



# “Storage-oxidation” cycling process for indoor benzene removal at room temperature

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## ABSTRACT

Non-thermal air plasma assisted “storage-oxidation” cycling process was applied to indoor benzene removal at room temperature and realized over TS-1 zeolite supported AgCu catalysts. AgCu/TS-1 catalyst showed not only promising C<sub>6</sub>H<sub>6</sub> capacity under humid condition in the storage phase, but also high oxidation efficiency of absorbed benzene with the assistance of non-thermal plasma (NTP) at a moderate discharge power of 6 W. Due to the generation of increased amounts of Cu<sup>+</sup> and active surface oxygen species resulting from the Ag–Cu interaction, the AgCu/TS-1 catalyst showed higher benzene storage and oxidation capacity than the other catalysts. Compared with the thermal regeneration, the good humidity tolerance, non-benzene release, and low energy cost was achieved in the non-thermal air plasma regeneration, which providing a promising way for indoor benzene purification.

## 1. Introduction

Physical adsorption and catalytic oxidation have been considered as the most promising methods for indoor C<sub>6</sub>H<sub>6</sub> removal [1–3]. However, it has been shown that traditional physical adsorption by activated carbon (AC) is facing the problem of hard to regenerate [4,5]. And in terms of catalytic oxidation, even on noble metals like Pt, Pd and Au catalysts, the temperature required for the complete oxidation of benzene (ca. 100–4000 ppm C<sub>6</sub>H<sub>6</sub>, GHSV = 10,000–60,000 h<sup>-1</sup>) is still higher than 150 °C [6–9], which result in the consequences of operational difficulties and high energy consumption.

In our previous work, we reported a novel energy-efficient catalytic removal of benzene by tandem temperature-pulse oxidation (TTPO) process over Pt/HZ(200) [10]. Benzene is firstly gathered at room temperature and stored in the channel of HZSM-5; after saturation the catalyst could be regenerated in situ by heating, the stored species being completely oxidized to CO<sub>2</sub> and H<sub>2</sub>O by Pt. The key issue for such a cycling process is the enhancement of benzene storage capacity under humid condition in order to prolong the catalyst's useful life for each cycle, as well as solving the problem of benzene release during temperature-rising stage, in which precious metal is needed (reaching the aim of benzene oxidation before desorption) and H<sub>2</sub>O existing must be avoid (huge amount of benzene will desorb in moisture containing regeneration).

Herein, as invoked by the characteristic of non-thermal plasma (NTP) [11], we attempted to substitute “temperature-pulse” oxidation by “NTP-pulse” regeneration to enable the whole “storage-oxidation” cycling process operated at room temperature. Since the oxidation regeneration by NTP is undertaken at room temperature, the possible release of benzene during “temperature-rising” stage could be avoided. Moreover, due to the reactive species such as O(3p) and OH generated by NTP in air, the stored benzene could be oxidized at room temperature without the catalysis by noble metals such as Pt [12]. TS-1 zeolite was selected as substrates for benzene storage based on its two characteristics: (i) 10-ring elliptical character of the channels renders TS-1 accessible for diffusion of C<sub>6</sub>H<sub>6</sub> (kinetic diameter of 5.8 Å); (ii) the excellent hydrophobic properties of TS-1 as compared with HZSM-5, enables it to store benzene under humid conditions [13]. Meanwhile, it is noticed that the unique characteristics of the d orbitals in Ag/Cu or Ag<sup>+</sup>/Cu<sup>+</sup> ions enable them to form bonds with unsaturated hydrocarbons in a nonclassical manner, which is broadly referred to as π-complexation. This π-complexation has been proved to be able to enhance HCHO and C<sub>6</sub>H<sub>6</sub> storage capacity in previous study [14–17].

Therefore, in this study, we propose a tandem “NTP-pulse” regeneration process which combines with benzene storage on AgCu/TS-1 catalyst for indoor benzene removal at room temperature, as depicted in Scheme 1. It is a cyclic process of enrichment of low concentration of C<sub>6</sub>H<sub>6</sub> on the TS-1 zeolite and a followed oxidation of the stored benzene

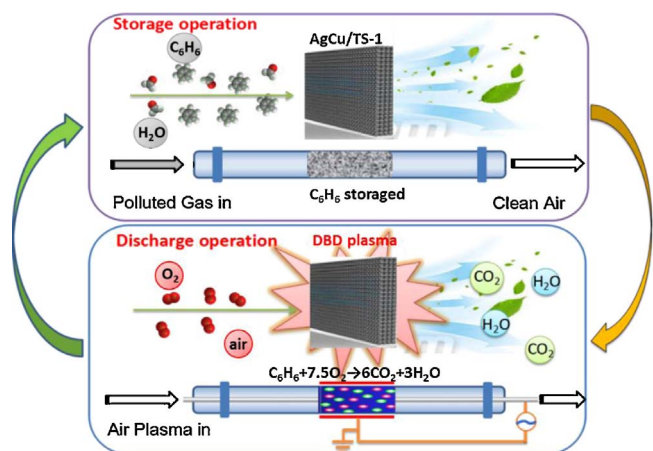
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**Scheme 1.** Schematic diagram of the proposed “storage-oxidation” cycling process for  $C_6H_6$  removal.

by assistance of NTP. The “NTP-pulse” only takes 1/10 time of storage time, providing an energy-efficient method for the synergy of plasma and catalysis.

## 2. Experimental details

### 2.1. Catalyst preparation

Ag and Cu catalysts with nominal metal loading of 1 wt% were prepared by conventional incipient wetness impregnation method using TS-1 (commercial samples) as support.  $AgNO_3$  and  $Cu(NO_3)_2$  were used as Ag and Cu precursors, respectively. The desired amount of  $AgNO_3$  was dissolved in needed deionized water. After impregnation, the sample was aged at room temperature overnight, followed by drying at  $110\text{ }^\circ\text{C}$  for 16 h and then calcined at  $450\text{ }^\circ\text{C}$  for 4 h in air. The obtained catalyst was denoted as Ag/TS-1 and Cu/TS-1.

0.5 wt%Ag0.5 wt%Cu/TS-1 (AgCu/TS-1) bimetal catalyst was prepared by the co-impregnation method. In a typical synthesis, first, desired  $AgNO_3$  and  $Cu(NO_3)_2$  were co-dissolved in a certain amount of deionized water. Then, the mixed solution was added dropwise to the TS-1 support. The impregnated samples were aged overnight at ambient temperature in darkness followed by drying at  $110\text{ }^\circ\text{C}$  for 12 h and calcined in air at  $450\text{ }^\circ\text{C}$  for 4 h.

### 2.2. Characterization techniques

Before characterization test, the samples were calcined in air at  $450\text{ }^\circ\text{C}$  for 4 h.

Specific surface areas (SBETs) of the catalysts were calculated from a multipoint Brunauer–Emmett–Teller (BET) analysis of the nitrogen adsorption and desorption isotherms at  $-196\text{ }^\circ\text{C}$  measured in a Quantachrome QUADRASORB SI gas adsorption analyzer. Prior to the measurement, the samples were degassed in vacuum at  $300\text{ }^\circ\text{C}$  for 10 h.

X-ray powder diffraction (XRD) analysis was conducted using a D/Max-2400 (Rigaku) instrument with  $CuK\alpha$  radiation ( $\lambda = 0.1542\text{ nm}$ ), operating at 40 kV and 100 mA; phase identification was achieved through comparison of XRD patterns to those of the Joint Committee on Powder Diffraction Standards (JCPDS).

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCALAB250 spectrometer using  $AlK\alpha$  radiation (1486.6 eV) as the X-ray source. The beam was monochromatized by a twin crystal monochromator, yielding a focused X-ray spot with a size of  $500\text{ }\mu\text{m}$ , at  $10\text{ mA} \times 5\text{ kV}$ . Curving fitting of the Ag 3d, Cu 2p and O 1s peaks were performed using XPSPEAK software.

Scanning electron microscopy (SEM) images were obtained on a QUANTA 450 instrument with an acceleration voltage of 3 kV.

Transmission electron microscopy (TEM) images of the samples were obtained on a JEOL JEM-2000EX microscope operated at 200 kV. Diluted suspensions of samples in ethanol were prepared and drop dried on carbon coated copper TEM grids.

### 2.3. Catalytic activity measurements

The catalytic activity evaluations include two processes: the storage process and the oxidation process. Both were carried out in a continuous flow fixed bed quartz microreactor at atmospheric pressure. 0.10 g catalyst (40–60 mesh) was sandwiched between quartz wool layers in the tube reactor. Before performing the experiment, the catalysts were pretreated in the  $N_2$  flow at  $450\text{ }^\circ\text{C}$  for 2 h. The storage process was carried out at room temperature, and 14 ppm  $C_6H_6$ /21%  $O_2$ /1.564%  $H_2O$  (relative humidity of 50%, at  $25\text{ }^\circ\text{C}$ ) was introduced into the reactor at a total flow rate of  $100\text{ ml min}^{-1}$ , corresponding to a gas hourly space velocity (GHSV) of  $30,000\text{ h}^{-1}$ . Gaseous  $H_2O$  was carried into the gas stream by passing  $N_2$  through a bubbler in a water bath at room temperature. The amount of water, expressed as the relative humidity (RH) at  $25\text{ }^\circ\text{C}$ , was controlled by adjusting the flow rate of  $N_2$ , while keeping the total flow unchanged. The inlet and outlet  $C_6H_6$  concentrations were measured by converting it to  $CO_2$  in a homemade  $C_6H_6$ -to- $CO_2$  converter ( $CuMn/\gamma-Al_2O_3$  catalyst) at  $450\text{ }^\circ\text{C}$  and determining the amount of  $CO_2$  formed by IRAS (SICK-MAIHAK-S710, Germany) [18]. In thermal regeneration, the same simulated air stream without benzene was switched into the reactor, with the temperature ramped to  $500\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C min}^{-1}$  and held there for 10 min. In plasma regeneration, air without benzene was switched to the catalyst-packed DBD, with discharge at input power of 6 W.

The  $C_6H_6$  storage capacities were determined at  $25\text{ }^\circ\text{C}$ . The examined parameter,  $C_6H_6$  storage capacity ( $N_{C_6H_6}$ ,  $\text{mmol}\cdot\text{g}_{\text{cat}}^{-1}$ ) are defined as follow:

$$N_{C_6H_6} \left( \text{mmol}/\text{g}_{\text{cat}} \right) = \frac{C_{C_6H_6}^{\text{in}} F_1 t_1}{W_{\text{cat}}} \quad (1)$$

where  $C_{C_6H_6}^{\text{in}}$  is the inlet  $C_6H_6$  concentration in the feed gas,  $F_1$  is the total flow rate,  $t_1$  is the breakthrough time and  $W_{\text{cat}}$  is the catalyst weight. Breakthrough time was defined as the time when outlet  $C_6H_6$  concentration reached 2% of feed concentration. A capillary-sampled quadrupole mass spectrometer with two-stage differential pumping (Omnistar™, Pfeiffer Vacuum, Germany) was used to examine the benzene desorption and the possible by-products at the discharge stage. The examined parameters, stored- $C_6H_6$  to  $CO_x$  oxidation efficiency ( $E_{C_6H_6 \rightarrow CO_x}$ , %), carbon balance ( $B_C$ , %),  $CO_2$  Selectivity ( $S_{CO_2}$ , %), CO selectivity ( $S_{CO}$ , %), and energy cost for remedying  $1\text{ m}^3$  air ( $E_c$ ,  $\text{kWh}\cdot\text{m}^{-3}$ )

$$E_{C_6H_6 \rightarrow CO_x} (\%) = \frac{n_{CO_x}^{\text{out}}}{6 \times n_{C_6H_6}^{\text{stored}}} \times 100\%, \quad (2)$$

$$B_C (\%) = \frac{n_{CO}^{\text{produced}} + n_{CO_2}^{\text{produced}} + 6 \times n_{C_6H_6}^{\text{desorption}}}{6 \times n_{C_6H_6}^{\text{stored}}} \times 100\%, \quad (3)$$

$$S_{CO_2} (\%) = \frac{n_{CO_2}^{\text{produced}}}{n_{CO_2}^{\text{produced}} + n_{CO}^{\text{produced}}} \times 100\%, \quad (4)$$

$$S_{CO} (\%) = \frac{n_{CO}^{\text{produced}}}{n_{CO_2}^{\text{produced}} + n_{CO}^{\text{produced}}} \times 100\%, \quad (5)$$

$$E_c (\text{kWh}\cdot\text{m}^{-3}) = \frac{P \times t_2 \times c}{n_{C_6H_6}^{\text{stored}} \times E_{C_6H_6 \rightarrow CO_x}}, \quad (6)$$

where  $n_{C_6H_6}^{\text{stored}} = C_{(C_6H_6)_a} F_1 t_1$ ,  $n_{CO_2}^{\text{produced}} = \int_0^{t_2} F_2 C_{CO_2} dt$ ,  $n_{CO}^{\text{produced}} = \int_0^{t_2} F_2 C_{CO} dt$ ;  $n_{C_6H_6}^{\text{desorption}} = \int_0^{t_2} F_2 C_{(C_6H_6)_d} dt$ ,  $C_{(C_6H_6)_a}$  and  $C_{(C_6H_6)_d}$  means

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