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Volatile Organic Compound Emissions During Cold-Starts of Motorcycles

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Today's catalytic converters do not reach their minimum operating temperatures until at least 120 seconds after cold-start of a motorcycle and during the warm-up period, 40-80% of total air pollutants are generally found in the emissions (Chan and Nien 1995; Boeham and Niksa 1996; Nichols and Weisel 1996; Velasco et al. 1997; Winebrake and Deaton 1999). Among these air pollutants, volatile organic compounds (VOCs), present a threat to health that is related to the amount of pollution, duration of exposure, and total dose (Kuo et al. 2000). A number of VOCs have been identified as important cancer risk factors in the environment. The VOC vapors might be absorbed rapidly by lungs and taken up readily by the gastrointestinal tract, but poorly through skin (Chang et al. 2002). The effects of VOCs on the central nerve system are related to dizziness, weakness, and confusion.

Some of VOCs are also precursors of photochemical smog and tropospheric ozone (Clarke and Ko 1996; Siegl et al. 1999; Leong et al. 2002). Activated carbons are commonly used to remove VOCs from air or water, but they require a relatively complex regeneration or disposal procedure.

Since 1982, malignant neoplasms have become the leading causes in death in Taiwan (Chen et al. 1996). Of which lung cancer has been considered as one of the major cancer deaths. Cr, Ni, Cd, As, and Be, found in the pleural fluid of patients with malignancy, are suspected causing lung cancer (Chen et al. 1996). Increasing exposures of Pb has been noted in the past decades simply due to the use of leaded gasoline in the automobiles. However, there is little evidence for the association of Pb with the risk of lung cancer (Gao 1996). Nevertheless the active metals such as Pt, Pd, Rh and Ce that are generally found in the catalytic converters may cause the adverse health effects. The major objectives of this work were to study VOC emissions during the cold-start of motorcycles and the chemistry of Rh, Pd, and CeO_2 on catalytic surfaces.

MATERIALS AND METHODS

Representative exhaust VOC emission measurements for the first 120 seconds were

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conducted with motorcycles (Kwang Yang Motor Co.) of different capacities (90 and 125 cc), model years (1991-2001), and fuel distribution systems. Exhaust samples were collected through a heated line to a dilution tube and into a Tedlar bag and analyzed within two hours of collection by capillary gas chromatography (Hewlett Packard HP5890 Series II) which was equipped with flame ionization and electron capture detectors. A HP-624 column (30 m × 0.53 mm i.d.) was used for separation of light aromatics. Chemical structure of Rh, Pd and Ce on catalytic surfaces of the catalytic converters was also studied by X-ray photoelectron spectroscopy (Fison ESCA 210 (VG Scientific) spectrometer with a Mg Kα X-ray (1253.6 eV) excitation source). The standard deviation of the binding energy measurements was ±0.3 eV.

RESULTS AND DISCUSSION

Motorcycles generally contribute about 25% of total VOC emissions in Taiwan. Aromatic VOCs (such as benzene, toluene, ethylbenzene, and xylenes) from cold-start emissions of motorcycles were separated, identified, and quantified. Species up to and including xylenes represent primarily products of partial combustion. Table 1 provides a list of the aromatic VOCs emitted from representative light-duty gasoline motorcycles at the cold-start stage (first 120 seconds). Toluene and xylenes are the most abundant aromatic VOCs in the motorcycle exhaust emissions. It should be noted that if compared with the 4-stroke unleaded gasoline automobile, the VOC emission from 2-stroke old motorcycles are relatively higher by at least 12 times. The exhaust VOC emission from a current technology 4-stroke motorcycle was similar to that from a gasoline-fueled automobile. The old 2-stroke motorcycle with high mileages of about 6800 km emitted more benzene and toluene than the new one during the cold-start tests.

Table 1. Major VOC concentrations (ppm) in cold-start emissions.

	2-stroke	2-stroke	4-stroke	4-stroke
Engine Volume (cc)	90	90	125	2,000
Fuel System	Carburetor	Carburetor	Carburetor	EFI
Mileage (km)	<1 (new)	6,800	<1 (new)	100,000 .
Benzene	31	51	1.0	0.9
Toluene	59	181	2.1	4.1
Ethylbenzene	29	30	1.5	2.4
Xylenes	101	117	2.7	6.0

In general, the catalytic converter of a motorcycle is used with its electronic carburetor system. In the VOC destruction efficiency tests, the motorcycle engines were conducted a warm start and lasted 10 minutes to reach its normal operating temperatures. Table 2 shows that the average VOC destruction efficiencies of the catalytic converters are found to vary significantly between new and old 2-stroke motorcycles. It is also noticed that benzene has a relatively low destruction efficiency in the exhaust gas, especially for the old and high-mileage motorcycles.

Table 2. VOC destruction efficiency after a warm start.

	2-stroke Motorcycle	2-stroke Motorcycle
Engine Volume (mL)	90	90
Fuel System	Carburetor	Carburetor
Mileage (km)	<1	6,800
Benzene	84%	75%
Toluene	90%	90%
Ethylbenzene	91%	88%
Xylenes	90%	85%

The catalytic converter is generally the major factor determining the destruction efficiency of VOCs in the exhaust gas (Dasch and Williams, 1991). The reduction of the catalytic activity in the converter may be due to at least two possibilities: thermal shock and overheating of the catalyst. By X-ray photoelectron spectroscopy, a high degree of oxidation of Pd (such as Pd(IV)) as well as the loss of Rh on the surfaces of the converter catalyst was observed (see Table 3). Note that the concentration of CeO_2 was also decreased on the surfaces of the catalyst.

Table 3. Oxidation states of catalytic active species on the converter catalysts of 90 cc new and old (mileage=6800 km) 2-stroke motorcycles studied by X-ray photoelectron spectroscopy.

Element	New Converter	Old Converter (Front Portion)	Old Converter (Rear Portion)
Ce	Ce(IV)	Ce(IV)	Ce(IV)
Pd	Pd(II)	Pd(IV)	Pd(II), Pd(IV)
Rh	Rh(II)	-	-

In summary, 29-117 ppm of aromatic VOCs (benzene, toluene, ethylbenzene, and xylenes) were emitted during the cold-start of 2-stroke, 90 cc motorcycles. Soon after the converter catalyst was activated, the destruction efficiencies of those VOCs were increased to 75-91%. A reduction in the VOC destruction efficiencies for the old and high-mileage 2-stroke motorcycles was found, probably due to the deactivation (the loss of Rh also and CeO_2 on the surface) of the converter catalysts.

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