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Communication

# Significant enhancement in water resistance of Pd/Al<sub>2</sub>O<sub>3</sub> catalyst for benzene oxidation by Na addition

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## ABSTRACT

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A series of Na-doped 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with different Na loadings were prepared by wet impregnation and tested for the catalytic oxidation of benzene. Suitable addition of Na had a remarkable promotion effect on water resistance and enhancement of low temperature activity of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. The optimal mole ratio between Na and Pd was 1:1. The properties of the prepared catalysts were characterized by X-ray diffraction (XRD), Brunauer Emmett Teller (BET), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), O<sub>2</sub>-temperature-programmed desorption (O<sub>2</sub>-TPD), and *in situ* DRIFTS. Results indicated that the addition of Na not only decreased the content of adsorbed water species but also increased the amount of liable surface oxygen species, which are likely the key factors for the excellent water resistance of the catalyst. Na addition also improved the mobility of the lattice oxygen species, which was favorable for catalytic activity. Moreover, the well-dispersed negatively charged Pd particles and suitable redox properties derived from Na addition also contributed to the improved performance and water resistance of the Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. *In situ* DRIFTS results revealed that benzene was oxidized to maleate and acetate species *via* intermediate o-benzoquinone species, which finally turned into harmless CO<sub>2</sub> and H<sub>2</sub>O.

Volatile organic compounds (VOCs) are a major contributor to air pollution [1]. Emissions of VOCs from industrial processes and transportation activities pose considerable harm to both the atmospheric environment and human health [2, 3]. Therefore, VOCs abatement is an important pollutant control issue.

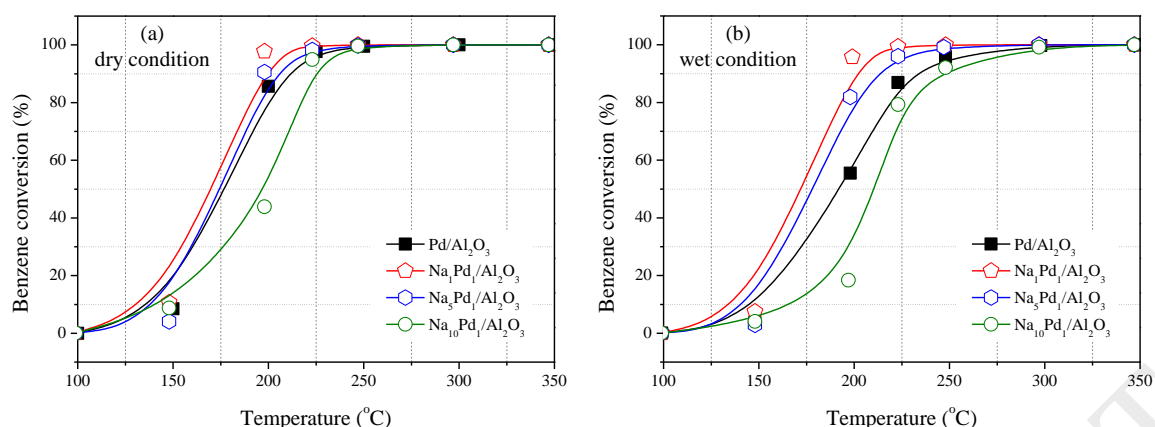
Catalytic oxidation is one of the most effective means for reducing VOCs emissions due to its high destruction efficiency, low NO<sub>x</sub> emissions, and minimal operation and energy costs [4], and has thus gained increasing interest [5-7]. Noble-metal-based catalysts, such as platinum (Pt) [8-11], gold (Au) [12], and palladium (Pd) catalysts [13, 14], are considered the most desirable candidates. Among them, Pd-based catalysts offer several advantages, including high activity, thermal stability, and low cost [13, 15]. As such, Pd-based catalysts have gained growing attention. For instance, Wang *et al.* [16] established a highly active and anti-coking Pd-Pt/SiO<sub>2</sub> catalyst for the elimination of toluene at low temperature. Zhu *et al.* [17] studied Al-doped TiO<sub>2</sub> mesoporous material supported by Pd for the complete oxidation of ethanol. Tang *et al.* [18] reported on the promotion effect of acid treatment on Pd-Ni/SBA-15 catalysts for complete oxidation of benzene vapor.

Pd-based catalyst supports are highly important, with performance tightly related to support type [4]. Al<sub>2</sub>O<sub>3</sub>, a porous support, is a desirable choice to load Pd, and has been investigated extensively for the catalytic oxidation of VOCs [13, 15, 19]. Huang *et al.* [15] studied the complete oxidation of o-xylene over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts at low temperature and found Pd/Al<sub>2</sub>O<sub>3</sub> to be the most active among Pt and Au noble metal catalysts. Kim and Shim [13] investigated the catalytic oxidation of benzene, toluene, and o-xylene VOCs over a 1 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and reported an activity order of o-xylene > toluene > benzene. Jiang *et al.* [19] prepared a monolithic Pt-Pd bimetallic catalyst supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for catalytic combustion of benzene series, which achieved good catalytic combustion for benzene and other aromatic hydrocarbons. While the above research has obtained credible achievements, the influence of water vapor on the activity of catalysts has not been emphasized, which is inevitable in practical application. More importantly, the presence of water vapor may severely inhibit the operation of catalysts.

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**Fig. 1.** (a) Benzene conversion over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts under dry conditions. Reaction conditions: 1500 ppm benzene, 20 vol% O<sub>2</sub>, N<sub>2</sub> balance, total flow rate = 300 mL/min, GHSV = 45,000 h<sup>-1</sup>. (b) Benzene conversion over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts under wet conditions. Reaction conditions: 1500 ppm benzene, 20 vol% O<sub>2</sub>, 2 vol% water vapor, N<sub>2</sub> balance, total flow rate = 300 mL/min, GHSV = 45,000 h<sup>-1</sup>.

The alkali metal Na can serve as electronic or textural promoters for catalysts in various catalytic processes [20]. Haneda *et al.* [21] have demonstrated good reactivity for NO decomposition over Co<sub>3</sub>O<sub>4</sub> with the addition of alkali metal Na. Li *et al.* [20] reported that Na addition had a remarkable promotion effect on Pd/TiO<sub>2</sub> catalysts for HCHO oxidation. As for Soot abatement, Rao *et al.* [22] have confirmed that Na addition is favorable for soot degradation over SnO<sub>2</sub> catalysts. Recently, we found the alkali metal Na is affirmative in enhancing water resistance and low temperature activity of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts in the elimination of VOCs.

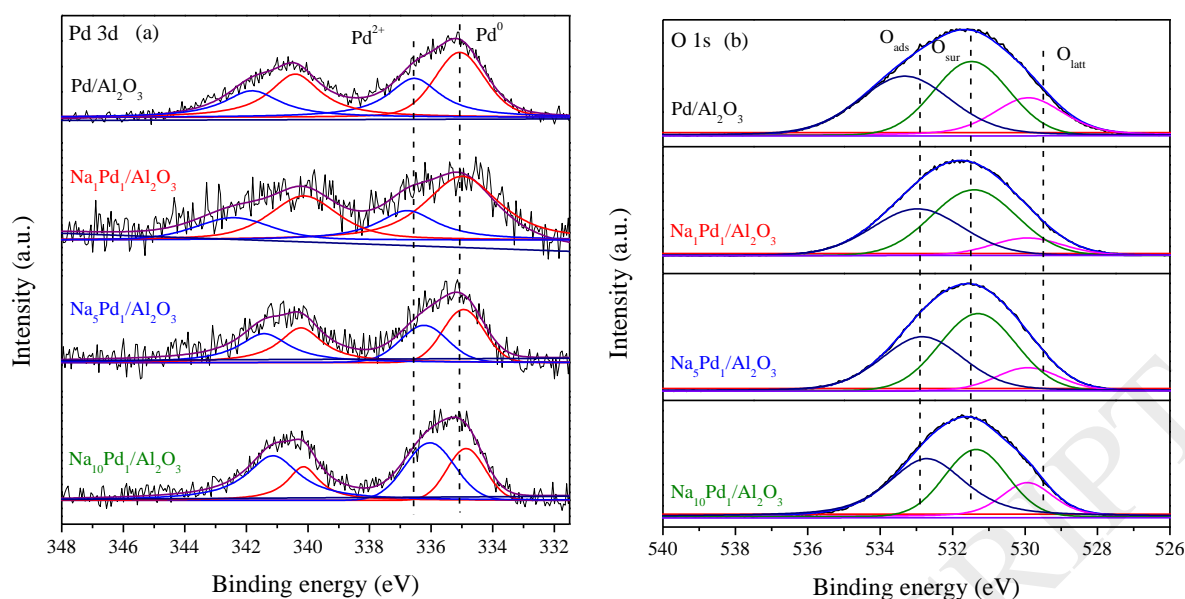
Herein, a series of Na-Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with different Na to Pd mole ratios were prepared via wet impregnation. Benzene, a major and difficult-to-decompose VOC in the environment [13], was chosen as the model compound to test the effect of Na addition on the water resistance of Pd/Al<sub>2</sub>O<sub>3</sub>. The catalysts were characterized by means of X-ray diffraction (XRD), Brunauer Emmett Teller (BET), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), O<sub>2</sub>-temperature-programmed desorption (O<sub>2</sub>-TPD), and *in situ* DRIFTS. Results showed that Na addition had a remarkable promotion effect on water resistance and improved low temperature activity. The well-dispersed Pd particles, abundant liable surface oxygen species, and enhanced mobility of lattice oxygen species derived from Na addition contributed to the good performance in the elimination of VOCs.

We prepared 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> and Na-doped 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, with different Na to Pd mole ratios of 1:1, 5:1, and 10:1, using wet impregnation. Four beakers filled with the same amount of deionized water were prepared. The same amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (5 g, SASOL, SBa-200) and 15% Pd(NO<sub>3</sub>)<sub>2</sub> solution (0.3325 g, Shanghai Jiu Ling Chemical Co., Ltd.) were then dissolved in the four beakers, respectively. Next, 0.025, 0.125, and 0.25 g of Na<sub>2</sub>CO<sub>3</sub> (Sinopharm Chemical Reagent Co., Ltd.) were added into the three solutions separately. After stirring for 3 h, the excess water of the aforementioned mixed solution was removed in a rotary evaporator at 60 °C. To decompose the metal salt adsorbed on the Al<sub>2</sub>O<sub>3</sub> supports, the samples were dried at 100 °C overnight, then calcined in air at 500 °C for 3 h. After the prepared samples cooled to room temperature, they were crushed and sieved through 40–60 mesh. Prior to activity testing and characterization, the catalysts were pre-reduced at 300 °C for 1 h in mixed gas of 5 vol% H<sub>2</sub> and balanced N<sub>2</sub> at a total flow rate of 300 mL/min. Finally, we denoted 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> and Na-doped 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with Na to Pd mole ratios of 1:1, 5:1, and 10:1 as Pd/Al<sub>2</sub>O<sub>3</sub>, Na<sub>1</sub>Pd/Al<sub>2</sub>O<sub>3</sub>, Na<sub>5</sub>Pd/Al<sub>2</sub>O<sub>3</sub>, and Na<sub>10</sub>Pd/Al<sub>2</sub>O<sub>3</sub>, respectively.

To verify the credibility of this study, Na-doped Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with Na and Pd mole ratios of 0.5:1, 20:1, and 40:1 were prepared, as per above, and named Na<sub>0.5</sub>Pd/Al<sub>2</sub>O<sub>3</sub>, Na<sub>20</sub>Pd/Al<sub>2</sub>O<sub>3</sub>, and Na<sub>40</sub>Pd/Al<sub>2</sub>O<sub>3</sub>, respectively.

The activity tests for the catalytic oxidation of benzene over Pd/Al<sub>2</sub>O<sub>3</sub> and Na-doped Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were performed in a continuous flow fixed bed reactor. The catalyst (40–60 mesh) was supported on a small plug of glass wool in the middle of a straight-tube quartz reactor. Before the activity tests, the catalysts were pretreated in mixed gas of 5 vol% H<sub>2</sub> and balanced N<sub>2</sub> at a total flow rate of 300 mL/min. The 1500 ppm benzene gas and 2 vol% water vapor were produced by a N<sub>2</sub> stream bubbling through a saturator filled with liquid benzene and water. The concentrations of benzene and water vapor were controlled by the flow rate of nitrogen or temperature of the water bath, which was kept at 36 °C. The reaction feed under dry conditions consisted of 1500 ppm benzene and 20 vol% O<sub>2</sub> in N<sub>2</sub>. We introduced 2 vol% water vapor into the mixed gas under wet conditions. The flow rate of the gas mixture through the reactor was 300 mL/min, corresponding to a gas hourly space velocity (GHSV) of 45,000 h<sup>-1</sup>. The benzene concentration was analyzed online by a gas chromatograph (GC; Agilent 7890B, HP-5 capillary column) with a flame ionization detector. CO<sub>2</sub> and O<sub>2</sub> concentrations were analyzed by the same GC equipped with a thermal conductivity detector (Porapak Q and HayeSep Q column).

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**Fig. 2.** XPS spectra of Pd/Al<sub>2</sub>O<sub>3</sub> and Na-doped Pd/Al<sub>2</sub>O<sub>3</sub> catalysts: (a) Pd 3d, (b) O 1s.

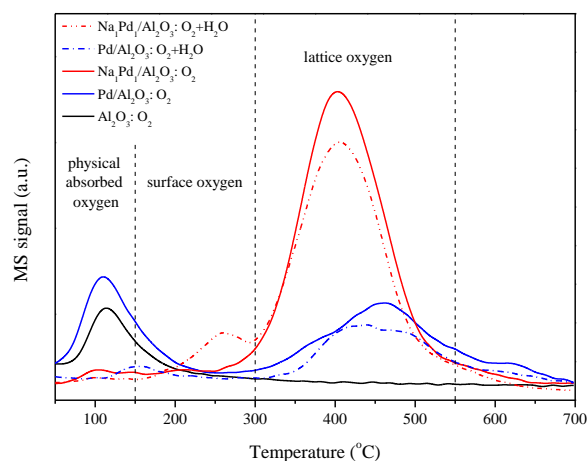
Powder XRD measurements were performed on an X'pert Pro instrument equipped with an X-ray source of Cu-K $\alpha$  at a  $2\theta$  angle ranging from  $5^\circ$  to  $90^\circ$ . Brunauer-Emmett-Teller (BET) surface area measurement was performed with N<sub>2</sub> adsorption/desorption isotherms on a Quantachrome QuadraSorb-evo system. TEM Images were obtained using a JEOL JEM-ARM2100F with 200 kV acceleration voltage. XPS measurements were carried out with an ESCALAB250 spectrometer using a monochromatic Al K $\alpha$  X-ray source (1486.6 eV). The binding energy was calibrated using the adventitious C 1s peak at 284.6 eV. The continuum spectra were fitted according to Gaussian-Lorentzian line shapes. The O<sub>2</sub>-TPD tests were carried out on a Micromeritics Autochem II 2920. The signals were monitored using an Ametek LC-D200M PRO Mass Spectrometer. *In situ* DRIFTS spectra were recorded on a Thermo Fisher 50 Fourier transform infrared (FT-IR) spectrometer equipped with an *in situ* diffuse reflectance chamber (Harrick) and high sensitivity MCT/A detector.

The Na loading effect on 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> was examined in terms of benzene oxidation, with results shown in Fig. 1. The conversion of benzene under dry conditions over different Na-doped Pd/Al<sub>2</sub>O<sub>3</sub> catalysts as a function of temperature is displayed in Fig. 1a. The complete conversion temperature of Pd/Al<sub>2</sub>O<sub>3</sub> was about 210 °C. When an appropriate amount of Na was doped, the conversion of benzene over the whole range was improved slightly, and Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> exhibited the best performance. The conversion of benzene under wet conditions over different Na-doped Pd/Al<sub>2</sub>O<sub>3</sub> catalysts is shown in Fig. 1b. Increasing the mole ratio from 0 to 5 significantly enhanced benzene conversion. Among them, Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> exhibited the highest benzene conversion, and the reaction temperature for >90% conversion (T<sub>90</sub>) was 196 °C. Increasing the mole ratio to 10 significantly decreased benzene conversion, indicating that there is an optimal amount of Na that can improve catalytic performance.

Comparison of benzene oxidation over the Pd-based catalysts is listed in Table S1 (Supporting information). Our catalysts exhibited outstanding combined performance. The CO<sub>2</sub> selectivity curves over different Na-doped Pd/Al<sub>2</sub>O<sub>3</sub> catalysts are plotted in Fig. S1 (Supporting information), which demonstrated the same trend as the conversion of benzene. As shown in Fig. S2 (Supporting information), suitable Na addition had a promotion effect on the Pd/Al<sub>2</sub>O<sub>3</sub> catalysts for benzene catalytic oxidation under both dry and wet conditions, and the optimal mole ratio between Na and Pd was 1:1.

To demonstrate the promotion effect of Na addition on water resistance of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, durability tests for Pd/Al<sub>2</sub>O<sub>3</sub> and Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> were carried out at 215 °C, as shown in Fig. S3 (Supporting information). It is clear that benzene conversion by Pd/Al<sub>2</sub>O<sub>3</sub> decreased from 96% to 90% when 2 vol% water vapor was introduced into the feed gas, however, benzene conversion by Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> was maintained at 97% at 215 °C, even after the introduction of water vapor. Comparison of the catalytic performances of Pd/Al<sub>2</sub>O<sub>3</sub> and Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> in dry and wet conditions is shown in Fig. S4 (Supporting information). Thus, the introduction of water vapor significantly reduced the activity of Pd/Al<sub>2</sub>O<sub>3</sub> but demonstrated little impact on the Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.

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**Fig. 3.** O<sub>2</sub>-TPD profiles of Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, and Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> samples.

The result of XRD shown in Fig. S5 (Supporting information) suggests that the Pd species were dispersed better on the surface of the Na-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support than the undoped one.

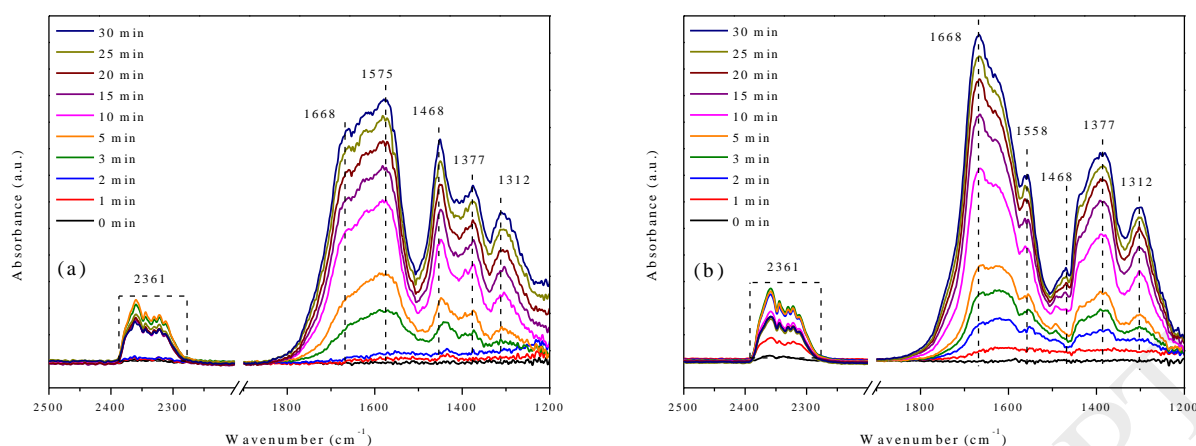
The specific surface areas ( $S_{\text{BET}}$ ) and pore volumes ( $V_{\text{pore}}$ ) of the catalysts listed in Table S2 (Supporting information) together with the STEM images shown in Fig. S6 (Supporting information) indicate that excess Na addition may block some pore openings and then inhibit reactants in gaining access to the active sites in the pores, thus leading to the decrease in catalytic activity and water resistance over the Na<sub>10</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.

SEM-EDS of the as-prepared catalysts was shown in Fig. S7 (Supporting information). It can be clearly seen that the percentages of weight for Pd of all the samples are around 1%, and the actual values of the Na to Pd mole ratios are close to the theoretical values.

The chemical states of the supported Pd and O species were characterized by XPS, with results shown in Fig. 2 and Table S3 (Supporting information). As shown in Fig. 2a, the Pd 3d<sub>5/2</sub> peaks could be divided into two peaks with binding energies of 335.1 eV [23] and 336.4 eV [24], assigned to metallic Pd (Pd<sup>0</sup>) and oxidized Pd (Pd<sup>2+</sup>), respectively. It is worth noting that the binding energy of Pd<sup>0</sup> derived from the sample with Na addition slightly shifted to lower binding energy compared to Pd/Al<sub>2</sub>O<sub>3</sub>, revealing that electrons are donated from the Na species to metallic Pd due to promoter-metal interaction [25]. Metallic Pd is more active than Pd oxide for total VOC oxidation [13, 15]. As shown in Table S3, the relative content of Pd<sup>0</sup> was higher than that of Pd<sup>2+</sup> in all Na-related catalysts, except Na<sub>10</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub>, with Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> exhibiting the highest amount of Pd<sup>0</sup>. Thus, the performance of Na<sub>10</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> was the weakest and the performance of Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> was the strongest.

Oxygen chemisorption can be enhanced by negatively charged metallic Pd species [26]. Thus, the O 1s XPS spectra of the catalysts were investigated, as shown in Fig. 2b. The O 1s spectra could be fit with three peaks at 529.9, 531.4, and 532.8 eV, which were assigned to lattice oxygen species (denoted as O<sub>latt</sub>), surface adsorbed oxygen species (named as O<sub>sur</sub>), and chemisorbed water and/or dissociated oxygen and/or hydroxyl species (labeled as O<sub>ads</sub>), respectively [27, 28]. Due to the higher mobility, the adsorbed oxygen (O<sub>sur</sub>) was deemed to be more reactive during oxidation [29], thus the high relative contents of adsorbed oxygen (O<sub>sur</sub>) on the catalyst surface could be favorable for benzene removal. The specific peak positions and relative contents of different oxygen species are listed in Table S3. The relative contents of O<sub>latt</sub> and O<sub>ads</sub> were decreased, whereas active O<sub>sur</sub> increased for both Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> and Na<sub>5</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub>. This is consistent with the excellent water resistance of the Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> and Na<sub>5</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. Conversely, the relative content of O<sub>ads</sub> was remarkably increased, whereas active O<sub>sur</sub> was decreased for Na<sub>10</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub>. This may be one of the most important reasons why Na loading cannot be doped redundantly. In brief, the addition of Na plays a crucial role in tuning the relative content of different oxygen species, which eventually influences the activity to a great degree. The Na 1s XPS was shown in Fig. S8 (Supporting information). On increasing the initial Na loading, the surface sodium content was observed to increase substantially.

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**Fig. 4.** *In situ* DRIFTS of benzene oxidation over Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> (a) and Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> (b) catalysts at different times. Reaction conditions: 1500 ppm benzene, 20 vol% O<sub>2</sub>, 2 vol% water vapor, N<sub>2</sub> balance, total flow rate = 100 mL/min, T = 200 °C.

The O<sub>2</sub>-TPD experiments were performed over the samples to identify and confirm the activity and mobility of different oxygen species, with results shown in Fig. 3. The desorption peaks between 50–150 °C were ascribed to physical adsorbed oxygen [30], the peaks obtained at 150–300 °C were attributed to the desorption of surface oxygen species such as O<sup>2-</sup> and O<sup>-</sup> [31], and the peaks above 300 °C were attributed to the evolution of lattice oxygen [32]. Compared with pure Al<sub>2</sub>O<sub>3</sub>, the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst displayed an obvious lattice oxygen desorption peak, indicating that Pd doping promoted lattice oxygen mobility. When Na was introduced to Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub>, the amount of physical adsorbed oxygen was decreased, but the mobility of the lattice oxygen was enhanced, because the desorption regions for the lattice oxygen moved toward lower temperatures and the amount was dramatically increased. This result indicates that surface oxygen species are facilitated from bulk oxygen species [33]. Therefore, the oxidative property of the catalyst is reasonably improved, which is consistent with the catalytic performance. After water vapor was introduced to interact with the surface of the catalysts, the main desorption peak of lattice oxygen decreased for both Pd/Al<sub>2</sub>O<sub>3</sub> and Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub>, indicating that the presence of water vapor deactivated the lattice oxygen species. However, a desorbed peak of surface oxygen species appeared from the Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, indicating that the absorbed water can be transformed into liable surface oxygen, which is favorable for oxidation reaction activity [34]. These findings are consistent with the XPS-O1s characterization and catalytic activity measurement results.

Based on these observations, the addition of Na not only improved the mobility of lattice oxygen, which helped facilitate redox reactions and enhance catalytic activity for benzene combustion, but also motivated the absorbed water to form liable surface oxygen species and promoted water resistance of the catalyst.

To elucidate the role of Na addition in the surface mechanism, *in situ* DRIFTS spectra were collected as a function of time in a mixture gas of benzene, O<sub>2</sub>, and water vapor at a fixed temperature of 200 °C, with the results illustrated in Fig. 4. Exposure of the Pd/Al<sub>2</sub>O<sub>3</sub> and Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts to the feed gas resulted in the appearance of several peaks within the range of 1200–2500 cm<sup>-1</sup>. In accordance with other reports, the broad peak around 2361 cm<sup>-1</sup> was attributed to the asymmetric stretch of carbonate species [35]. The band at 1668 cm<sup>-1</sup> was assigned to the C=O stretching vibration of surface o-benzoquinone-type species [36]. The bands at 1575 cm<sup>-1</sup> and 1468 cm<sup>-1</sup> were assigned to the C=C stretching vibrations of surface phenolate species [36]. Bands corresponding to carboxylate species such as formate and acetate were detected at 1558, 1450 and 1377 (CH<sub>2</sub> stretching vibration) cm<sup>-1</sup> [15, 37]. The band at 1312 cm<sup>-1</sup> was assigned to a surface maleate species [38]. As shown in Fig. 4a, as the reaction proceeded, the surface o-benzoquinone-type species (1668 cm<sup>-1</sup>), phenolate species (1575 cm<sup>-1</sup> and 1468 cm<sup>-1</sup>), acetate species (1377 cm<sup>-1</sup>), maleate species (1312 cm<sup>-1</sup>) and CO<sub>2</sub> (2361 cm<sup>-1</sup>) were gradually produced. Thus, it can be concluded that benzene was oxidized into o-benzoquinone, phenolate, maleate, acetate species and CO<sub>2</sub> on the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst at 200 °C in the presence of benzene, O<sub>2</sub>, and water vapor mixture.

In comparison to Fig. 4a, similar bands at 1688, 1377, and 1312 cm<sup>-1</sup> can be observed in Fig. 4b as the reaction proceeded. A new band at 1558 cm<sup>-1</sup> corresponding to acetate species emerged. It is quite different to Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> the surface phenolates species (1468 cm<sup>-1</sup>) cannot be observed until 10 min later. Since phenolate species are very active and can be easily oxidized into benzoquinone [37], the presence of phenolate species indicated the exhaustion of the original liable surface oxygen species on the catalysts. The replenishment of gaseous oxygen to oxygen vacancies clearly decelerated the rate of oxidation. This finding indicates that Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> is more active than Pd/Al<sub>2</sub>O<sub>3</sub>. Moreover, the band intensities of surface organic species on Na<sub>1</sub>Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> were relatively higher than that on Pd<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub>, confirming that Na addition indeed promotes activity. The *in situ* DRIFTS spectra under both dry and wet conditions were compared and displayed in Fig. S9 (Supporting information). Based on these results, a reaction mechanism was proposed and is displayed in Fig. S10 (Supporting information).

The water resistance of the 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst during benzene oxidation was significantly promoted by the suitable addition of Na, with the Na and Pd mole ratio of 1:1 found to be optimal. The appropriate addition of Na led to the formation of well-dispersed and



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negatively charged metallic Pd particles, which facilitated oxygen adsorption. Proper Na addition promoted the transformation of absorbed water into liable surface oxygen species. In addition, the mobility of the lattice oxygen species was also significantly improved, which contributed to the enhanced catalytic activity and water resistance.

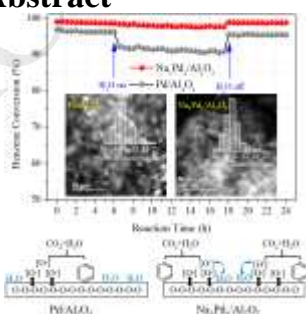
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### Graphical Abstract



Appropriate Na addition led to the formation of well-dispersed metallic Pd particles, which facilitated oxygen adsorption. Proper Na addition further promoted the transformation of absorbed water into liable surface oxygen species and improved the mobility of the lattice oxygen species, which contributed to enhanced catalytic activity and water resistance.