutants only at the narrow λ window as indicated in Fig. 1, although an increase of fuel consumption of conventional gasoline engine vehicles has occurred due to the usage of TWCs and their requirement for the stoichiometric λ to achieve best performances [17].

Technological developments in internal combustion engines for automobiles, especially in the last 10 to 20 years, have progressively extended the lean limit for homogeneous charge combustion stability, thereby achieving significantly improving fuel efficiency with lower engine-out emissions of pollutants, particularly NO_x and CO₂ [11,18]. Since the first introduction of LB gasoline engines by Toyota in Japan in 1984 and more ad-vanced LB engines in 1994 in both Japan and Europe [19,20], this engine technology has been widely used for gasoline-fueled vehicles in worldwide automobile markets, representatively Japan and Europe. Modern LB gasoline engines are generally operated with a λ value between 1.22 and 1.43, as shown in Fig. 1. However, if a combustion mixture of air and fuel is too lean, it can lead to combustion instability with consequent loss of efficiency and drivability. Under lean conditions (λ > 1.22), the increase in HCs emissions is due to lower combustion temperatures, which leads to significantly lower exhaust temperatures, typically 800-850 °C, compared to the stoichiometric engines with exhaust temperatures up to 1,100 °C [17]. Conventional TWCs could not be successfully used for the LB engines operating at complete LB conditions to sufficiently reduce NO_x [15,21]; therefore, a new effective deNO_x catalyst for lean NO_x engines is required to meet the phase-in of the Tier 2 standards and this will be covered in Chapter 4.

2-2. Diesel Engine Vehicles

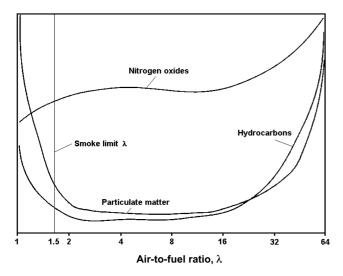


Fig. 2. Relationship between normalized air-to-fuel ratio (λ) and exhaust emissions for a diesel engine [16].

Diesel automobiles are thermally more efficient than conventional gasoline ones because of their operation at higher compression ratios ranging from 14 to 24 (8-10 for gasoline engines) and fewer pumping losses. Very broad λ ranges from about 1.38, corresponding to an actual AFR value of about 20.0 based on the stoichiometric one of 14.5 for cetane (C16H34) as a light diesel oil, at a high load, to over 6.9 at light loads are normally used for diesel engine vehicles; however, engine operation at $\lambda < 1.5$ needs to be avoided because of the formation of large amounts of soot and smoke, and of poor fuel economy [16]. The generalized variation of emissions with λ for a diesel engine is shown in Fig. 2. Modern diesel engines give less CO₂ production and much lower HCs and CO emission levels than those from conventional and LB gasoline engines. Although diesel vehicles emit much less amounts of NO_x than gasoline engines, the NO_x emissions should be controlled to meet future exhaust standards. Catalyst-based approaches, such as diesel oxidation catalysts (DOCs), catalyzed diesel particulate filters (CDPFs), and NO_x storage-reduction (NSR), can have a greater potential for controlling the engine-out emissions when existing diesel fuel is replaced to ultra low sulfur diesel fuel from 2006, as mandated by the EPA [1,19,22,23], and these technologies will be discussed in Chapter 4.

3. Current and Future Automotive Emission Standards for Passenger Cars, Light-duty Trucks and Medium-duty Passenger Vehicles in the United States

Many concepts in the Tier 2 standard program have been incorporated from the National Low Emission Vehicle (NLEV) program finalized by the EPA on December 16, 1997 and phased-in nationally from model year (MY) 2001 through 2003 only for LDVs and light light-duty trucks (LLDTs). The new standard program takes the corporate averaging approach and other provisions from the NLEV; however, the main focus on automotive emission reductions was moved on to NO_x from NMOG and LDVs and LDTs all were included in this program. Heavy-duty passenger vehicles (HDPVs) were subsequently introduced in this new standard program.

The Tier 2 program is compatible with that of CalLEV II running from MYs 2004 through 2010, although the certification Bins for the corporate averaging are somewhat different with those of the CalLEV II program [7]. Ultimate corporate average NO_x standards to be met for all of LDVs and LDTs of automakers under the Tier 2 regulations will be complete according to two different phasein schedules, regardless of fuel. Until the final Tier 2 standards are fully phased in, interim non-Tier 2 standards apply separately to LDVs/LLDTs and heavy light-duty trucks (HLDTs). Manufacturers can use all Bins for interim or Tier 2 vehicles during the phasein years, and the Bins system and the choice of the individual Bins are discussed in detail below.

3-1. Weight Category of Vehicles

To understand how the Tier 2 emission standards are applied to a variety of automobiles in the United States, two principal rules are very important: first, the same Tier 2 standards are used for all passenger cars, LDTs and MDPVs if these vehicles are included in the same weight rating category, as stated earlier, and second, the basic rule is no consideration of different fuel types [1]. Thus, it is very useful to understand the EPA system for classifying LDVs and trucks.

All vehicles and trucks, less than 8,500 lbs gross vehicle weight rating (GVWR), which is the curb weight of the vehicle plus its maximum recommended load of passengers and cargo, are included in the light-duty category of motor vehicles. Light trucks are categorized to LLDTs≤6,000 lbs GVWR and HLDTs>6,000 lbs GVWR, as listed in Table 3. The first group is LDVs/LLDTs that include all LDVs and all LDT1s and LDT2s, and secondly HLDTs consist of LDT3s and LDT4s. Heavy-duty passenger vehicles, such as large SUVs and passenger vans, between 8,500 and 10,000 lbs GVWR for personal transportation were recategorized as MDPVs in this new Tier 2 standard program on October 29, 1999 [6]. This vehicle category may include other types of multipurpose vehicles in the future, depending on new vehicle designs of car makers. Because the MDPVs are designed primarily for the transport of persons and have a capacity of not more than 12 persons, vehicles that have been designed for a legitimate work function as their primary use, such as the largest pick-up trucks, the largest passenger vans, and cargo vans would be excluded from this MDPV category; therefore, these vehicles would continue to be categorized as heavy-duty (HD) and

Table 3. Category of light-duty	v vehicles and trucks and	1 medium-dutv	passenger vehicles

Category	Characteristics
LDV (light-duty vehicles)	A passenger car or passenger car derivative seating 12 passengers or less
LLDT (light light-duty trucks)	Any LDT rated at up through 6,000 lbs GVWR. Includes LDT1s and LDT2s
HLDT (heavy light-duty trucks)	Any LDT rated atgreater than 6,000 lbs GVWR. Includes LDT3s and LDT4s
MDPV (medium-duty passenger vehicles)	A heavy-duty passenger vehicle rated at less than 10,000 lbs GVWR

Note. GVWR: gross vehicle weight rating (=vehicle weight plus rated cargo capacity).

	Bin#		L	imit values (g/mil	e)	
	DIII #	NO _x	NMOG	СО	НСНО	PM
Temporary Bins	11 ^a	0.9	0.280	7.3	0.032	0.12
	$10^{b,c,d}$	0.6	0.156/0.230	4.2/6.4	0.018/0.027	0.08
	$9^{b,e,f}$	0.3	0.090/0.180	4.2	0.018	0.06
Permanent Bins	8^e	0.20	0.125/0.156	4.2	0.018	0.02
	7	0.15	0.090	4.2	0.018	0.02
	6	0.10	0.090	4.2	0.018	0.01
	5	0.07	0.090	4.2	0.018	0.01
	4	0.04	0.070	2.1	0.011	0.01
	3	0.03	0.055	2.1	0.011	0.01
	2	0.02	0.010	2.1	0.004	0.01
	1	0.00	0.000	0.0	0.000	0.00

Table 4. Tier 2 full useful life emission standards for passenger cars, light-duty trucks, and medium-duty passenger vehicles

Note. NMOG: non-methane organic gases. Multiple each limit value by 0.622 to compare it to that in Table 2.

^aThe Bin # applies only to MDPVs and expires after model year 2008.

^bDeleted at end of 2006 for LDVs and LLDTs, and 2008 for HLDTs.

^eThe higher NMOG, CO and HCHO values apply only to HLDTs and expire after 2008.

^dOptional temporary NMOG standard of 0.280 g/mile applies for qualifying LDT4s only.

^eThe higher NMOG value applies only to HLDTs and expires after 2008.

^fOptional temporary NMOG standard of 0.130 g/mile applies for qualifying LDT2s only.

would be subject to applicable HD standards. Consequently, three different vehicle categories, i.e., LDV/LLDT, HLDT and MDPV, are used for the Tier 2 program, and all motor vehicles having the same weight category apply the same Tier 2 exhaust standards, irrespective of fuel and engine types.

3-2. Tier 2 Bins System

The Tier 2 Bins system can be designated to temporary and permanent Bins, as classified in Table 4. The temporary emission standards in the Tier 2 program are Bins # 9, 10 and 11, while the permanent full useful life standards are Bins # 1 to 8, and all manufacturers must use only these Bins to certify their Tier 2 vehicles being produced after MY 2008. The term "full useful life" represents 10 years and 120,000 miles for LDVs and LLDTs and 11 years and 120,000 miles for HLDTs and MDPVs, as defined by the US EPA [6], and only full useful life standards will be covered in this review. Bins # 9 and 10 among the temporary standards are available only during the interim period and will be eliminated after MYs 2006 for all LDVs and LLDTs and 2008 for HLDTs. Bin # 11 is applied only for MDPVs and will be listed out from the Bins category after MY 2008. The higher standards for NMOG CO and HCHO in the same Bin # in Table 4 can be used to certify their emissions from HLDT vehicles, prior to full phase-in of the Tier 2 program, which may give flexibility to a manufacturer during the phase-in years.

All NO_x emissions from Tier 2 vehicles with the Bins above 0.07 g/mile may be offset by NO_x emissions from Tier 2 vehicles certified to the Bins below 0.07 g/mile [6]. Such focus on NO_x reductions allows NMOG emissions to be floating in that the extent of the fleet NMOG emission depends on the combination of Bins used to meet the NO_x standard; however, any combination of vehicles meeting the 0.07-g/mile average NO_x standard may have average emission levels less than 0.09 g NMOG/mile [1]. The actual value would vary by manufacturer depending on the sales mix of the ve-

hicles for complying with the average fleet NO_x standard. It is expected that the overall NMOG emissions are progressively improved because HLDT vehicles that had not been covered by the NLEV regulations were included in this Tier 2 program. Consequently, manufacturers would use all the Bins during the phase-in years regardless of whether they certify their Tier 2 vehicles or interim vehicles, but the permanent eight Bins with a single standard emission value for each pollutant will be used after full phase-in until 2010.

3-3. Corporate Average Fleet NO_x Standards

Not only both manufacturers of LDVs, LDTs and MDPVs and their importers in the United States but also all exporters of the vehicles to US are ultimately required to meet the fleet NO_x standard of 0.07 g/mile every MY, as included in Table 5 [1]. Regardless, all the manufacturers can have the flexibility to certify their Tier 2 vehicles using the Tier 2 Bins system, which allows a combination of different sets of exhaust emission standards and will be discussed in detail later. However, the Bins # should be chosen so that their corporate sales-weighted average NO_x emission values for their full useful life Tier 2 vehicles are no more than the 0.07 g/mile standard.

Until MY 2008, it is believed that each automotive manufacturer will determine its own year-end corporate average NO_x emission level by computing a sales-weighted average of the full useful life NO_x standards using the various Bins and will comply with the average fleet NO_x standard for its Tier 2 vehicles. If a manufacturer meets a corporate average NO_x emission value below 0.07 g/mile, this car maker can have credits for the difference and can trade the credits to other manufacturers or use them in years when its average value exceeds the 0.07-g/mile NO_x standard [1]. All manufacturers can apply advanced engine design and control and emission control technologies to different vehicles in a more cost-effective manner than under a single set of standards that all vehicles have to meet.

						Y	'ear			
	2001	2002	2003	2004	2005	2006	2007	2008	2009+later	Average fleet NO _x standard (g/mile)
LDV/LLDT	NLEV	NLEV	NLEV	75%	50%	25%				0.30
(Interim)				max.	max.	max				
LDV/LLDT	early	v banking		25%	50%	75%	100%	100%	100%	0.07
(Tier 2+Evap.)	а	a	a							
HLDT	early	v banking						50%	100%	0.07^b
(Tier 2+Evap.)	a	a	a	a	a	a	a			
HLDT	Tier 1	Tier 1	Tier 1							$0.20^{b,e}$
(Interim)	а	а	а	25%	50%	75%	100%	50%		
MDPV	HDE	HDE	HDE	c,d	d	d	d	max.		
(Interim)										
MDPV	early	v banking						50%	100%	0.07^{b}
(Tier 2+Evap.)	a	a	a	a	a	a	a			

Table 5. Tier 2 and interim non-Tier 2 phase-in and exhaust averaging sets

Note. Bold lines around shaded areas indicate averaging sets.

^aAlternative phase-in provisions permit manufacturers to deviate from the 25/50/75% 2004-2006 and 50% 2008 phase-in requirements and provide credit for phasing in some vehicles during one or more of these model years.

^bHLDTs and MDPVs must be averaged together.

^cRequired only for manufacturers electing to use optional NMOG values for LDT2s or LDT4s and MDPV flexibilities during the appli cable interim program and for vehicles whose model year commences on or after the fourth anniversary date of the signature of this rule. ^dDiesels may be engine-certified through the 2007 model year.

^e0.60 NO_x cap applies to balance of LDT3s/LDT4s, respectively, during the 2004-2006 phase-in years.

3-4. Phase-in Schedules of Tier 2 Program

3-4-1. Phase-in Approach for Tier 2 LDVs and LLDTs

In MY 2004, 25% of the total LDV and LLDT vehicles sold by automobile manufacturers were in compliance with the Tier 2 full useful life standards [1], and the standard program was phased in 50% in 2005, 75% in 2006, and 100% from 2007 for this vehicle category, as seen in Table 5. In doing this during the phase-in years, manufacturers can certify their vehicles using one of the available Bins # or more likely a mix of the Bins # 1-10 in Table 4, but they must meet the 0.07 g NO_x/mile corporate average standard for their Tier 2 LDVs and LLDTs each model year.

Because manufacturers have the flexibility to introduce the Tier 2 LDV and LLDT vehicles until MY 2006, a maximum of 25% of the vehicles in that year can use the interim standards, which will be separately discussed below, as an alternative phase-in schedule. The LDVs and LLDTs with the interim standards up to the year 2006 should meet the corporate average fleet NO_x value of 0.30 g/ mile based on the full useful life. If a manufacturer needs to obtain NO_x credits in MYs 2005-2006 to be used in later years or to be sold to other manufacturers, it should achieve corporate average standards below 0.07 g NO_x/mile, as mentioned previously. Manufacturers introducing early Tier 2 vehicles certified by the Bins 1 or 2 have also additional NO_x credits [1].

3-4-2. Phase-in of Tier 2 Standards to HLDTs

Final Tier 2 standards for HLDTs (LDT3s and LDT4s) with 6,000 <GWVR≤8,500 lbs will be phased in later and ended later than that for LDVs and LLDTs. The Tier 2 emission standards will be applied to each manufacturer of HLDTs as follows [1]: 50% in MY 2008 and 100% in MY 2009 (Table 5). The 0.07-g/mile corporate

average fleet NO_x standard must be met for the Tier 2 HLDTs during the phase-in years, as for the LDVs and LLDTs. Both early Tier 2 NO_x credits and alternative phase-in approach that still result in 100% phase-in by 2009 are allowed to HLDTs manufacturers, which can be expected to promote early introduction of Tier 2 HLDTs with a greater flexibility in the phase-in of the interim HLDTs standards. 3-4-3. Phase-in of Tier 2 Standards to MDPVs

As for HLDTs discussed above, all MDPVs must meet the final Tier 2 standards up to MY 2009 via 50% phase-in in MY 2008, as indicated in Table 5 [1]. Prior to MY 2009, car makers can certify their non-Tier 2 MDPVs using interim standards, for which the MDPVs must be grouped with non-Tier 2 HLDTs. Manufacturers must optimize a fleet of MDPVs and HLDTs so as to meet 0.07 g NO_x/mile as the corporate average standard required. It can be a solution for early phase-in of the Tier 2 program to MDPVs to generate NO_x credits as for HLDTs. HD engine standards could be used for diesel MDPVs to certify their exhaust emissions until MY 2007; however, they are not available from MY 2008 even for diesel MDPVs. 3-5. Phase-in Schedules for Interim Standards

As in the case of the Tier 2 standard program, the interim regulations focus primarily on significant reduction in NO_x emissions from automobiles but also provide reductions in NMOG beyond the NLEV levels. The two groups consisting of LDVs and LLDTs, and HLDTs have separate interim average NO_x standards during the phase-in period. From MY 2004, the interim provisions described below were applied for all the Table 3 vehicle categories not certified to the Tier 2 standards. Interim vehicles were certified by using the same Bins as Tier 2 vehicles; however, Bins # 9-11 in Table 4 will be used only during the phase-in years. Bins # 9 and 10 were completely phased out after MYs 2006 for LDVs and LDTs and will be so in 2008 for HLDTs, and Bin # 11 only for MDPVs will be discontinued after MY 2008.

3-5-1. Phase-in of Interim Standards to LDVs and LLDTs

All MY 2004 and later LDVs and LLDTs not complying with the Tier 2 phase-in were subject to an interim corporate average NO_x standard of 0.30 g/mile, and this NO_x emission standard was continued until 2006, as included in Table 5. The interim standards for the LDVs and LLDTs were designed to hold the extent of their NO_x emissions to NLEV levels [6]; therefore, this interim program would give substantial NO_x emission reductions from LDT2s in the early years of the program, because the LDT2s must meet the 0.30-g/mile NO_x average, which is significantly lower than a 0.50 g/ mile average in the NLEV program. The phase-out regulations were applied for LDVs and LLDTs category up to 75% in MY 2004 and were implemented each year-maximum 50% in MY 2005 and 25% in MY 2006, as seen in Table 5.

3-5-2. Phase-in of Interim Standards to HLDTs

The interim program provides a chance to significantly reduce exhaust emissions from HLDTs to manufacturers and may allow adequate lead time before they must bring their HLDTs into complete compliance with final Tier 2 standards. The interim standards for HLDTs were phased in from MY 2004 and their manufacturers were required to meet a corporate average fleet NO_x standard of 0.20 g/mile through MY 2007. As shown in Table 5, the phasein of the 0.20-g/mile NO_x standard to HLDTs plus MDPVs was 25% in MY 2004 and were 75 and 100% in the respective later MYs 2006 and 2007 via 50% phase-in in 2005. The interim program will remain at a maximum of 50% in effect through 2008 to cover HLDTs not yet phased into the Tier 2 standards. Interim HLDTs not subject to the interim corporate average NO_x standard during the applicable phase-in years are certified to the least stringent Bins so that they have a cap of NO_x emissions at 0.60 g/mile [6], and these vehicles are not included in the average fleet to determine compliance with the interim 0.20 g NO_x/mile standard. This alternative approach is to allow more time for manufacturers to bring the more difficult HLDTs to the Tier 2 program.

3-5-3. Phase-in of Interim Standards to MDPVs

All MDPVs were included in the Tier 2 program from MY 2004 and are required to meet the final Tier 2 standards in 2009 and later [1]. Because the MDPVs were grouped with HLDTs for the phasein of the interim program, the interim standards based on a corporate average full useful life NO_x standard of 0.20 g/mile were applied for 25% of total MDPVs sales including HLDTs in MY 2004 and were phased in 50, 75 and 100% in the respective years of MYs 2005, 2006 and 2007, as seen in Table 5. The total sales of HLDTs and MDPVs certified to the interim standards cannot exceed maximum 50% in MY 2008. This means that at least 50% of total MDPVs sales must comply with the Tier 2 standards. Manufacturers would be required to certify their MDPVs using Bin # 11, which is effective only for MDPVs in MYs 2004-2008, and they may continue to use the Bin for certifying their interim vehicles until MY 2008; however, the vehicles must be included in the 0.20 g NO,/mile fleet average. The 0.9 g NO_x/mile Bin is the highest Bin available; therefore, this NO_x regulation acts as the cap for MDPV vehicles not yet phased in to the interim standards.

Up to MY 2007, diesel engine-equipped MDPVs can be certi-

Table 6. Evaporative emission standards for light-duty vehicles and trucks and medium-duty passenger vehicles

Vehicle category	3 day diurnal +hot soak (g/test)	Supplemental 2 day diurnal+hot soak (g/test)
LDVs	0.95	1.2
LLDTs	0.95	1.2
HLDTs	1.2	1.5
MDPVs	1.4	1.75

Note. The values are a gram of hydrocarbons emitted per test.

fied to the heavy-duty engine (HDE) standards that are engine-based standards but not GVWR-based ones as in the Tier 2 program, and such engine-certified diesel MDPVs would be excluded from the interim averaging pool for determining the NO_x emission level because they are required to comprise a separate averaging set under the averaging, banking and trading requirements applicable to HD diesel engines. This engine-based certification for diesel MDPVs is to provide phase-in time and flexibility to manufacturers who may have limited experience with chassis certifying vehicles containing such engines. All diesel MDPVs from MY 2008 must be chassis-certified and included either in the interim regulations or in the final Tier 2 program. In MY 2009 and later, all MDPVs including diesels must be in compliance with the final Tier 2 standards. 3-6. Evaporative Emission Standards

All Tier 2 vehicles such as LDVs, LDTs and MDPVs must comply with the more stringent evaporative emission standards given in Table 6. The phase-in requirements in evaporative emissions of HCs from gasoline-, natural gas-, liquefied petroleum gas (LPG)-, ethanol- and methanol-fueled vehicles must not exceed the Tier 2 diurnal plus hot soak standards for the full three diurnal test sequence and for the supplemental two diurnal test one; these test sequences have been described in detail elsewhere [6]. The Tier 2 evaporative standards were and will be phased in according to the same mechanism as the Tier 2 exhaust ones, i.e., MYs 2004-25, 2005-50, 2006-75 and 2007-100% for LDVs and LLDTs, and 50% beginning in MY 2008 for HLDTs and MDPVs. As for the exhaust standards, interim standards would be also available for these vehicle categories. The higher standards for HLDTs and MDPVs than those applicable for LDVs and LDTs are to provide allowance to greater nonfuel emissions due to larger vehicle size [1].

3-7. Other Emission Standards

Many emission standards except for the Tier 2 exhaust standards discussed above have been defined in the Tier 2 program, and these standards are additionally applied for Tier 2 vehicles, depending on their categories [1]. Manufacturers should meet running loss, refueling emission and spitback standards. All new Tier 2 LDVs, LDTs and MDPVs cannot exceed 0.05 g/mile in HCs upon the running loss test, regardless of fuel used. The Tier 2 refueling emission standards for all gasoline-, diesel- and methanol-fueled LDVs, LDTs and MDPVs are an emission value of 0.20 g HC per gallon, corresponding to 0.053 g per liter, of fuel dispensed, and all Tier 2 LPG-fueled LDVs, LDTs and MDPVs must meet 0.15 g HC per gallon (0.04 g per liter) of fuel dispensed. The Tier 2 spitback standards for gasoline- and methanol-fueled LDVs, LDTs and MDPVs must meet 0.15 g HC per gallon (0.04 g per liter) of fuel dispensed. The Tier 2 spitback standards for gasoline- and methanol-fueled LDVs, LDTs and MDPVs are defined dispensed.

ter 3.

as amounts equal to or smaller than 1.0 g HCs (carbon if methanol-fueled) per fuel dispensing spitback test. All these standards are subject to the same phase-in compliance as the Tier 2 exhaust standards.

Cold temperature exhaust emission standards are applicable only to gasoline LDVs, LDTs and MDPVs with a useful life of 50,000 miles. The standard for LDVs and LDT1s is 10.0 g CO/mile, while LDT2s, LDT3s, LDT4s and MDPVs must not exceed 12.5 g CO/ mile. Certification short test exhaust emission standards for all gasoline-fueled LDVs, LDTs and MDPVs are applied to be: HCs must be less than 100 ppm based on hexane for certification and selective enforcement audit (SEA) testing and 220 ppm as hexane for in-use testing; CO must be within 0.5% for certification and SEA testing and 1.2% for in-use testing. Highway NO_x exhaust emission standards represent that the maximum projected NO_x emissions measured upon the federal Highway Fuel Economy Test [6] must not be greater than 1.33 times the applicable FTP (Federal Test Procedure) NO, standard to which the manufacturer certifies the test group. Both the projected emissions and the product of the NO_x standard and 1.33 must be rounded to the nearest 0.01 g/mile before being compared. This highway NO, standard is not applicable to MDPVs. Supplemental exhaust emission standards applicable to all Tier 2 gasoline- and diesel-fueled LDVs and LDTs but not to MDPVs and alternative or flexible fueled LDVs and LDTs when operated on a fuel other than gasoline or diesel are based on 4,000 miles and full useful life. Details of these supplemental exhaust emission standards can be found elsewhere [6].

4. Catalytic Emission Control Technologies for Meeting Future US Tier 2 Standards

Sophisticated approaches to internal engine combustion and catalyst-based emission control technologies are required to meet the future emission legislations being phased in up to MY 2009 for all the LDVs, LDTs and MDPVs in Table 3, and one of them would be a systematic integration between advanced internal combustion technologies and advanced exhaust aftertreatment ones. Particularly, the catalyst-based technologies will play a large role in achieving the future engine-out limits for NOx, PM, CO and HCs, and their performances and feasibility are engines-dependent and vary significantly with legislated emission levels, exhaust temperature and compositions, GVWR, vehicle infrastructure, fuel economy and so forth. The vehicles should ultimately meet the legislated emission target which is the US Tier 2 Bin # 5 with an NO_x emission limit of 0.07 g/mile [1], indicating that all the catalyst-based single and multi-staged systems must have conversion efficiencies greater than 90% to be an effective, viable emission control technology for vehicle applications, because the FTP cycle can tolerate engine-out levels of 0.70 g NO_x/mile [24]. The exhaust temperature and compositions during the FTP cycle depend on the types of engines, such as traditional and LB gasolines and diesels, and as well as on the relationship between engine size and vehicle weight.

All the indicated points may primarily determine the applicability of the catalytic emission control technologies to reductions in the emission of the major pollutants from the vehicles listed in Table 3. It is our major concern to understand the operating principle of commercial and emerging catalytic emission control technologies and their requirements and limitations in vehicle applications and to examine potential ways of facilitating a systematic integration between

facturer certifiesthese technologies is anticipated to give significant improvements
in the emission controls with some economic and engineering dis-
advantages, i.e., larger catalyst volume, higher pressure drop and
less fuel economy, and such attempts are in progress extensively.andards applica-
andards applica-4-1-1. TWC System

The TWCs have been widely employed to simultaneously catalyze the removal reaction for NO₂, CO and HCs from conventional gasoline-fueled automotives being operated near stoichiometric AFR conditions. Oxidation catalysts were first introduced into MY 1975 automobiles in the United States to lower unburned HCs and CO emissions from stoichiometric gasoline engine passenger cars and these first generation catalytic converters are usually called to "twoway catalysts" [12,25]. A multifunctional automotive catalyst coupled with a closed-loop control electronic fuel-injection system in combination with a λ sensor was begun to be used for gasoline passenger cars in the early 1980s in the United States since some MY 1977 vehicles in California fitted out it to substantially reduce NO_x, and this may be an old version of modern TWC systems [12,25,26]. The typical operating conditions and their related performances of the TWCs have been discussed in the previous Section 2.1. The modern TWCs are the state-of-the-art technology to simultaneously reduce all NO₂, HCs and CO from stoichiometric gasoline-powered vehicles, and layered washcoating and thermal-resistant, high cell density and thin-walled catalyst supports and their new designs such as hexagonal cell structure will be soon-to-be-used on advanced TWCs systems for meeting the ultimate Tier 2 Bin # 5 standards [25].

the catalysts-based technologies for multi-staged combinations, there-

by bringing out future scientific and engineering challenges of each

approach to advanced gasoline and diesel vehicles to which much

tighter exhaust standards will be in force until MY 2009. However,

it is not intended to make a comprehensive focus on such catalytic

solutions to meet the future Tier 2 standards discussed in the Chap-

4-1. Commercially-proven Catalytic Emission Control Technologies

and PM, from modern gasoline and diesel vehicles up to their future

emission targets motivates an intense effort to highly improve cur-

rently available catalytic emission control technologies, including

the TWCs, NSRs, DOCs, DPFs and CDPFs mentioned in Sections

2.1 and 2.2. These technologies may be a benchmark in develop-

ing new catalytic solutions to meet the future Tier 2 standards, but

all the approaches have requirements and limitations in vehicle applications, as compiled in Table 7. A systematic integration between

The need to reduce the automotive pollutants, particularly NO_x

Even for the advanced TWCs with highly technological achievements, there are a few limitations in commercial applications to advanced gasoline-driven vehicles, i.e., LB gasoline and gasoline direct injection (GDI) engines, as seen in Table 7. Modern TWCs consisting of active noble metals, such as Pt, Pd and Rh, with numerous promoters, are difficult to be transposed as a way of controlling NO_x, HCs and CO emissions from the LB gasoline and GDI vehicles because large amounts of engine-out excess O₂ transfer easily the Rh to an inactive phase, RhO_x, during the automotive catalysis [27,28]. The same problem exists for diesel engine vehicles because these are also operated under highly LB conditions as discussed in Section 2.2. Consequently, a new, cost-effective catalyst-based technology to reduce NO_x emissions from such LB automobiles needs

		Engin	e			
Catalytic technology ^a	Gaso	oline		Direct	Requirements and limitations	
	Conventional	LB	GDI	- Diesel		
TWC	\checkmark				No working under lean operating conditions	
NSR			\checkmark		Very weak sulfur tolerance	
					• Poor NO _x storage performance at low temperatures	
					 Continuous or periodical regeneration 	
					 Thermal spike at temperatures around 650 °C 	
					• Post injection with fuel penalty	
					Large catalyst volume	
DOC					• Low catalytic efficiency	
					• No way of NO _x reduction	
DPF					• Continuous or periodical regeneration (every 400-500 km	
					• OBH system to heat to 600-650 °C	
					• Post injection with fuel penalty	
					Weak sulfur tolerance	
					• No way of NO _x reduction	
CDPF					Continuous or periodical regeneration	
					• High thermal durability	
					• Post injection with fuel penalty	
					• Low performances in NO _x reduction	
					• Weak sulfur tolerance	
					• Relatively higher pressure drop	

Table 7. Commercially-available catalytic emission control technologies for light-duty vehicles and trucks and medium-duty passenge	r
vehicles	

Note. The \sqrt{s} represent the commercial application of each emission control technology to the specified vehicles.

"Systems strongly integrated between each technology are being employed to meet the Tier 2 standards, and such approaches will be continued.

to meet the future NO_x regulatory requirements in the US Tier 2 program.

4-1-2. NSR Catalyst

NSR catalytic systems are employed for current GDI vehicles to alleviate NO_x emissions and are one of the most viable solutions to advanced LB gasoline and GDI vehicles for meeting the future Tier 2 NO_x standards, which was first commercialized by Toyota in 1994 [19,29]. Nitrogen oxides are removed from the gas stream under lean operating conditions and stored on BaO existing in the NSR catalysts as barium nitrate compounds. The BaO particles covered completely by the nitrates are exposed to fuel-rich conditions for a certain time to regenerate the catalytic sites for adsorbing NO_x and the overlayer nitrates are reduced, thereby releasing NO that is further reduced to N₂ on neighbor noble metal sites. A detailed description of the NSR mechanism on Al₂O₃-supported noble metal-based BaO catalysts has been given in the literature [29,30].

A critical drawback to this technology as noted in Table 7 is that the catalysts possess very weak tolerance to SO_2 which is strongly accommodated on the NO_x adsorption sites as surface sulfate groups and have relatively poor performances in the NO_x storage at low temperatures [31,32]; there- fore, an on-board heating (OBH) system capable of thermal spike at temperatures near 650 °C needs to release the sulfates out from the catalytic sites [32,33]. Such temperatures cannot be normally achieved even for advanced diesel engines in the future. The exhaust temperatures of many light-duty diesel vehicles fall in the temperature range below 350 °C, and NSR catalysts are hardly regenerated at this temperature; therefore, a variation of the NSR catalytic systems, such as a combination of TWC and NO_x trap catalysts, low oxygen storage TWC and lean NO_x trap, is under development to improve the catalyst regeneration and system performances [34,35]. Odorous H₂S can be produced from NSR aftertreatment systems during their high-temperature regeneration, although its emission levels are controlled by improving the selectivity for SO₂ during desulfation processes using rich/lean wobbling strategies [36]. Finally, an impediment to this catalytic technology requires large volumes of the NSR catalysts which can be several times greater than the engine cylinder displacement and has a fuel economy penalty (5-7%), depending on the duration and frequency of the regeneration events.

4-1-3. DOC System

The DOC technology is essential to meet current regulations for exhaust emissions from modern diesel-driven vehicles, and more stringent future legislations, such as Tier 2 standards, require advanced DOC systems to significantly reduce HCs, CO and SOF (soluble organic fraction) emissions. The catalysts consisting of precious metals, predominantly Pt or Pd, are focused on the oxidation of condensable HCs which would mainly form diesel soot, although they play an additional role in oxidizing CO and light HCs [37]. The catalytic control of the SOF emissions enables the DOCs to reduce total PM emissions by 25-50%, depending on the constituents of the total PM. In an effort to upgrade such noble metal-based DOCs, advanced approaches to the washcoating of the precious metals and their optimal content and distribution are recently in extensive progress; as a representative example, zeolitic materials are substantially introduced into the washcoating processes for achieving intermediate adsorption of HCs from diesel engine cars at low exhaust temperatures as well as for allowing easier cracking of longchain HCs [38,39].

The current DOCs have a crucial disadvantage that is no way to remove NO_x from diesel engine vehicles, as noted in Table 7, although the addition of zeolites to the traditional DOCs helps to convert NO_x, up to ~30%, in the presence of engine-out HCs even within a certain temperature window and the principle of NO_x removal reaction on these advanced DOCs is very similar to lean NO_x catalysis that will be discussed later. Another limitation to this technology is insufficient capability of DOCs to reduce PM up to its future emission targets; consequently, even advanced DOCs may be required to be a systematic integration with (C)DPFs and deNO_x solutions.

4-1-4. DPF and CDPF Technology

The filter-based approaches to PM emission controls for diesel automotives have been the topic of the intense R&D activities during the last 20 years due to incomplete oxidation of soot cores over DOCs being loaded onto monolithic carriers [40]. Significant reduction in PM emissions from diesel vehicles is achieved by using diesel particulate filters alone (DPFs) or lined with catalysts (CDPFs) that help to oxidize the deposited PM at low temperatures and are frequently used for diesel applications since the first commercial use by Engelhard for diesel Mercedes-Benz cars sold in California in 1985. Diesel particulates are mechanically filtered and collected in the (C)DPFs and simultaneously burned off on them upon either active regeneration with fuel burners and electrical heaters [41-43] or passive ones with fuel-borne catalysts (FBCs) and catalytic coatings [44-48]. Numerous thermally resistant porous filter media, including ceramic monoliths, woven silica, fiber coils, ceramic foam, wire mesh and sintered metal foam, and regeneration techniques have been studied to date, but only a few of the media for DPFs reached system maturity and many other materials are being investigated as good candidates as well. Currently, cordierite and silicon carbide (SiC) are widely employed for DPFs materials [49].

The extent of the reduction for the PM should be at least 90% based on the total particulate mass to comply with the future standards for LDVs and LDTs such as US Tier 2 and EURO V [6]. Advanced DPF technology capable of complete elimination (+99%) of fine particulates with their diameters less than 100 nm has been reported [50] and this is of particular interest in future diesel applications because major concern over PM emissions is now moving on the number of nano-sized particulates from the total mass emitted. The state-of-the-art wall-flow monolith type surface filters, being used commonly in commercial diesel vehicle applications since the first introduction by Corning Inc. [50a], such as NO,aided CRT (Johnson Matthey), DPX (Engelhard), MINE-X Sootfilter (DCL), DuraTrap (Corning), SMF-CRT (HJS), SXS-CX (CEP) and DPNR (Toyota) give us PM trapping efficiencies greater than 95% based on the particulate number, depending on application conditions and systems combination. CDPF-based PM emission control strategies will be continued by all car manufacturers to meet the future Tier 2 standards for diesel vehicles, but NO, emissions may be reduced by using either a serial combination of a CDPF with a deNO_x catalyst or single-step deNO_x catalyst-coated DPF processes as in the case of the DPNR system (redesigned as "D-CAT" package from 2004) which consists of an NSR-washcoated DPF following a DOC and was first fitted to Toyota CRDDI engineequipped Avensis sold in the United Kingdom and Germany [51,52].

Fuel-borne catalysts (FBC), such as Pt- Ce-, Fe-, Cu-, Li- and Na-based fuel additives, have been investigated to incorporate catalytically-active materials directly into the soot particles being produced during the internal combustion process [53-55], and such FBCaided (C)DPF systems can significantly reduce the burn-off temperatures of diesel particulates from 600-650 to 250 °C or less, thereby facilitating the regeneration of the DPFs at much lower temperatures. Some FBCs have been already introduced onto the automotive market, representatively Pt- (Clean Diesel Technologies), Fe-(3M), Ce- (Rhodia, Millennium Chemicals) and Cu-based (Engine Control Systems, Lubrizol) FBCs. All these approaches to diesel particulate emissions have some drawbacks to be resolved in the near future, as noted in Table 8; therefore, an effort will be continued to develop more advanced technology to control particulate emissions from modern diesel vehicles. Consequently, more advanced (C)DPF systems with an FBC-assisted passive regeneration, as the complicated system of PSA Peugeot-Citroen [56], are believed to be a solution to particulates emissions from diesel LDVs and LDTs, based on space requirements, cost, relative simplicity, technological status and future emission legislations.

4-2. Emerging - but with Many Challenges - Catalytic Emission Control Technologies

Extensive studies are underway to develop advanced aftertreatment systems for controlling exhaust emissions from gasoline and diesel engine-equipped vehicles, thereby meeting the future Tier 2 standards of the United States and the EURO ones of EU. A variety of approaches, such as lean NO_x catalysis (LNC), selective catalytic reduction with urea (urea-SCR) and hydrocarbons (HC-SCR) and plasma-assisted catalysis (PAC), have been proposed for the aftertreatment of principal pollutants, i.e., unburned and/or partially burned HCs, CO and NO_x, from advanced engine vehicles [23]. All these catalyst-based emission control technologies may be specific and limited in engine applications, as noted in Table 8, and recent studies and major challenges of each technology will be covered below.

4-2-1. HC-SCR Technology

The HC-SCR approach is widely recognized to be a potential technology for engine-out NO_x emission controls of advanced internal combustion engines. Since the deNO_x technology was successfully established with Cu-zeolites in the presence of excess oxygen [57,58], this has received great attention as a promising NO_x emission control for oxygen-rich mobile sources and because un(partially)burned HCs and CO present in the exhaust stream of the automotives can be simultaneously removed upon the catalytic NO_x reduction. There have been intensive investigations for a huge number of catalysts that can catalyze selectively the reduction of NO_x by HCs even in the presence of excess oxygen, and based on numerous earlier works, the effect of SO₂ on NO removal activity was moderate, whereas H₂O resulted in serious catalyst deactivation even with small amounts [15].

Some engineering advantages can be achieved by using HC-SCR processes to remove NO_x from those engines. The first of such ad-

Current and future US Tier 2 vehicles program and catalytic emission control technologies to meet the future Tier 2 standards 219

		Engin	e				
Catalytic technology ^a	Gase	oline		- Diesel	Requirements and limitations		
	Conventional	LB	GDI	- Diesei			
HC-SCR	+	+	+	_	Substantial use of HCs as reductants		
					 Temperatures greater than 350 °C 		
					• No way of PM reduction		
					 Post injection with fuel penalty 		
Urea-SCR ^b	_	_	_	-	• Use of urea solutions as a reductant		
					• Insufficient space to install the infrastructure for urea injection		
					• NH ₃ slip during load changes		
					Large catalyst volume		
					• Frequent refilling of urea solution		
Passive LNC	_	_	_	+	Low catalytic efficiency		
					• Production of N ₂ O with significant amounts		
					• Weak sulfur tolerance		
					• High thermal stability		
PAC		_	_	_	• Substantial use of HCs as reductants		
					 Selective activation of HCs to oxygenated HCs 		
					• On-board plasma generation system		
					• Production of toxic chemicals and radicals		
					• Fuel economy penalty		
					• Weak durability of plasma devices		

Table 8. A potential of catalyst-based em	ission control technologi	ies for light-duty vehicles	s and trucks and medium	-duty passenger vehicles
				· · · · · · · · · · · · · · · · · · ·

Note. The signs + and - represent the respective high and low possibilities in vehicle applications.

^{*a*}A systematic combination of a technology with either another one or the proven solutions in Table 7 would give a greater potential in vehicle applications.

^bCommercialized for heavy-duty trucks and buses.

vantages no longer requires external reductants unlike urea-SCR applications. Not only can raw fuels appropriate for reducing NO_x be directly supplied into the engine exhaust stream using post-injection technique which may be available particularly for modern diesel vehicles with Common Rail injection systems which have been first developed by Daimler-Benz and Bosch in 1997 [59], but they are also added to the cylinder in a way of secondary injection for yield-ing lighter HCs which tend to have performance benefits in deNO_x reaction over raw fuels injected over or in the front of the catalyst bed. Another one is on-board application without any installation of additional infrastructure, unlike urea-SCR processes for heavy-duty diesel NO_x emission controls under LB conditions.

Regardless, there are some challenges in commercial applications of HC-SCR catalysts to deNO_x controls, including somewhat low catalytic activity, poor hydrothermal stability and very weak tolerance to H₂O vapor present in the LB engine exhaust stream [26, 60,61], although excellent water tolerance and hydrothermal durability during deNO_x reaction with HCs have been documented for a Fe-MFI and Co-BEA catalyst [62-65]. The most urgent challenge in commercializing HC-SCR technology as aftertreatment systems for vehicle applications is to explore the diverse role of H₂O in catalyzing the selective NO_x reduction with HCs. Consequently, this SCR technology would be one of the most promising solutions to attain future legislated NO_x emission limits, and a variety of the state-of-the-art HC-SCR processes have been extensively reviewed [15]. The potential use of Fe-zeolites for deNO_x SCR reaction will be dealt with in another program of this study. 4-2-2. "Passive" LNC Technology

The LNC approach was motivated to lower NO_x from LB gasoline and diesel vehicles under lean conditions, for which not only would unburned HCs, present in the exhaust stream at concentration levels of 50-1,300 ppm [17], be used for selective reducing agents, normally known as "passive" LNC, but additional HCs could be also introduced into either the cylinder via secondary fuel injection or the exhaust stream via direct fuel injection to enhance deNO_x performances of lean NO, catalysts, generally called "active" LNC that is commonly dubbed as "HC-SCR" to distinguish it from the former deNO_x catalysis. Supported precious metals, such as Pt, Rh and Pd, allow the selective NO, reduction at low temperatures, and among these passive LNC catalysts supported Pt samples are particularly active at temperatures below 250 °C. They are shown to have stable activity and hydrothermal durability even under realistic conditions [66,67]; therefore, this LNC technology can be utilized for removing NO_x from advanced Common Rail diesel direct injection (CRDDI) engines, based on the active temperature region, and such CRDDI vehicles readily allow subsequent use of on-board diesel fuel as a reductant.

The LNC technology is still confronted with future challenges to be resolved: relatively low deNO_x efficiency, by 50% or less, because of small amounts of engine-out HCs, large amounts of N₂O production which is known to be one of the greenhouse gases, and very narrow operating window (\leq 30 °C). Supported Ag systems are much more preferable to the supported precious metals because of no N₂O formation [68]. These catalysts require higher temperatures (300-500 °C), depending mainly on reductants used, for the maximum NO_x reduction in the presence of HCs than common exhaust ones of diesel-fueled passenger vehicles. Modern diesel vehicles with the FTP 75 cycle gave exhaust temperatures ranging from 130 to 330 °C with a typical average one of 250 °C [69], and the respective temperature ranges of 80-180 °C with a peak exhaust temperature of 230 °C and 180-280 °C with a maximum temperature of 440 °C were exhibited during the Economic Commission for Europe (ECE) cycle and extra-urban driving cycle (EUDC) tests for the diesels [17,70]. The maximum NO_x reduction temperatures can be shifted towards much lower ones when substantially using H₂ under simulated LB conditions [71].

4-2-3. Urea-SCR Technology

The urea-SCR deNO_x catalysis has been extensively studied with a variety of catalysts for the last decade and this SCR technology is a well-established deNO₂ solution to stationary diesel combustion sources [72,73]. The deNO_x technology is basically governed by the same principle as NH₃-SCR reaction over catalysts because of the production of NH₃ via urea decomposition under appropriate thermal conditions. The urea-SCR system is currently employed as an NOx removal technology for heavy-duty diesel trucks and buses in EU. It is comprised basically of a catalyst, a storage tank for urea solution, and a urea feed system [74] but the latter two components must be much more concise and controllable for vehicle applications. The controlled injection of urea as the reducing agent into the hot engine-out stream produces NH₃ which reacts with NO₂ on the surface of the catalyst, typically V_2O_5 -WO₃ (or MoO₃)/TiO₂. The standard NH₃-SCR catalysts are commonly used to lower NO₂ emissions from automotive diesel engines, but other SCR catalysts, such as Cu- and Fe-zeolites, have recently been investigated for diesel vehicle applications [75-77]. Although the mobile SCR system gives very high deNO_x efficiency, it has many differences in application environments, such as load and engine-speed variations and precise control of urea feed, compared to stationary urea-SCR processes.

There are a few limitations to using this technology for abating automobile engine-out NO_x emissions, as stated in Table 8. The first one is insufficient space of at least LDV and LLDT vehicles to install additional infrastructures for supplying the urea solution [23,78], although this SCR technology assists the manufacturers of heavyduty diesel trucks and buses in complying with the future stringent exhaust emissions, like commercialized SINO, (Siemens) and VHRO (MAN) systems. Secondly, a very precise electronic control unit is required to prevent or minimize NH3 slip, which must be about 10 ppm or less for practical vehicle applications, during load changes, when the urea solution is sprayed into the engine exhaust stream for on-board NH₃ production [79]. Thirdly, the urea-SCR-based NO_x reduction system needs catalyst volumes much larger than the engine cylinder volume, depending on the future legislations. Finally, the urea solution commonly used for heavy-duty applications is a mixture of ~35% urea in water and the remainder of the solution does not add to deNO_x performances, thereby requiring frequent refilling.

4-2-4. PAC Technology

The PAC systems utilize the plasma to oxidize NO into NO_2 which

then reacts with appropriate reductants over $deNO_x$ SCR catalysts; however, these PACs still possess challenging tasks (Table 8) to resolve the formation of toxic byproducts and the catalyst deactivation due to the deposition of the organic products during the course of the reaction as well as to prepare cost-effective and durable onboard plasma devices [23,80]. Consequently, these technologies are not yet adequate for commercial applications to even advanced diesel and gasoline engine vehicles.

4-2-5. New Combustion Technology

Recently, homogeneous charge compression ignition (HCCI) engines have received great attention because of engine efficiency as high as advanced diesel engines and low CO_2 emissions, and give quite low NO_x (<20 ppm) and PM (under detection limits) emissions but very high CO and HCs emissions [81]. Therefore, a new catalytic emission control technology should be developed to reduce such high CO and HCs emissions from the HCCI engines, although the NO_x and PM emission levels are quite lower than that in complying with the Tier 2 program, and CO_x -based catalysts would be a good candidate for HCCI engine applications [82]. If this new combustion technology becomes more available in the near future, after-treatment may become much less important.

5. Concluding Remarks

The new Tier 2 program defining very stringent emission standards for LDVs, LDTs and MDPVs was begun from the 2004 model year and will be fully phased in until 2009, depending on the vehicle categories. It is of particular interest in significantly lowering NO_x and PM emissions. The principal rule for successful implementation of these regulations to all the Tier 2 vehicles is the use of the same standards if these vehicles are included in the same weight rating category, irrespective of fuel and engine types being used. Not only manufacturers of the vehicles and their importers in the United States but also all exporters of the vehicles to US should ultimately meet the new Tier 2 standards. However, some flexibilities such as interim standards and NO_x credits are provided for all manufacturers, importers and exporters during the phase-in years. Although a systematic approach combining advanced engine and fuel injection technology, advanced emission control technology and fuel quality improvement is required to maximize an effectiveness in an effort to reduce the emissions from new vehicles, the advanced catalyst-based control technologies are expected to be an ultimate solution to achieve large reductions in automotive emissions from Tier 2 diesel and gasoline vehicles.

ACKNOWLEDGMENT

The author thanks a partial grant-in-aid of Daegu University for this research.

REFERENCES

- 1. US EPA, Control of air pollution from new motor vehicles: Tier 2 motor vehicle emissions standards and gasoline sulfur control requirements, Vol. 65, No. 28, Rules and Regulations, Federal Register (2000a).
- 2. European Communities, *Off. J. Eur. Commun. L* 350, **41**, 1 (1998a).
- 3. European Communities, Off. J. Eur. Commun. L 350, 41, 58

Current and future US Tier 2 vehicles program and catalytic emission control technologies to meet the future Tier 2 standards 221

(1998b).

- Commission of the European Communities (CEC), Communication from the commission - A review of the Auto-Oil II Programme, COM(2000) 626 Final, Brussels (2000).
- European Union, (a) Off. J. Eur. Union L 291, 45, 20 (2002); (b) Off. J. Eur. Union L 76, 46, 10 (2003).
- 6. US EPA, *Control of emissions from new and in-use highway vehicles and engines*, Code of Federal Regulations (CFR), Title 40, Chapter 1, Subchapter C, Part 86, Federal Register (2000b).
- California EPA, Motor vehicle pollution control devices, California Code of Regulations (CCR), Title 13, Chapter 1, Article 2, California Office of Administrative (2003).
- 8. Commission of the European Communities (CEC), *Commission staff working paper Fiscal incentives for motor vehicles in advance of EURO 5*, COM(2005) 43, Brussels (2005a).
- 9. Commission of the European Communities (CEC), *Proposal for a regulation of the European Parliament and of the Council on type approval of motor vehicles with respect to emissions and on access to vehicle repair information, amending Directive 72/306/EEC and Directive ../..EC*, COM(2005) 683 Final, Brussels (2005b).
- European Commission, Preliminary draft proposal for a regulation of the European Parliament and of the Council relating to emissions of atmospheric pollutants from motor vehicles (EURO 5), Office for Official Publications of the European Union, Brussels (2005).
- J. Leyrer, E. S. Lox and W. Strehlau, *Design aspects of lean NO_x catalysts for gasoline and diesel applications*, *SAE* 952495 (1995).
- 12. K. C. Taylor, Catal. Sic. Technol., 5, 119 (1984).
- 13. A. Fritz and V. Pitchon, Appl. Catal. B, 13, 1 (1997).
- T. J. Truex, R. A. Searles and D. C. Sun, *Platimum Metals Rev.*, 36, 2 (1992).
- M. H. Kim and I. S. Nam, New opportunity for HC-SCR technology to control NO_x emissions from advanced internal combustion engines, Catalysis (Vol. 18), Spivey, J. J., ed., The Royal Society of Chemistry, Cambridge, 2005, p. 116 and there-in references.
- A. Faiz, C. S. Weaver and M. P. Walsh, *Air pollution from motor vehicles: Standards and technologies for controlling emissions*, Office of the Publisher, The World Bank, Washington, D.C. (1996).
- J. Kaspar, P. Fornasiero and N. Hickey, *Catal. Today*, **77**, 419 (2003).
- A. Konig, G Herding, B. Hupfeld, T. Richter and Weidmann, *Topics Catal.*, 16/17, 23 (2001).
- N. Miyoshi, S. Matsumoto, K. Katoh, T. Tanaka, J. Harada, N. Takahashi, K. Yokota, M. Sugiura and K. Kasahara, *Development* of new concept three-way catalyst for automotive learn burn engines, SAE 950809 (1995).
- 20. F. Zhao, M. C. Lai and D. L. Harrington, *Prog. Energy Combust.* Sci., 25, 437 (1999).
- 21. H. Cheng, G Chen, S. Wang, D. Wu, Y. Zhang and H. Li, *Korean J. Chem. Eng.*, **21**, 595 (2004).
- 22. D. Fino, P. Fino, G. Saracco and V. Specchia, *Korean J. Chem. Eng.*, **20**, 445 (2003a).
- 23. T. V. Johnson, *Diesel emission control in review*, *SAE* 2001-01-0184 (2001).
- R. Aneja, B. Bolton, A. B. Oladipo, Z. Pavlova-MacKinnon and A. Radwan, Advanced diesel engine and aftertreatment technology

development for Tier 2 emissions, in Proceeding of The 9th Diesel Engine Emissions Reduction Conference, Session 8, Newport, RI, Aug. 24-28, p. 1 (2003).

- 25. Manufacturers of Emission Controls Association (MECA), *Tier2/LEV II emission control technologies for light-duty gasoline vehicles*, MECA, Washington, DC (2003).
- T. Kreuzer, E. S. Lox, D. Lindner and J. Leyrer, *Catal. Today*, 29, 17 (1996) and there-in references.
- 27. M. Iwamoto and N. Mizuno, J. Auto. Eng., 207, 23 (1993).
- M. Petersson, T. Holma, B. Andersson, E. Jobson and A. Palmqvist, J. Catal., 235, 114 (2005).
- 29. N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. I. Matsumoto, T. Tanizawa, T. Tanaka, S. S. Tateishi and K. Kasahara, *Catal. Today*, **27**, 63 (1996).
- L. J. Gill, P. G. Blakeman, M. V. Twigg and A. P. Walker, *Topics Catal.*, 28, 157 (2004).
- A. Amberntsson, M. Skoglundh, S. Ljungstrom and E. Fridell, J. Catal., 217, 253 (2003).
- G. Fornasari, F. Trifiro, A. Vaccari, F. Prinetto, G Ghiotti and G Centi, *Catal. Today*, **75**, 421 (2002).
- 33. R. Mital, J. Li, S. C. Huang, B. J. Stroia, R. C. Yu, J. A. Anderson and K. Howden, *Diesel exhaust emissions control for light duty vehicles*, *SAE* 2003-01-0041 (2003).
- 34. Y. Tamura, S. Kikuchi, K. Okada, K. Koga, T. Dogahara, O. Nakayama and H. Ando, *Development of advanced emission control technologies for gasoline direct injection*, SAE 2001-01-0254 (2001).
- 35. J. R. Asik, D. A. Dobson and G M. Meyer, Suppression of sulfide emission during lean NO_x trap desulfation, SAE 2001-01-1299 (2001).
- A. Sassi, R. Noirot, C. Rigaudeau and G Belot, *Topics Catal.*, 30/31, 267 (2004).
- 37. F. C. Galisteo, R. Mariscal, M. L. Granados, J. L. G Fierro, R. A. Daley and J. A. Anderson, *Appl. Catal. B*, **59**, 227 (2005).
- U. D. Standt and A. Konig, *Performance of zeolite-based diesel* catalysts, SAE 950749 (1995).
- 39. J. A. Martens, A. Cauvel, F. Jayat, S. Vergne and E. Jobson, *Appl. Catal. B*, **29**, 299 (2001).
- B. A. A. L. van Setten, M. Makkee and J. A. Moulijn, *Catal. Rev.*, 43, 489 (2001).
- 41. K. Hayashi, Y. Ogura, K. Kobashi, H. Sami and A. Fukami, *Regeneration capability of wall-flow monolith diesel particulate filter with electric heater*, SAE 900603 (1990).
- H. Suto, T. Mikami, H. Hirai and M. Hori, *Evaluation of diesel particulate filter systems for city buses*, SAE 910334 (1991).
- 43. H. Luders, P. Stommel and R. Backe, *Applications for the regeneration of diesel particulate traps by combining different regeneration systems*, *SAE* 970470 (1997).
- 44. K. N. Pattas and A. M. Stamatelos, *A trap oxidizer for the turbocharged diesel engine*, *SAE* 910137 (1991).
- 45. G. Voss and G Rice, *Catalyzed diesel soot filters*, *SAE* 950156 (1995).
- G. Saracco, N. Russo, M. Ambrogio, C. Badini and V. Specchia, *Catal. Today*, 33, 60 (2000).
- 47. S. Sasaki, *Device for purifying the exhaust gas of an internal combustion engine*, US Patent 6490857 (2002).

- 48. D. Fino, N. Russo, C. Badini, G Saracco and V. Specchia, *AIChE J.*, **49**, 2173 (2003b).
- 49. J. Adler, Int. J. Appl. Ceramic Technol., 2, 429 (2005).
- A. Mayer, J. Czerwinski, U. Matter, M. Wyser, P. Scheidegger, D. Kieser and M. Weidhofer, VERT: Diesel nano-particulate emissions Properties and reduction strategies, SAE 980539 (1998).
- 50a. J. S. Howitt and M. R. Montierth, *Cellular ceramic diesel particulate filter*, *SAE* 810114 (1981).
- 51. J. McDonald and B. Bunker, *Testing of the Toyota Avensis* DPNR at the U.S. EPA-NVFEL, SAE 2002-01-2877 (2002).
- 52. J. McDonald, Progress in the development of Tier 2 light-duty diesel vehicles, SAE 2004-01-1791 (2004).
- B. Krutzsch and G Wenninger, Effect of sodium and lithiumbased fuel additives on regeneration efficiency of diesel particulate filters, SAE 922188 (1992).
- 54. J. Lahaya, S. Boehm and P. Ehrburger, *Springer Ser. Chem. Phys.*, **59**, 307 (1994).
- 55. P. Zelenka, W. Reczek, W. Mustel and P. Rouveirolles, *Towards securing the particulate trap regeneration: A system combining a sintered metal filter and cerium fuel additive*, SAE 982598 (1998).
- 56. O. Salvat, P. Marez and G. Belot, "Passenger car serial application of a particulate filter system on a Common Rail direct injection diesel engine," SAE 2000-01-0473 (2000).
- W. Held, A. Konig, T. Richter and L. Puppe, "Catalytic NO_x reduction in net oxidizing exhaust gas," *SAE* 900496 (1990).
- M. Iwamoto, *Decomposition of NO on copper ion-exchanged zeolite catalysts*, in Proceedings of Meeting on Catalytic Technology for Removal of Nitrogen Monoxide, Tokyo, Japan, Jan., p. 17 (1990).
- 59. A. Peters, H. J. Langer, B. Jokl, W. Muller, H. Klein and K. Ostgathe, *Catalytic NO_x reduction on a passenger car diesel common rail engine*, *SAE* 980191 (1998).
- 60. M. Shelef, Chem. Rev., 95, 209 (1995).
- S. Y. Chung, S.-H. Oh, M. H. Kim, I. S. Nam and Y. G Kim, *Catal. Today*, 54, 521 (1999).
- T. Tabata, M. Kokitsu, H. Ohtsuka, O. Okada, L. M. F. Sabatino, and G Bellussi, *Catal. Today*, 27, 91 (1996).
- 63. X. Feng and W. K. Hall, J. Catal., 166, 368 (1997).
- 64. H. Y. Chen and W. M. H. Sachtler, Catal. Today, 42, 73 (1998).
- 65. K. Krishna and M. Makkee, Catal. Today, 114, 23 (2006).
- 66. R. Burch, P. J. Millington and A. P. Walker, *Appl. Catal. B*, **4**, 65 (1994).
- 67. J. M. Garcia-Cortes, M. J. Illan-Gomez, A. L. Solano and C. Sali-

nas-Martinez de Lecea, Appl. Catal. B, 25, 39 (2000).

- X. She and M. Flytzani-Stephanopoulos, J. Catal., 237, 79 (2006) and there-in references.
- R. Blint, Discovery of new NO_x reduction catalysts for CIDI (diesel) engines using combinatorial techniques, in Proceedings of The First AccelrysWorld Conference, San Diego, CA, Feb. 23-26, p. 123 (2003).
- 70. K. M. Adams, J. V. Cavataio and R. H. Hammerle, *Appl. Catal. B*, 10, 157 (1996).
- S. Satokawa, J. Shibata, K. I. Shimizu, A. Satsuma and T. Hattori, *Appl. Catal. B*, **42**, 179 (2003).
- 72. M. Koebel, M. Elsener and T. Marti, *Combust. Sci. Tech.*, **121**, 85 (1996).
- M. Koebel, M. Elsener and M. Kleemann, *Catal. Today*, **59**, 335 (2000).
- 74. C. J. Brodrick, M. Farsh-chi, H. A. Dwyer, D. Sperling, S. W. Gouse, W. Doelling, J. Hoelzer and M. Jackson, *Urea-SCR system demonstration and evaluation for heavy-duty diesel trucks*, SAE 1999-01-3722 (1999).
- 75. L. Xu, R. W. McCabe and R. H. Hammerle, *Appl. Catal. B*, **39**, 51 (2002).
- 76. J. H. Park, H. J. Park, J. H. Baik, I. S. Nam, C. H. Shin, J. H. Lee, B. K. Cho and S. H. Oh, *J. Catal.*, **240**, 47 (2006).
- 77. K. Krocher, M. Devadas, M. Elsener, A. Wokaun, N. Soger, M. Pfeifer, Y. Demel and L. Mussmann, *Appl. Catal. B*, 66, 208 (2006).
- 78. P. G. Blakeman, G R. Chandler, G.A. John and A. J. J. Wilkins, Investigation into NO_x aftertreatment with urea SCR for light-duty diesel vehicles, SAE 2001-01-3624 (2001).
- 79. M. Koebel, G. Madia and M. Elsener, *Recent advances in the development of urea-SCR for automotive applications*, *SAE* 2001-01-3625 (2001).
- J. Hoard, Plasma-catalyst for diesel exhaust treatment: Current state of the art, SAE 2001-01-0185 (2001).
- K. Epping, S. Aceves, R. Bechtold and J. Dec, *The potential of HCCI combustion for high efficiency and low emissions*, *SAE* 2002-01-1923 (2002).
- 82. M. H. Kim, S. H. Chang and J. S. Kim, CoO_x/TiO₂ catalysts for controlling engine-out emissions from HCCI engines - Room-temperature CO oxidation, in Proceedings of the Korean Environmental Sciences Society Conference, Seoul, May 20-21, p. 218 (2005).