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Article

Study of the role of alkaline sodium additive in selective hydrogenation of phenol

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ABSTRACT

The selective hydrogenation of phenol to cyclohexanone is an important process in the chemical industry. However, achieving high selectivity at high conversion rates is highly challenging, particularly under continuous reaction conditions. Here, we found that the presence of Na alkaline additives (NaX, X = CO₃²⁻, HCO₃⁻, or OH⁻) on Pd/Al₂O₃ not only promoted the phenol conversion from 8.3% to >99% but also increased the cyclohexanone selectivity from 89% to >97% during the continuous hydrogenation of phenol on a fixed bed reactor. After 1200 h of continuous reaction, no activity or selectivity attenuation was observed and the turnover number was approximately 2.9×10^5 . Density functional theory calculations, spectroscopic, and dynamics studies demonstrated that the addition of NaX greatly promoted phenol adsorption and hydrogen activation, thereby improving catalytic activity. Simultaneously, the formation of a “C=O-Na-” intermediate inhibited the excessive hydrogenation and intermolecular coupling of cyclohexanone, leading to high selectivity.

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1. Introduction

Cyclohexanone is generally a vital industrial raw material for the production of caprolactam and adipic acid, which are the primary stocks for the synthesis of nylon [1,2]. Cyclohexane oxidation [3–5] and phenol hydrogenation [6–10] are two main methods for producing cyclohexanone. The cyclohexane oxidation route is generally employed in the industry due to its relatively low cost [11,12]. However, the harsh reaction conditions and yield of undesirable byproducts lower the cyclohexanone selectivity and complicate the recovery/separation steps [11,13,14]. Following the hydrogenation route, phenol can be hydrogenated to cyclohexanone in a “one-step” or a “two-step” process [15,16]. The “two-step” process involves the hydrogenation of phenol to cyclohexanol over Ni catalysts, followed

by the dehydrogenation to cyclohexanone over Cu/Zn catalysts [17,18]. The “one-step” hydrogenation, otherwise known as the selective hydrogenation of phenol to cyclohexanone, demonstrates its ascendancy in several ways. For instance, tedious product separation steps can be avoided and costs would be reduced in the absence of the endothermic dehydrogenation step [17,19]. Additionally, phenol is a well-known model compound of bio-oil and its direct hydrogenation and hydrolysis are of great significance for sustainable chemistry [20].

Catalytic hydrogenation reactions of some high-boiling liquid compounds are traditionally operated in flasks and stirred tank reactors [21–24]. Some extra steps such as reactor cleaning and catalyst separation are inevitable due to the discontinuous nature of the batch process, which leads to increased production costs [25]. Besides, the product yield and efficiency

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are always low due to the inferior heat and mass transfer in the batch liquid-phase reactions [26,27]. Nowadays, researchers are focusing on developing more environmentally acceptable and efficient processes [28,29]. The goals would be realized in continuous gas-phase reactions that demonstrate their advantages in safety enhancement, waste minimization, and efficiency maximization [26,30,31]. Specifically, compared to those of the liquid-phase reaction, gas-phase hydrogenation of phenol exhibits more merits, including continuous manipulation, in situ activation of used catalysts, and no filtering and separating steps [14,15,32,33].

Pd-based catalysts, which exhibit outstanding catalytic activity and cyclohexanone selectivity, are demonstrated to be the best choice for the selective hydrogenation of phenol in both gas and liquid phases [1,8,34,35]. Besides metal components, supports always play important roles in catalytic reactions [6]. For example, our recent works demonstrated that the use of nitrogen-rich porous carbon materials as basic hosts to construct binary Pd/mpg-C₃N₄ or Pd/CNx as hetero-catalysts and these Pd-based catalysts have been shown to be highly active and selective for hydrogenating phenol in aqueous media [19,36,37]. Even though these carbon supported catalysts are very efficient in batch hydrogenation reactions, there are two main problems hindering their applications for continuous hydrogenation of phenol. On the one hand, the shape molding of carbon supported catalysts is relatively difficult. On the other hand, the molding process often leads to a great loss of the catalyst activity. Metal oxides such as Al₂O₃ are well-established carriers for continuous hydrogenation in the industry. However, the metal catalysts directly supported by Al₂O₃ generally show the disadvantages of poor activity and selectivity, and yet some promoters such as alkali and alkaline earth metals (Na, K, Ca, Cs) are always added to improve the catalytic performance [7,38–40]. These additives generally promote catalysts in three ways. First, they modify the electronic surrounding of the active sites, which is beneficial for H₂ activation or substrate adsorption, leading to increased activity [7,39,41–45]. Second, the addition of promoters affects the acid-base sites of the supports, and thus changes the adsorption/desorption equilibrium of the reaction species [6,18,46–49]. Third, they enhance the dispersion of active components and stability of the catalysts [7,46,50,72,73].

Although considerable works have revealed the benefits of alkaline additives for improving the catalytic performance of transition-metal catalysts, there are still controversies about their mechanisms of action for phenol hydrogenation [6,7,18,38,41,51,52] and a comprehensive understanding of the impact of Na additive is still unavailable. Herein, a series of Na-Pd/Al₂O₃ catalysts with different Na alkaline additives (Na₂CO₃, NaHCO₃, and NaOH) were prepared and studied in detail for the gas-phase hydrogenation of phenol. Preliminary kinetics, density functional theory calculations, and spectroscopic studies demonstrated that the addition of NaX promoted phenol adsorption and H₂ activation, and improved the catalytic activity. The formation of “-C=O-Na-” between the carbonyl group in cyclohexanone and the Na species in the Na-Pd/Al₂O₃ catalyst effectively inhibited the excessive hydrogenation and

coupling reaction of cyclohexanone, leading to increased selectivity. Due to the Na alkaline promoters, the phenol conversion was boosted from 8.3% to >99% and the cyclohexanone selectivity increased from 89% to >97%. No activity or selectivity decay was observed even after 1200 h of continuous reaction.

2. Experimental

2.1. Materials

PdCl₂ was purchased from Aladdin and granular Al₂O₃ (diameter 0.5–1.0 mm) was used as received from ZIBO HENGHUAN LVYE Co., Ltd. Unless otherwise stated, all solvents and chemicals were of analytical grade and used without further treatment.

2.2. Catalyst synthesis

The Na-Pd/Al₂O₃ catalysts were prepared by a stepwise impregnation method. In detail, an appropriate amount of a 20 mg·mL⁻¹ H₂PdCl₄ solution (PdCl₂ was dissolved in 0.6 M HCl solution) was initially mixed with 4 mL of deionized water, after which granular Al₂O₃ was added. The mixture was maintained at room temperature for 4 h, and then dried at 70 °C for 2 h. Subsequently, 5 mL of Na alkali (Na₂CO₃, NaHCO₃ or NaOH) solution was added. The mixture was maintained at room temperature for 3 h, and then dried at 60 °C overnight. Finally, the Na-Pd/Al₂O₃ catalysts were obtained by reducing with H₂ at 300 °C for 3 h. The additive-free Pd/Al₂O₃ catalyst was prepared in the same way, except that the Na alkali solution was replaced by pure deionized water. Regardless of the kind of additives, the catalysts supported by the Na promoters were unified and represented as Na-Pd/Al₂O₃. The specific catalyst was referred to as Na₂CO₃-Pd/Al₂O₃, NaHCO₃-Pd/Al₂O₃, or NaOH-Pd/Al₂O₃ when necessary.

2.3. Characterization

Powder XRD patterns were collected on a model D/tex-Ultima TV instrument using Cu K_α radiation (1.54 Å). The sample was scanned in the 2θ range from 10° to 85° (5° min⁻¹). XPS information was obtained using a scanning X-ray microprobe (PHI 5000 Versa, ULAC-PHI, Inc.) using an aluminum anode (Al 1486.6 eV) X-ray source with C as the internal standard (C 1s = 284.6 eV). ICP-AES measurements were performed on a PerkinElmer Optima OES 8000 instrument, and the samples were dissolved in concentrated nitric acid in a 120 °C oven with hydrothermal treatment for 12 h. Nitrogen adsorption analysis was performed at 77 K using a Micromeritics ASAP 2020 to access the surface areas and pore distributions. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area (S_{BET}). The pore size distribution (PSD) plots were calculated based on the desorption branch of the isotherm, according to the Barrett-Joyner-Halenda (BJH) model. The Pd dispersion was determined by CO chemisorption at 30 °C, using a CHEMBET-3000 instrument (Quantachrome Co.). Prior to the experimental trials, each sample was reduced un-

der H₂ flow at 250 °C for 1 h, purged with He at the same temperature for 0.5 h, and then cooled to 30 °C. Finally, CO pulses were injected into the sample bed every 5 min until no further consumption of CO was detected. The temperature-programmed reduction of H₂ (H₂-TPR) was conducted with a FINESORB-3010 apparatus equipped with a thermal conductivity detector (TCD). Before a TPR run, the catalysts were pretreated in Ar at 300 °C for 1 h. After cooling to 30 °C, TPR was performed under a 10% H₂/Ar gas mixture, at a flow rate of 30 mL·min⁻¹ with a temperature ramp of 10 °C·min⁻¹.

2.4. Catalytic reaction

The hydrogenation of phenol was carried out in a fixed bed vertical glass reactor ($h = 348$ mm, $d = 6$ mm) equipped with an electronically controlled furnace, fitted with a glass frit carrying the catalyst. Phenol was placed in a heating tank (70 °C), to maintain its liquid-phase state, and injected through a liquid chromatography pump. The H₂ stream was controlled using a mass flow controller. All the catalytic data were acquired at 160 °C. The products were analyzed by GC equipped with an FID detector every hour. The conversion of phenol (Conv.) was calculated as the mol of reacted phenol per mol of total phenol fed. The selectivity of cyclohexanone (Sel. (C=O)) was calculated as the mol of produced cyclohexanone per mol of reacted phenol, and the selectivity of cyclohexanol (Sel. (-OH)) was calculated as the mol of produced cyclohexanol per mol of reacted phenol. The TOF value was defined as the mol of phenol reacted per hour per mol of surface Pd atom (the calculation of surface Pd atoms was derived from the results of CO chemisorption and ICP-AES.). The TON value was defined as the mol of phenol reacted per mol of total Pd. The carbon balance was >99% in the case of selectivity near 99%.

2.5. TPD measurement

The adsorption and desorption of phenol were performed in the same reactor for phenol hydrogenation. N₂ was used as a carrier gas and was controlled by a mass flow controller. To remove the surface hydroxyl groups and the adsorbed oxygen, 0.6 g of the catalyst was swept by N₂ at 250 °C at a speed of 25 mL·min⁻¹, for 1 h. After pretreatment, the sample was cooled in the carrier gas to 160 °C. Subsequently, phenol was supplied through a syringe pump at a speed of 0.010 mL·min⁻¹. Phenol was adsorbed for 1 h at a rate of 25 mL·min⁻¹ N₂. Subsequently, the N₂ (60 mL·min⁻¹) continued to purge for 1 h without the flow of phenol to remove the weakly adsorbed species. Afterward, the temperature program desorption was carried out from 160 to 560 °C at a heating rate of 5 °C·min⁻¹. The outlet of the reactor was sealed by a cold trap filled with ethanol solution to collect the desorbed molecules. The collected solution was detected by GC every 5 min. Dodecane was used as the internal standard for the quantitative analysis of the desorbed substances. The adsorption and desorption of cyclohexanone were evaluated by the same method. The cyclohexanone was supplied through a syringe pump at 0.034 mL·min⁻¹.

2.6. DFT calculations

Density functional theory (DFT) calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) [53,54]. The spin-polarized projector augmented wave (PAW) method [55,56] and the RPBE electron exchange-correlation functional [57] of the generalized gradient approximation (GGA) were applied in our calculations. The kinetic energy cut-off for the wave function expanded in the plane-wave basis was set as 400 eV. A $p(6 \times 6)$ supercell containing 4-layer slabs with 144 atoms for Pd(111) was modeled. The periodic condition was employed along the x and y directions. The vacuum space along the z direction was set to 15 Å to eliminate the interaction between neighboring slabs. The upper two layer atoms of the model in the cell were allowed to relax during the structure optimization and the bottom two layer atoms were fixed. The Brillouin-zone integration was performed along with a $2 \times 2 \times 1$ Monkhorst-Pack grid for the different surface slabs. The relaxation was halted when the force residue on the atom was smaller than 0.02 eV·Å⁻¹. The transition states were calculated using the climbing image nudged elastic band (CI-NEB) method [58].

The adsorption energy (E_{ads}) was calculated as follows: $E_{\text{ads}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{adsorbate}}$, where E_{total} was the calculated total energy of the adsorption system, E_{surface} was the energy of the clean catalyst, and $E_{\text{adsorbate}}$ was the energy of the gas-phase molecule. The energy barrier was defined as $E_a = E_{\text{TS}} - E_{\text{IS}}$, where E_{TS} and E_{IS} were the total energies of the transition state and the initial state, respectively.

3. Results and discussion

3.1. Selective hydrogenation of phenol to cyclohexanone

The hydrogenation of phenol was carried out over the prepared Pd-based catalysts. Each catalyst was evaluated on-line for 11 h and the output was sampled and analyzed once per hour. For precision, the conversion and selectivity from more than 6 samples were calculated at the steady state, and the average values are presented in Table 1. As is shown, the doping of NaHCO₃ and NaOH additives raised the phenol conversion from 8.3% to >99%, and the addition of Na₂CO₃ improved the phenol conversion to 88% (Table 1, entries 1–4). The addition of Na₂CO₃, NaHCO₃, and NaOH additives enhanced the cyclohexanone selectivity from 89% to >99%, 97%, and 95%, respectively (Table 1, entries 1–4). This indicated that the promoting effects followed the order of NaHCO₃ > NaOH > Na₂CO₃. The GC-MS results revealed that besides cyclohexanone (Sel. = 89%) and cyclohexanol (Sel. = 2.6%), the intermediate, 2-cyclohexen-1-ol (Sel. = 3.0%), and bicyclic coupling products (Sel. = 5.4%) appeared in the additive-free Pd/Al₂O₃ system. Thus, the relatively low selectivity of cyclohexanone over the additive-free Pd/Al₂O₃ catalyst originated from the generation of cyclohexanol and the occurrence of coupling reactions. After 1200 h of continuous reaction, no activity or selectivity attenuation was observed over the NaOH-Pd/Al₂O₃ catalyst, and the turnover number was approximately 2.9×10^5 (Fig. S1). In summary, it can be seen that the Na additives play

Table 1The results of catalytic phenol hydrogenation over different catalysts ^a.

Entry	Catalyst	Additive	Pd content ^d (wt%)	Na content ^d (wt%)	H ₂ /Phenol molar ratio	Conv. (%)	Sel. (C=O) (%)	Sel. (-OH) (%)
1	Pd/Al ₂ O ₃	— ^b	0.6	— ^b	3.0	8.3	89	2.6
2	Pd/Al ₂ O ₃	Na ₂ CO ₃	0.6	3.0	3.0	88	>99	0.5
3	Pd/Al ₂ O ₃	NaHCO ₃	0.6	3.0	3.0	>99	97	2.4
4	Pd/Al ₂ O ₃	NaOH	0.6	3.0	3.0	>99	95	3.2
5	Pd/Al ₂ O ₃	Na ₂ CO ₃ * ^c	0.6	3.0	3.0	9.0	92	2.9
6	Pd/Al ₂ O ₃	NaHCO ₃ * ^c	0.6	3.0	3.0	9.9	91	2.2
7	Pd/Al ₂ O ₃	NaOH* ^c	0.6	3.0	3.0	11	97	2.1
8	Pd/Al ₂ O ₃	NaHCO ₃	0.6	1.0	3.0	28	93	4.3
9	Pd/Al ₂ O ₃	NaHCO ₃	0.6	5.0	3.0	72	>99	0.1
10	Pd/Al ₂ O ₃	NaHCO ₃	0.6	7.0	3.0	58	>99	0.3

^a Reaction conditions: catalyst = 0.6 g; H₂ = 25 mL·min⁻¹; T = 160 °C. ^b No additive. ^c Na additives physically mixed with the additive-free Pd/Al₂O₃ catalyst. ^d The theoretical loading.

an extremely important role in the performance of the catalysts. All the Na-Pd/Al₂O₃ catalysts prepared here exhibited much better catalytic performance than the previously reported catalysts did (Table S1). For further insight into the role of Na additives, a series of characterizations were performed to understand the exact origin of the enhanced activity and selectivity.

3.2. Analysis of catalytic activity differences

The Pd contents in Pd/Al₂O₃, Na₂CO₃-Pd/Al₂O₃, NaHCO₃-Pd/Al₂O₃, and NaOH-Pd/Al₂O₃ catalysts, measured by ICP, were 0.53, 0.47, 0.45, and 0.45 wt%, respectively (Table 2). The Na contents in Na₂CO₃-Pd/Al₂O₃, NaHCO₃-Pd/Al₂O₃, and NaOH-Pd/Al₂O₃ catalysts were very close to the theoretical loading of 3 wt%. The addition of Na promoters had no significant effect on the shape of N₂ sorption isotherms (Fig. S2), *i.e.*, it had a negligible effect on the textural structures of the catalysts. The specific BET surface area (*S*_{BET}) of the additive-free Pd/Al₂O₃ catalyst was calculated to be 216 m² g⁻¹ and the BJH pore volume was 0.65 cm³ g⁻¹ (Table 2, entry 1). The *S*_{BET} decreased to 198, 193, and 193 m² g⁻¹ and the pore volume was reduced to 0.63, 0.53, and 0.56 cm³ g⁻¹ after modification with Na₂CO₃, NaHCO₃, and NaOH, respectively (Table 2, entries 2–4). It can be explained by the fact that the addition of Na species occupied a small number of pores [50]. In summary, the diversification in these structural parameters was too little to be considered as the factor deciding the catalytic performance.

The XRD patterns of all the catalysts showed no characteristic peaks indicative of crystalline Pd and Na components (Fig. S3). The Pd loading was relatively low; consequently, the Na species were well dispersed on the catalysts. The Pd dispersion calculated from the CO chemisorption (Pd:CO = 1:1) increased

from 31.8% to 36.6%, 40.2%, and 41.5% after loading with Na₂CO₃, NaHCO₃, and NaOH additives, respectively. The promotion degrees of different Na additives in Pd dispersion followed the sequence of NaOH > NaHCO₃ > Na₂CO₃ (Table 2). The increase in Pd dispersion may be attributed to the reaction between NaX and the Pd precursor ion, which forms alkaline Pd substances, *i.e.*, PdCO₃, Pd(HCO₃)₂, or Pd(OH)₂. These alkaline Pd substances, bounded to the acid sites of Al₂O₃, play important roles in re-dispersing metal particles and retarding the migration of Pd NPs during the following reduction process. The negative peak (70–90 °C) on the H₂-TPR spectrum of the additive-free Pd/Al₂O₃ indicated that the Pd NPs on Pd/Al₂O₃ were relatively large (Fig. S4) [59–62]. In contrast, no negative peak was observed for the Na-Pd/Al₂O₃ catalysts, implying that the Pd surface encircled with Na species inhibited the formation of β-PdH. The relatively highly dispersed Pd NPs on the Na-Pd/Al₂O₃ catalysts increased the number of active sites, and in turn, enhanced the catalytic activity for phenol hydrogenation.

The chemical states of Pd were determined by XPS (Fig. S5). The contents of metallic Pd (Pd⁰) calculated from the XPS peak fitting in additive-free, Na₂CO₃-, NaHCO₃-, and NaOH-Pd/Al₂O₃ were 55.2%, 92.6%, 75.0%, and 82.3%, respectively (Table 2). Furthermore, it can be observed that the Na additives changed the electronic structure of the Pd metals (Fig. 1(a)). Comparing to that over the additive-free Pd/Al₂O₃ catalyst, the binding energies (B.E.) of the Pd 3d orbital over the Na₂CO₃-, NaHCO₃-, and NaOH-Pd/Al₂O₃ catalysts negatively shifted by 0.23, 0.27, and 0.07 eV, respectively. When the Na content was increased to 5 wt%, the Pd B.E. of NaHCO₃-Pd/Al₂O₃ was shifted by 0.34 eV. These results implied that the Na species supplied electrons to Pd, thereby forming the Pd-Na coordination complexes [46,49,63]. To further understand the electronic structure of

Table 2

Textural properties of different catalysts.

Entry	Catalyst	Additive	Pd content ^a (wt%)	Na content ^a (wt%)	<i>S</i> _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Pd ⁰ /(Pd ⁰ +Pd ⁿ⁺) ratio ^b (%)	Pd dispersion ^c (%)
1	Pd/Al ₂ O ₃	—	0.53	0.00	216	0.65	8.81	55.2	31.8
2	Pd/Al ₂ O ₃	Na ₂ CO ₃	0.47	2.91	198	0.63	8.91	92.6	36.6
3	Pd/Al ₂ O ₃	NaHCO ₃	0.45	2.89	193	0.53	7.93	75.0	40.2
4	Pd/Al ₂ O ₃	NaOH	0.45	2.85	193	0.56	8.40	82.3	41.5

^a Determined by ICP. ^b Originated from the XPS peak split. ^c Determined by CO chemisorption.

Fig. 1. (a) XPS spectra of Pd/Al₂O₃ and Na-Pd/Al₂O₃. (b) The amounts of the electrons transferred from the Na species to Pd in three Na-Pd/Al₂O₃ catalysts.

the catalysts, DFT calculations were performed to study the charge distributions of the Pd surfaces. According to the catalyst preparation method, the loading of alkaline Na additives (0.13 mol%) was much higher than the loading of Pd (0.0056 mol%). Therefore, it can be deemed that the alkaline Na promoters were distributed on both the metal Pd surface and the Al₂O₃ support. For comparison, the Pd/Al₂O₃ catalyst, physically mixed with three types of Na additives, was used for the catalytic hydrogenation of phenol. The results showed that the physical mix with Na promoters brought about a slight increase in phenol conversion and cyclohexanone selectivity, and slight inhibition in cyclohexanol generation (Table 1, entries 5–7). Compared to the performance of the catalysts with chemical added Na promoters, the inferior improvement of the physical mix implied that the Na additives functioned effectively within an appropriate distance from the Pd active sites [64]. Thus, we reputed that the alkaline Na promoters distributed on the Pd surface played a significant role in the hydrogenation reaction and established the DFT models for the alkaline Na additives distributed on the surface of Pd. The Na additives on the prepared catalysts should be in the form of Na₂CO₃, Na₂O, or NaOH (NaHCO₃ was converted to Na₂CO₃ or Na₂O) after the reduction under H₂ atmosphere at 300 °C, according to which the calculation models were constructed, as shown in Fig. S6. The figure showed that Na species interacted with Pd mainly from O with a Na–O distance of 0.22–0.24 nm, and the Na atom was relatively far from the Pd surface (0.28–0.30 nm). Besides, Na₂CO₃, Na₂O, and NaOH transferred 0.43, 0.80, and 0.34 e of electrons to the Pd surface, respectively (Fig. 1(b)), showing the same trend concluded from the XPS results. It was widely accepted that Pd in an electron-rich state has an increased ability to activate H, which explained why the phenol hydrogenation activity was significantly improved after adulterating with Na additives [65–67].

DFT calculations were performed to understand whether and how Na worked to alter the adsorption behaviors of the phenol molecule. As shown in Fig. S7, the adsorption energy of phenol ($E_{\text{ads-phenol}}$) on the pure Pd (111) surface was similar to that on three Na-containing catalytic systems. From the opti-

mized configurations of phenol adsorption on different catalysts, the distance between the phenolic hydroxyl H and the Pd surface decreased from 3.1 to 2.5 Å after doping with Na additives. It can be inferred that the addition of Na may facilitate the dissociation of O–H bonds. Therefore, the dissociative adsorption energy of phenol ($E_{\text{dis-phenol}}$) was calculated over four catalysts (Fig. 2). In the additive-free Pd/Al₂O₃ system, $E_{\text{ads-phenol}}$ (–0.42 eV) was not much different from $E_{\text{dis-phenol}}$ (–0.48 eV). However, the $E_{\text{dis-phenol}}$ values on the Na₂CO₃-, Na₂O-, and NaOH-Pd surfaces (–0.88, –0.82, and –0.80 eV) were much lower than the $E_{\text{ads-phenol}}$ values (–0.44, –0.45, and –0.54 eV). Low values mean more stable adsorption configurations. By comparing the $E_{\text{ads-phenol}}$ with the $E_{\text{dis-phenol}}$ on four catalyst systems, it can be concluded that doping with Na additives made phenol prone to dissociative adsorption. For confirmation, phenol-TPD experiments were performed. The catalyst with the best performance, NaHCO₃-Pd/Al₂O₃, was chosen as the

Fig. 2. The optimized configurations and calculated energies for phenol dissociative adsorption over the (a) pure Pd, (b) Na₂CO₃-, (c) Na₂O-, and (d) NaOH-Pd surfaces. The blue, white, grey, red, and violet balls represent Pd, H, C, O, and Na, respectively.

subject. Unless otherwise specified, the following, Na-Pd/Al₂O₃, refers to NaHCO₃-Pd/Al₂O₃ catalyst. In the phenol-TPD spectra, the peak in the range of 160–250 °C was attributed to the physical and weak chemical adsorption of phenol (Fig. S8(a)). Furthermore, comparing the desorption temperature and total adsorption amount of phenol on Pd/Al₂O₃ (360 °C and 495 mg g⁻¹_{Pd}) with those on the Na-Pd/Al₂O₃ catalyst (485 °C and 593 mg g⁻¹_{Pd}) (Fig. S8(b)), it can be concluded that the addition of Na significantly enhanced the adsorption of phenol. Therefore, the addition of Na additives to the Pd/Al₂O₃ systems promoted not only H₂ activation but also phenol adsorption, which jointly enhanced the catalytic activity. As revealed in Fig. S9, the TOF values on both catalysts were minutely affected by the temperature, *i.e.*, the apparent activation energies of phenol hydrogenation on both Pd/Al₂O₃ and Na-Pd/Al₂O₃ were very small and they were almost the same if considering the experimental error. In conclusion, the difference in TOF values between Pd/Al₂O₃ and Na-Pd/Al₂O₃ originated mainly from the intrinsic activities of the Pd metal sites. The addition of Na altered the dispersion and electronic structure of Pd, which brought about enhanced ability of the active sites to activate substrates.

3.3. Analysis of catalytic selectivity differences

To further explore the reasons for selectivity differences, the hydrogenation of cyclohexanone was evaluated on the same device used for the phenol hydrogenation. The conversions of cyclohexanone over the Pd/Al₂O₃ and Na-Pd/Al₂O₃ catalysts were 34% and 9.3%, respectively (Table 3). A large number of coupling products (Sel. (-CP) = 90%) was generated over the Pd/Al₂O₃ catalyst, according to the GC-MS analysis, including dicyclohexane, cyclohexyl-ether, 1,1'-bicyclohexyl-2-one, 2-cyclohexylcyclohexanol, and 1-cyclohexyl-cyclohexene. (Fig. S10). However, the yields of cyclohexanol were the same (3.5%) on both catalysts. The results showed that the Na additives reduced the cyclohexanone conversion by inhibiting the coupling reactions. Subsequently, the cyclohexanone chemisorption was studied on Na-free and Na-containing catalysts. The amount of desorbed cyclohexanone in the temperature range of 160–250 °C was mainly attributed to the physical and weak chemical adsorption types (Fig. S11(a)). Two distinct desorption peaks (260 °C on Pd/Al₂O₃ vs. 310 °C on Na-Pd/Al₂O₃) manifested that the Na additive changed the adsorption strength of cyclohexanone. Besides, the phenol adsorption (485 °C) on Na-Pd/Al₂O₃ was much stronger than that of cyclohexanone (310 °C), and the adsorption amount of phe-

nol was more than 5 times higher than that of cyclohexanone (Figs. S8(b) and S11(b)). Hence, when phenol was fed as the substrate, the stronger adsorption of phenol forced cyclohexanone out and suppress the further reaction of cyclohexanone over Na-Pd/Al₂O₃. When cyclohexanone was fed, the weakly adsorbed cyclohexanone abandoned rich Pd sites for H₂ activation, resulting in excessive hydrogenation reactions (Table 3).

DFT calculations were further performed to explore the reason for the selectivity disparity. As shown in Fig. 3, the presence of the Na-based species in three Na-Pd catalysts released cyclohexanone from the Pd surface, while cyclohexanone was eventually bonded with Na species, forming the “-C=O-Na-” conformation. The values of adsorption energy of cyclohexanone ($E_{\text{ads-cyclohexanone}}$) over the three Na-Pd catalysts were -0.70, -0.79, and -0.69 eV, which were far lower than that over the pure Pd surface (-0.06 eV) (Fig. 3). Although the formation of “-C=O-Na-” influenced the sooth desorption of cyclohexanone, it could effectively protect cyclohexanone from further reaction [8]. Afterward, we prepared Na-Pd/Al₂O₃ catalysts with different Na (NaHCO₃) contents and used them for phenol hydrogenation. With increasing the Na content, the phenol conversion increased first, reached maximum at 3.0 wt% of Na, and then dropped (Table 1, entries 3, 6–8). The textural properties of the catalysts with different Na contents indicated that a large amount of Na species occupied the pore structures (Table S2). Excessive Na additives covered the Pd sites, leading to reduced activity toward phenol hydrogenation. As the Na content increased from 0.0 wt% to 7.0 wt%, the selectivity of cyclohexanol decreased from 2.6% to <0.3%. Cyclohexanone selectivity remained >99% when the Na content was higher than 5 wt%. The adsorption manner of phenol depended on the acid-base sites around the metal [68]. An increase in the NaHCO₃ content enhanced the basicity of the catalyst. The acid-base reaction would occur between phenol (weak acid) and the basic sites of the catalyst, and thus it can be said that the strong alkalinity of Na-Pd/Al₂O₃ catalysts further promoted the dissociative adsorption of phenol. Besides, the dissociative

Table 3

The results of catalytic cyclohexanone hydrogenation over different catalysts ^a.

Entry	Catalyst	Conv. (%)	Sel. (-OH) ^b (%)	Sel. (-CP) ^c (%)	Yield (-OH) ^d (%)
1	Pd/Al ₂ O ₃	34	10	90	3.5
2	Na-Pd/Al ₂ O ₃	9.3	39	61	3.5

^a Reaction conditions: catalyst = 0.6 g; H₂ = 25 mL·min⁻¹; H₂/cyclohexanone molar ratio = 3.0; T = 160 °C. ^b The selectivity of cyclohexanol. ^c The selectivity of the coupling products. ^d The yield of cyclohexanol.

Fig. 3. The optimized configurations and calculated energies for cyclohexanone adsorption over the (a) pure Pd, (b) Na₂CO₃-, (c) Na₂O-, and (d) NaOH-Pd surfaces.

adsorption of phenol on Pd favored the formation of cyclohexanone, as demonstrated by Ge *et al.* [69]. Accordingly, the increased basicity of the Na-Pd/Al₂O₃ catalysts can be considered as one reason to explain the excellent cyclohexanone selectivity [46,70]. Based on the above analysis, the enhanced selectivity over Na-Pd/Al₂O₃ was attributed to four advantages. (1) The stronger adsorption of phenol promoted cyclohexanone desorption, thereby avoiding the excessive reactions; (2) the formation of “-C=O-Na-” inhibited the further reaction of cyclohexanone; (3) alkaline Na additives improved the basicity of the catalysts, thereby promoting phenol dissociation adsorption and hydrogenation to cyclohexanone; (4) the relatively small Pd NPs decreased the possibility of phenol co-adsorption that caused the coupling reactions [71].

3.4. Proposed mechanism of phenol hydrogenation over the Na-Pd/Al₂O₃ catalyst

Based on the experimental data and theoretical calculations, a possible mechanism was proposed to understand the function of Na additives in phenol hydrogenation (Fig. 4). Na promotes the dissociation of phenol into phenoxyl on the Pd surface. An appropriate amount of H₂ is activated on the highly dispersed and electron-rich Pd sites. These activated H atoms are capable of hydrogenating phenoxyl to cyclohexanone rapidly. Next, Na species would interact with cyclohexanone through a “-C=O-Na-” unit, which inhibits further reactions of cyclohexanone, such as excessive hydrogenation or intermolecular coupling. In addition, phenol adsorbed stronger than cyclohexanone did on Na-Pd/Al₂O₃. The produced cyclohexanone would be quickly forced out by phenol, ensuring high cyclohexanone selectivity at elevated conversions of phenol. For cyclohexanone hydrogenation, excessive H atoms activated on the Pd metals will hydrogenate cyclohexanone to cyclohexanol, while the formation of the “-C=O-Na-” intermediate inhibits the coupling reactions.

4. Conclusions

To conclude, we demonstrated that Na alkaline additives

Fig. 4. Proposed mechanism of phenol hydrogenation over the Na-Pd/Al₂O₃ catalyst.

can dramatically improve the catalytic performance of Pd/Al₂O₃ catalysts for phenol hydrogenation to cyclohexanone under continuous reaction conditions. The action mechanism of the additives was studied in detail. Na additives can modify the conversion and selectivity by mainly three aspects: (1) Na additives promote phenol adsorption on Pd active sites strongly through dissociation into a phenoxyl group. (2) An appropriate concentration of H₂ activated on the highly dispersed and electron-rich Pd NPs hydrogenates the benzene ring of phenoxyl to form cyclohexanone rapidly. (3) Once cyclohexanone is formed, the “-C=O-Na-” between the carbonyl and Na species inhibits the excessive hydrogenation and coupling reactions, which guarantees a high cyclohexanone selectivity. On the additive-free Pd/Al₂O₃ catalyst, less exposed active sites and the competitive adsorption of phenol and H on the catalyst resulted in relatively low catalytic activity. On the other hand, relatively large Pd particles can simultaneously adsorb two or more phenol molecules, thereby resulting in coupling reactions, which reduce the catalytic selectivity. Generally, this exploration of the role of Na additives may provide a direction for catalyst design and expand the applications of Na alkaline additives in industrial catalysis.

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Supplementary data

Supplementary material related to this article can be found in a word file.

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Graphical Abstract

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Study of the role of alkaline sodium additive in selective hydrogenation of phenol

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A comprehensive understanding of the role of Na additives in the continuous hydrogenation of phenol to cyclohexanone in the gas phase.

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碱性钠添加剂在苯酚选择性加氢中的作用

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摘要: 环己酮是重要的大宗化工原料, 其下游产品广泛应用于纺织品、电子电器、塑料工业、石油化工和医药等领域。苯酚选择性加氢副产物少, 制备得到的环己酮纯度高, 在工业上被认为是最具潜力的高品质环己酮生产工艺。然而, 由于环己酮容易过加氢到环己醇, 因此如何在维持催化剂高活性的前提下, 提高催化剂对环己酮的选择性是苯酚选择性加氢催化剂开发的重点和难点。相关工作表明, 碱助剂的添加有利于提高过渡金属催化剂的催化性能, 但这些助剂在催化反应中的作用机理尚不明确, 在苯酚加氢中的作用机制亦存在争议。本文使用不同碱性钠助剂(Na_2CO_3 , NaHCO_3 和 NaOH), 通过分步浸渍法制备了一系列的 $\text{Na-Pd/Al}_2\text{O}_3$ 催化剂, 并利用一氧化碳(CO)化学吸附, X射线光电子能谱(XPS), 密度泛函理论计算(DFT)等手段研究了钠助剂的加入如何提高苯酚气相选择性加氢的催化活性。

对系列 $\text{Na-Pd/Al}_2\text{O}_3$ 催化剂进行苯酚气相加氢测试后发现, 由于碱性钠助剂的添加, 苯酚转化率从8.3%提高到 > 99%, 环己酮选择性从89%提高到 > 97%, 连续1200 h的反应后未观察到性能衰减, 表明该催化体系具有优异的稳定性。CO化学吸附结果表明, 添加 Na_2CO_3 , NaHCO_3 和 NaOH 后, Pd分散度分别从31.8%增加到36.6%、40.2%和41.5%。这可归因于钠助剂和Pd前驱体离子之间反应形成的碱性Pd物质, 如 PdCO_3 , $\text{Pd}(\text{HCO}_3)_2$, $\text{Pd}(\text{OH})_2$ 等与 Al_2O_3 的酸性位点结合, 促进金属颗粒的分散。XPS结果显示, 添加 Na_2CO_3 , NaHCO_3 和 NaOH 后, 金属态Pd的含量从55.2%分别增加到92.6%, 75.0%和82.3%。DFT结果也表明, 吸附在Pd表面的钠助剂会向Pd转移0.34–0.80个电子, 与XPS结果相符, 均说明了钠助剂可以调控Pd的电子结构, 使Pd处于富电子状态, 并促进 H_2 在Pd表面的活化。进一步的DFT研究表明, 不同的钠助剂均可以将苯酚的解离吸附能从-0.48 eV降至-0.80 eV左右, 说明钠助剂可以促进苯酚的酚羟基解离形成酚氧基。 H_2 在高分散且富电子的Pd纳米颗粒表面被快速活化形成H原子, 与酚氧基反应形成环己酮。另一方面, 环己酮的羰基和钠助剂之间形成的“ -C=O-Na- ”结构能有效地抑制了环己酮的过加氢和偶联反应。

关键词: 环己酮; 苯酚; 碱助剂; 机理; 选择性加氢

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