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Operando Raman-online FTIR investigation of ceria, vanadia/ceria and gold/ceria catalysts for toluene elimination

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ABSTRACT

Toluene oxidation on three ceria catalysts, CeO_2, VO_x/CeO_2 and Au/CeO_2, was investigated by an *operando* Raman-online FTIR reactor cell. The reactive surface oxygen sites were preferred sites for vanadium and gold deposition. The deposited vanadium existed as V^{5+}, while most of the gold was in Au^+ state and roughly a third of ceria was in the reduced Ce^{3+} state. The Au/CeO_2 and CeO_2 catalysts (T^*_{50} = 260 and 290 °C) were more active and selective toward the complete oxidation of toluene than VO_x/CeO_2 catalyst (T^*_{50} = 370 °C), where T^*_{50} refers to the temperature for 50% of CO_2 yield. The η^2-peroxide $O_2^{2-}{}_{ads}$ was detected on Au/CeO_2 and CeO_2 catalysts, where toluene molecules preferentially adsorbed parallel to the surface *via* π-bonding. Au/CeO_2 gave complete combustion producing mainly CO_2. On the other hand, η^1-superoxide $O_{2\,ads}^-$ was found on VO_x/CeO_2 catalyst and the toluene molecule adsorbed *via* σ-bonding forming carbenium ions on the vanadia Brønsted acid sites. This catalyst produced significant amount of benzaldehyde as partial oxidation byproduct and CO (<25%). The nature of the active sites, configurational adsorption of toluene and the reactive oxygen species play important roles in the catalyst activity and selectivity leading to a large contrast in the catalytic behavior of the CeO_2, VO_x/CeO_2 and Au/CeO_2 catalysts.

1. Introduction

Volatile organic compounds (VOCs) are important indoor air pollutants. Most VOCs are irritants that cause discomfort and psychological stresses to the occupants. Many VOCs can trigger autoimmune response (e.g. asthma, eczema) and airway inflammation causing respiratory distress [1,2], while others such as formaldehyde, benzene and toluene are known or suspected carcinogens [3,4]. Studies have shown that catalytic oxidation is effective in removing airborne VOCs [5] and ceria is one of the most promising catalysts [6]. Ceria has a large capacity for oxygen storage and displays good redox property [7]. Ceria itself is active enough to catalyze the oxidation of hydrocarbons including toluene. The numerous defects in ceria in form of oxygen vacancies or polarons are believed to be responsible for its unique catalytic properties [7–10].

Noble metals supported on ceria are reported to be more active and selective for catalytic oxidation of VOCs [11]. Ousmane and coworkers [12] reported Au/CeO_2 catalyst is more active than gold supported on TiO_2 and Al_2O_3. Ceria could stabilize gold at high dispersion (<2.5 nm) to yield catalysts of high activity and selectivity. Transition metal oxide catalysts including CuO, V_2O_5, MnO_x, ZrO_2, Co_3O_4 and related mixed oxides have been shown to be active for VOCs abatement [5,13]. Vanadia in particular is an attractive catalyst for VOC oxidation not only because of its high turnover frequency, but also its tolerance to SO_2, H_2S, NO_x, organosulfur compounds as well as organochloride compounds that are ubiquitous in the environment [14,15]. Dai's group [16] reported that VO_x/CeO_2 can deliver complete conversion of 1,2-dichloroethane oxidation at 250 °C with no observable deactivation over 360 h.

There are still considerable debates as to the exact reaction mechanism for VOCs oxidation on ceria catalysts [17,18]. The present work employed an *operando* Raman reactor cell with an online FTIR to investigate toluene oxidation on ceria catalysts (CeO_2, VO_x/CeO_2, Au/CeO_2) to gain a better understanding of the "working" catalyst and identify the surface species during reaction, in order to establish the structure-activity relationship at a molecular level.

2. Experimental

2.1. Preparation of ceria catalysts

Ceria (CeO_2) was prepared from 0.01 M $Ce(NO_3)_3$ solution obtained by dissolving $Ce(NO_3)_3{\cdot}6H_2O$ salt (99%, Sigma-Aldrich)

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in warm deionized distilled (DDI) water. The pH of the solution was adjusted gradually from pH 4.5 to pH 9 with the addition of 0.5 M NH_4OH (BDH) solution. The original clear solution changed to light pink and then to light yellow following vigorous stirring (ca. 1000 rpm). The yellow slurry obtained overnight, was washed repeatedly with warm, distilled water (60 °C) and centrifuged in JA-14 rotor (14,000 rpm) until the supernatant's pH was neutral. The solids were vacuum dried at 65 °C for 4 h, followed by calcination in flowing air (1000 sccm) at 300 °C for 2 h to produce the CeO_2 catalyst (Ce1).

The 2.5 wt% vanadia on ceria catalyst (2.5VCe) was obtained by an impregnation method. Briefly, 0.5 g ceria (Ce1) powder was first dispersed in 250 ml DDI by ultrasound for 30 min to obtain a suspension. The vanadia precursor, $(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$, was obtained by boiling an equal volume mixture of 0.02 M NH_4VO_3 (98%, Nacalai Tesque) and 0.04 M $(NH_4)_2C_2O_4$ (99%, Sigma-Aldrich) solutions. Afterward, a 0.024 g $(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$ crystal was dissolved in 50 ml DDI water and added to the Ce1 suspension and the mixture was placed in a rotary evaporator kept at 65 °C under a rotation speed of 120 rpm. The resulting paste was then dried in vacuum at 65 °C for 2 h, before calcining in 1000 sccm flowing air at 300 °C for 2 h to produce a bright yellow 2.5VCe catalyst.

The 2.5 wt% gold on ceria catalyst (2.5AuCe) was prepared by the following procedure. 0.5 g Ce1 was dispersed by ultrasound in 250 ml DDI water before the drop-wise addition of a 0.001 M gold solution. The solution was prepared from $HAuCl_4\cdot xH_2O$ (99.999%, Sigma-Aldrich) after adjusting the pH to 8.5 by adding 0.05 M NH_4OH solution. After vigorous mixing at 1200 rpm at 80 °C for 2 h, the mixture was cooled to room temperature and stirred overnight. The resulting slurry was washed repeatedly with warm, distilled water (60 °C) and centrifuged (14,000 rpm) to remove ammonium and chloride ions. The paste was then vacuum dried at 65 °C for 4 h, and calcined in 1000 sccm flowing air at 300 °C for 2 h. The Ce1, 2.5VCe and 2.5AuCe catalysts were stored in sealed containers under dry atmosphere before use.

2.2. Characterization of ceria catalysts

The Ce1, 2.5VCe, 2.5AuCe catalysts were examined by JEOL 2100 high resolution transmission electron microscopy (HRTEM) operated at 200 kV with a resolution of 0.29 nm. A selected area electron diffraction (SAED) and interplanar d-spacing measurement were carried out by Gatan Digital Micrograph program. The catalyst powder was dispersed in ethanol (Absolute, Merck) and deposited on a holey carbon TEM grid. The catalysts were also analyzed by the PANalytical X'pert model X-ray diffractometer (XRD) and Physical Electronics 5600 X-ray photoelectron spectroscopy (XPS). The XRD patterns was obtained from powder X-ray diffractometer with X-ray source of Cu anode, wavelength of 1.5406 Å and graphite monochromator. The samples were grounded into fine powder and then placed in a glass sample holder. The XPS was equipped with a 150 W monochromatic Al Kα X-ray source ($h\nu$ = 1486.6 eV) and Kratos Axis Ultra DLD spectrometer. The spectra were calibrated with the C1s peak at 285.0 eV. The catalyst was placed on an indium foil (99.99%) and outgassed under ultra-high vacuum. Nitrogen physisorption was carried out in a Beckman Coulter SA 3100 surface area analyzer. The 0.1 g catalyst was outgassed in vacuum at 200 °C before nitrogen adsorption at −196 °C. The adsorption and desorption isotherm data were used to calculate the Brunauer-Emmett-Teller (BET) surface area, pore volume and the Barrett-Joyner-Halenda (BJH) pore size distribution.

2.3. Operando reaction study

The toluene oxidation reaction was carried out in an *operando* fixed bed reactor cell made of optical-grade quartz. The reactor fitted snuggly into an insulated heating block as shown in Fig. 1 [19]. The reaction temperature was monitored by a type 2 thermocouple (thermocoax) inserted into the catalyst bed and controlled by a temperature programmer unit (PID Eng&Tech). The catalyst was observed *in situ* by a Renishaw micro-Raman System 1000 using a LEICA DMILM microscope with a 20× long-distance objective lens and the spectra were obtained under Argon laser (514 nm) excitation at 4 scans and 30 s acquisition time. The composition of the reaction gases were analyzed by an on-line ThermoNicolet 6700 Fourier transformed infrared (FTIR) spectrometer fitted with a thermostated (120 °C) gas cell. The spectra were collected from 650 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and sampling interval of 9.85 s. FTIR calibrations were made and the details are discussed in the Supplementary Information Part 1 (SI. Part 1).

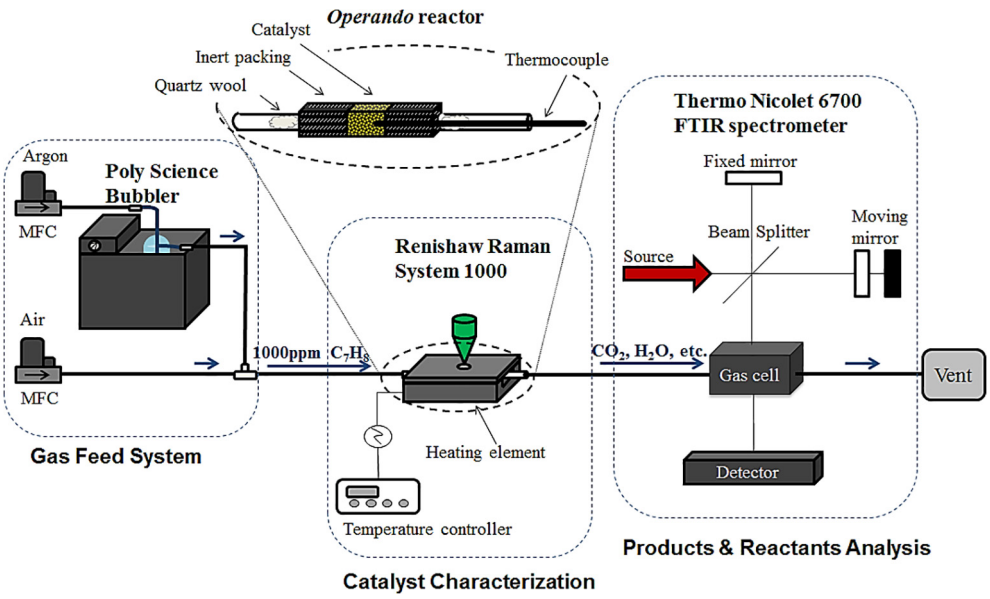

Fig. 1. Schematic diagram of the *operando* reactor setup equipped with *in situ* Raman and online FTIR spectrometers.