



# Photocatalytic synthesis of oxygenated hydrocarbons from diesel fuel for mobile deNOx application

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## ABSTRACT

Photocatalytic partial oxidation of dodecane has been studied as a model reaction of diesel fuel conversion to oxygenated hydrocarbons (OHCs) as an effective nitrogen oxide (NOx) reductant in selective catalytic reduction (SCR) systems. Thus, TiO<sub>2</sub>-based photocatalysts produced OHCs composed mainly of C<sub>1</sub>-C<sub>6</sub> aldehydes under UV irradiation, and TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxide photocatalysts showed higher selectivity and yield to OHCs than pristine TiO<sub>2</sub> by diluting contiguous Ti sites and suppressing complete oxidation to CO<sub>2</sub>. The effects of reaction variables were studied in detail. A novel scheme of NOx after-treatment system for diesel engine exhaust line was proposed involving the new photocatalytic reaction, where on-board photocatalytic partial oxidation of a small amount of diesel fuel produced OHCs that were supplied to the deNOx system as NOx reductant. Although further improvement is needed in the selectivity for OHCs as well as the system operability, the proposed scheme could be a more environment-friendly option than the reduction by urea, currently considered the most promising technology.

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## 1. Introduction

Diesel engine vehicles are the major source of harmful nitrogen oxides (NOx) emission on the road. Especially NOx emission from heavy duty diesel vehicles accounts for almost 30% of total emission despite the number of vehicles is limited to only 2% in California, USA [1]. The fact that all diesel cars must satisfy Bin 5 (NOx ≤ 0.07 g/mi) [2] and Euro VI (NOx ≤ 80 mg/km) [3] compliance to be sold in the USA and Europe markets drives diesel car manufactures to develop more efficient NOx after-treatment technology than the past [4].

There have been a huge number of reports concerning lean NOx selective catalytic reduction (SCR) technology categorized by reducing agent such as urea (or ammonia) [5–7], hydrocarbon (HC) [8], oxygenated hydrocarbons (OHCs) [2,9–12], and hydrogen [13]. These reports show highly practical potential of lean NOx SCR technology for application to the exhaust line of real diesel engine vehicle fleet with more than 50% NOx conversion at relatively low temperatures of 200–250 °C, similar to diesel exhaust temperatures under lean conditions. These technologies are proposed on the assumption that those highly effective reductants such as NH<sub>3</sub>, HCs (short and long chain alkanes and

alkenes), and OHCs (alcohols and aldehydes) are sufficiently produced somehow and delivered to the exhaust gas after-treatment convertor filled with a NOx reducing catalyst. In reality though, the reducing gases in the engine exhaust stream are insufficient; NH<sub>3</sub> (none), HCs-OHCs (0–600 ppm carbon, varied by driving condition) [14,15] and H<sub>2</sub> (almost none). Thus, additional supply of reducing agents to the NOx SCR convertor is necessary for practical application. Currently, urea is considered the most promising reductant because it generates NH<sub>3</sub>, the strong reductant of NOx at low temperatures. Yet, ammonia is toxic and carrying a urea tank on board is neither convenient nor safe. Also conversion of urea into ammonia does not reach 100%. Diesel fuel itself can be directly used as a convenient reductant, but it is not reactive enough at the diesel exhaust temperatures under lean conditions [16,17].

As an alternative technology to supply NOx reductants on board, herein we report photocatalytic partial oxidation of dodecane, a model compound of diesel fuel, into OHCs by using TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxide photocatalysts in a simple continuous flow reaction system that could be installed in the vehicle (Scheme 1 and Fig. S1 of Supporting information, SI). The performance of the photocatalytic reactions that we report here, especially selectivity to OHCs, is still rather low for practical applications. Further, installation of the photocatalytic reactor with a UV lamp inside the vehicle may not be convenient or energy-efficient. But if further improvement is achieved in the reaction selectivity and

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the system operability, it could be more environment-friendly than carrying the urea tank on board. The system produces OHCs below 100 °C, which are efficient NO<sub>x</sub> reductants and safer than NH<sub>3</sub>. By using a very small amount of diesel fuel, the system does not generate a significant fuel penalty (e.g., 6 mol of acetaldehyde can be produced from 1 mol of dodecane). In a scientific point of view, the number of study regarding photocatalytic partial oxidation of organic compound is rather scarce than that of photocatalytic mineralization or total oxidation process [18,19]. To the best of our knowledge, this work is the first experimental research of photocatalytic partial oxidation of a diesel-like molecule at low temperatures (<100 °C) without water.

## 2. Experimental

### 2.1. Catalyst synthesis

The TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxide was synthesized under typical hydrothermal conditions. (Better termed “solvothermal” with almost non-aqueous solutions accompanied by heating in a Teflon autoclave reactor.) Thus, titanium (IV) isopropoxide (TTIP, 97%, Sigma-Aldrich), tetraethyl orthosilicate (TEOS, 98%, Acros Organics), tetrabutyl ammonium hydroxide solution (TBAOH, 1 M in methanol, Sigma-Aldrich), 2-propanol (100%, JT baker) were used without further purification. Mixed oxide of Ti/Si = 0.11 was made as follows: 3 × (TTIP + TEOS) mole of 2-propanol, 0.0334 mol of TEOS, 0.5 × (TTIP + TEOS) mole of TBAOH, 0.00371 mol of TTIP, 3 × (TTIP + TEOS) mole of distilled H<sub>2</sub>O were dropped into the Teflon autoclave bottle in this order. This transparent yellowish solution was hydrolyzed at 170 °C for 15 h followed by filtering with 500 ml of distilled H<sub>2</sub>O. Sample powder was dried overnight at 100 °C and calcined at 500 °C for 10 h. Other samples with different ratios were synthesized in a similar way with different precursor mole ratios. Details of this synthesis procedure are illustrated in Table S1 and Scheme S1 of SI. Commercial TiO<sub>2</sub> in anatase form (98.5%) was obtained from Junsei.

### 2.2. Catalyst characterization

The textural properties such as surface area, total pore volume, pore size distribution, and microporosity of TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxide were determined using N<sub>2</sub> physisorption measurements. The N<sub>2</sub> adsorption-desorption isotherms were obtained at 77 K using a nanoPOROSITY-XQ nanoporosity and surface area analyzer (Mirae-si, Korea). The surface areas were calculated by using the Brunauer-Emmett-Teller equation in a relative pressure range ( $P/P_0$ ) of 0.05–0.20 assuming a cross-sectional area of 0.162 nm<sup>2</sup> for N<sub>2</sub> molecule. The total pore volume and pore size distribution were determined from the amount of N<sub>2</sub> adsorbed at the highest relative pressure of  $P/P_0 = 0.995$ . The pore diameter and pore size distribution plots were determined by applying the Barrett-Joyner-Halen-

da (BJH) model to the desorption isotherm. Microporosity was assessed by adapting *t*-plot method setting 3.5–7.0 Å as a statistical thickness range.

The crystalline phase of the products was determined using X-ray diffractometer (Mac Science Co., M18XHF) with monochromatic Cu K $\alpha$  radiation at 40 kV and 200 mA. UV-Vis DRS were taken by UV-2401PC Shimadzu). The X-ray absorption fine structure (XAFS) measurements were conducted on beam line 7D of Pohang Accelerator Laboratory (PAL) in Korea and beam line 7C of Photon Factory (PF) in Japan. The spectra for K-edges of Ti ( $E_0 = 4966$  eV) were taken in transmission mode at room temperature. The intensity of incident beam was monitored with He-filled IC Spec ionization chamber and that of transmitted beam with N<sub>2</sub>-filled ionization chamber. The obtained data were analyzed with Athena in the IFEFFIT 1.2.9 suite of software programs [20].

Images of HRTEM, EELS, and SAED pattern were taken by HR-STEM-2200FS (JEOL JEM-2200FS with Image Cs-corrector) at National Center for Nanomaterials Technology, Korea. The XPS spectra were obtained with a VG-Scientific ESCALAB 220 IXL spectrometer equipped with a hemispherical electron analyzer and a Mg K $\alpha$  ( $h\nu = 1253.6$  eV) X-ray source. The FTIR analysis was performed with a Perkin Elmer Spectrum 2000 Explore machine. Each sample was made in 30 mg pellet diluted with KBr. The ICP analysis was conducted with ICP AES (Spectro-Vision).

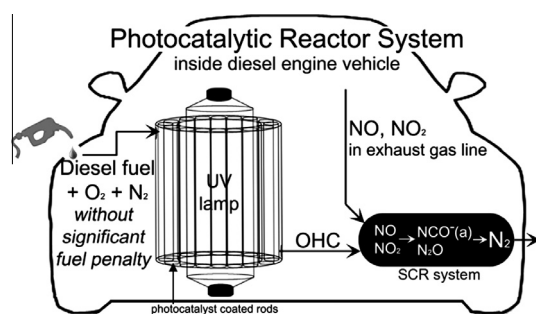
### 2.3. Photocatalytic partial oxidation of dodecane

Photocatalytic reactions were performed in a continuous flow system shown in Fig. S1. The carrier gas (Ar) flew through a dodecane saturator immersed in a constant temperature silicon oil bath. A 450 W Hg lamp (7825-34, Ace Glass) without cutoff filter was used as a UV-Vis source. Light intensity was 0.81 W/cm<sup>2</sup> measured by a photometer (ORIEL 70260 with 70282 head). Tubular quartz glass was used as a cooling jacket and a light window, in which cooling water was circulated. Ethanol solution of photocatalyst powders was sprayed over the glass rod on a 300 °C hot plate for coating. Product compounds were analyzed by an on-line gas chromatograph (HP 6890) equipped with a DB-5 column (Agilent Technology, 125-5532) and 2 auto sampling valves for TCD and FID analysis. The products were identified with a GC (HP 6890)-MS (HP 5973) equipped with a DB-5 ms column (Agilent Technology, 122-5563).

## 3. Results and discussion

### 3.1. Identification of products from photocatalytic partial oxidation of dodecane over TiO<sub>2</sub>

Since photocatalytic partial oxidation of a diesel-like molecule in the anhydrous flow system has never been studied before, we first tried to understand the reaction behavior depending on operating variables. Thus, at the beginning, we used commercial anatase phase TiO<sub>2</sub> (Junsei) as the photocatalyst. Of course, TiO<sub>2</sub> is the best known photocatalyst for total oxidation of organic chemicals to carbon dioxide or pollutants mineralization in various environmental applications [21–23]. Yet, photocatalytic partial oxidation is also possible although examples are rare [24–26]. At first, we performed the photocatalytic reaction with 21% O<sub>2</sub> in Ar to mimic air-like atmosphere at 160 °C using TiO<sub>2</sub> loaded on the quartz beads or rods as a photocatalyst. During the reaction, thermal decomposition of dodecane was not observed at these low temperatures (<160 °C) when light was turned off. We observed production of a large number of oxygenated hydrocarbons (OHCs) from photocatalytic partial oxidation of dodecane. Because of this complicated product profile and since there was no previous reports on the reaction, we conducted a careful product analysis.



**Scheme 1.** A photocatalytic partial oxidation system attached to exhaust line in diesel engine vehicle.

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