Synergy between Palladium and Potassium Species for Efficient Activation of Carbon Monoxide in the Synthesis of Dimethyl Carbonate

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A potassium ion containing Pd/NaY catalyst is introduced that effectively activates the CO molecule for the carbonation of methyl nitrite to synthesize dimethyl carbonate. The potassium ions play a dual role during the activation of CO. Doping the catalyst with potassium enhances the electron density of Pd active species, which strengthens the Pd–C atoms interaction and thus more strongly activates the CO molecule. Further, the

the O atom of linear adsorbed carbonyls to form a Pd–CO···K⁺ structure, which further activates the C–O bond. Both experimental analyses and density functional theory calculations indicated that the combination of potassium and Pd species facilitates the activation of CO in the carbonylation reaction.

charge-balancing potassium cations in the zeolite interact with

Introduction

Dimethyl carbonate (DMC) can be widely used in versatile chemical syntheses owing to its great reactivity towards nucleophile molecules.^[1] In addition, it is nontoxic, safe, and excellently soluble, thus can be extensively used as a solvent in the paint and battery industry and as an oxygen-containing fuel additive.^[2] Vapor-phase carbonylation of methyl nitrite (MN) catalyzed by supported Pd-based catalysts has been considered a promising path to produce DMC.^[3] Previous researches reported that active-carbon-supported PdCl2-CuCl2 is one of the most active catalysts.^[1a] However, the deactivation of the catalyst caused by the loss of chloride is still the main bottleneck. In addition, chloride-containing systems usually suffer from many problems such as the color of DMC, the corrosion of reaction apparatus, and so on. Chloride-free Pd/NaY catalysts, prepared by conventional liquid-ion exchange methods, have attracted much attention on the account of their good catalytic stability.^[3,4] However, their catalytic activity is not as good as that of PdCl₂-CuCl₂ supported on activated carbon. Therefore, the modification of Pd/NaY catalyst is necessary to obtain better carbonylation reactivity.

For the carbonylation of MN to synthesize the DMC system, the activation of CO is one of the most important factors.^[5] Hence, it is desirable to address this issue to improve carbonylation reactivity. Adding additives is usually considered as an effective means. However, there have been limited studies on the introduction of dopants into the Pd/NaY catalyst.

A potassium promotion effect on supported noble-metal catalysts has been widely reported in the literature. Doping a Pd/C catalyst with potassium ions increased the rate of hydrogen production by 1-2 orders of magnitude from vaporphase formic acid decomposition.^[6] The addition of potassium ions activates Pt absorbed on silica or alumina and, consequently, the low-temperature water gas shift reaction activity.^[7] The facilitation effects considered are deviations in the electronic and structural nature of the noble metals caused by the doping potassium species, which is beneficial to the activation of reactants. Therefore, the introduction of potassium ions into the Pd/NaY catalyst probably further activates the CO molecule for the carbonylation of MN to synthesize DMC. Additionally, Silvia Bordiga et al.^[8] reported that the electric field induced by alkali metal cations polarized the CO molecule. This polarization is thus speculated to facilitate the activation of the CO molecule to some extent. Aimed to effectively activate CO, it is therefore of interest to combine potassium ions and Pd species in the catalyst (e.g., by decorating the Pd/NaY catalyst with potassium ions). The cooperative activation is expected to promote CO for better participation in the reaction, thereby obtaining excellent catalytic performance. In this way, it is convenient to control the reactivity by adjusting the amount of noble metal and/or alkali metal.

A series of potassium-promoted Pd/NaY catalysts were prepared through liquid-ion-exchange technology. The catalysts were evaluated under the same condition in a fixed-bed microreactor. The results clearly demonstrated an improvement in catalytic activities that were achieved by the addition of potassium to Pd/NaY catalyst. Low-temperature N₂ adsorption, TEM, and XRD studies were performed to detect the physical nature of unpromoted and potassium-promoted catalysts. The chemical properties of all samples were determined by X-ray photoelectron spectroscopy (XPS), CO temperature-programmed desorption (TPD) and CO adsorption IR spectroscopy. Density

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functional theory (DFT) calculations were employed to uncover the underlying causes of potassium promotion effect in more detail.

Results and Discussion

In Table 1 and Figure S1 (XRD results, Supporting Information), the physical properties and crystal structures of the undoped and doped K catalysts are shown. Only slight changes are observed relative to NaY zeolite, indicating that doping insignificantly impacts the textural properties of the catalyst. To discuss the effects of potassium on carbonylation performances, the catalysts labeled as Pd/KNaY(*i*) (*i* represents the K/Pd molar ratio) were evaluated under the same reaction conditions in a fixed-bed microreactor. The results (Table 1) indicate that the doped catalysts differ in activity from the undoped ones owing to the amount of potassium. The space time yield (STY) of

DMC reaches up to 696 g $L^{-1}h^{-1}$, an increase of 25% in comparison with the STY achieved over undoped catalyst. The selectivity to DMC increases from 80.8% to 86.3%. Notably, the turnover frequency (TOF, calculated by the moles of DMC per mole Pd per hour) increases steadily at low K/ Pd molar ratios, reaching a maximum at K/Pd = 3.6, and then decreases as this ratio further increases. The STY and selectivity of DMC follow the same trend, but the STY and selectivity of MF exhibit a contrary tendency with the potassium loading. The DMM results are slightly different because of the limitations of zeolite pores.

To explore the potassium promotion effect in the carbonylation reaction, a series of characterizations were employed. TEM images (Figure 1) depict the morphology of Pd active species in the catalysts. The well-defined {200} and {111} facets identify the particles on all catalysts.^[9] Active-species Pd particles uniformly disperse in NaY zeolite, which provide a clue to the high reactivity of these materials. Compared with the original sample, the addition of potassium did not cause any relative enlargement of the supported Pd particles. In other words, the Pd particle size is found to be independent of the presence and abundance of potassium species, excluding variations in diameter as a possible cause of the differences in the observed catalytic activity.

It has been shown in the literature that the introduction of potassium ions modifies the electronic and structural properties of supported noble metals. Thus, XPS was performed to determine the changes in the electronic nature of Pd species caused by the potassium dopant (Figure 2). The peaks at approximately 338 eV and approximately 335 eV are assigned to



Figure 1. a-d) TEM images of undoped and K-doped Pd/NaY catalysts and f) their crystal facets.

Table 1. The structural properties and catalytic activity ^[a] of NaY ^[b] zeolite and Pd/KNaY() ^[c] catalysts.													
Catalysts	Pd loading ^[d] [wt%]	Dispersity ^[e] [%]	TOF ^[f] [h ⁻¹]	STY $[g L^{-1} h^{-1}]$			Sel. based on MN [%]			S_{BET} [m ² g ⁻¹]	Pore vol. ^[g] [ml g ⁻¹]	Pore width ^[h] [Å]	E _a ^[i] [kJ mol ⁻¹]
				DMC	DMM	MF	DMC	DMM	MF	_	_		
Pd/NaY	0.99	91.8	167.5	550	33.6	32.5	80.8	6.2	13.0	699	0.29	8.5	60.3±1.2
Pd/KNaY(1.8)	0.98	88.9	180.3	613	37.8	22.7	83.8	5.9	10.3	710	0.33	8.0	42.5 ± 1.0
Pd/KNaY(3.6)	0.97	90.3	196.9	696	35.9	21.5	86.3	5.4	8.3	730	0.32	7.7	33.4 ± 0.9
Pd/KNaY(4.9)	0.97	91.1	162.1	567	38.6	31.5	80.0	9.3	10.7	685	0.31	7.5	37.6 ± 0.8
Pd/KNaY(6.5)	0.98	89.6	153.0	519	37.3	33.3	78.6	8.1	13.3	650	0.29	7.3	37.0 ± 1.4

[a] Reaction conditions: gas hourly space velocity (GHSV) = 8000 h⁻¹, CO/MN/N₂ = 3.3:20:76.7 (vol.%), T = 383 K, P = 0.2 MPa. [b] Physical properties of NaY zeolite: S_{BET} : 698 m²g⁻¹, Pore vol.: 0.31 mLg⁻¹, Pore width: 8.6 Å. [c] Pd/KNaY(i) catalysts: *i* represents the molar ratio of K/Pd, KNaY denotes the K-doped NaY zeolite as the carrier to load the Pd active species. [d] Determined by ICP–OES. [e] Determined by CO chemisorption characterization. [f] Calculated by the moles of DMC per mole Pd per hour. [g] Pore volume was determined by the t-plot method. [h] Pore width was calculated using the Horvath–Kawazoe method. [i] E_a was calculated based on Arrhenius equation.



Figure 2. Pd 3d XPS spectra of undoped and K-doped Pd samples.

the oxidation and metallic states of Pd, respectively.^[10] The two states of Pd species are clearly distinguished for the original Pd/NaY catalyst. With an increasing potassium level, the peaks of oxidation and metallic states of Pd begin to overlap and finally become a single peak. Additionally, the band energies of Pd species gradually decline regardless of the oxidation and metallic state, which suggests that the electron density of Pd species is progressively enhanced.^[11] Therefore, the assumption is proposed that the addition of potassium decorates the electronic nature of Pd active species and, consequently, the carbonylation reactivity.

For the MN carbonylation reaction system, the activation of CO plays an important role. In the light of the observed effects of potassium on the electronic properties of Pd species, we speculate this function may further affect desorption and/or adsorption of CO on the active species, and finally influences the catalytic performances. The CO TPD was thus employed to verify the conjecture. In Figure 3, the CO TPD spectra and the results of peak fitting for undoped and doped catalysts are shown. The spectrum of parent sample is composed of three peaks. With increasing potassium levels, the areas of peak (I)



Figure 3. CO TPD spectra of Pd/NaY catalysts with different K/Pd mole ratio.

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and (III) decrease, whereas the area of peak (II) increases. The dominant moderate-level adsorption observed suggests that the introduction of potassium modulates the CO adsorption strength such that CO molecule is more able to participate in subsequent reaction.^[12] Moreover, the CO desorption peaks (I) and (II) (Figure 3) move to higher temperature at the lower K/Pd molar ratio until the ratio reaches 3.6, and then shifts in the opposite direction. Peak (III) also drifts to higher temperatures but disappears when K/Pd exceeded 3.6. These phenomena were caused by changes in the Pd–CO interaction intensity. Specifically, these results indicate that the Pd–CO interaction strength is improved by adding a certain amount of potassium ions, but it is counterproductive if added in excess.

Further experiments were conducted to understand the influences of potassium on the adsorption properties of CO molecule in more detail. In Figure 4, the FTIR spectra of CO adsorbed onto the undoped and K-doped catalysts are shown.



Figure 4. FTIR spectra of CO (1 atm) adsorbed onto Pd/NaY and K-promoted Pd/NaY catalysts at 25 °C. a) 2200–2080 cm⁻¹, b) 2082–2000 cm⁻¹, c) 2008–1800 cm⁻¹, d) 1720–1800 cm⁻¹.

The bands at approximately 2170, 2162, and 2100 cm⁻¹ are attributed to carbonyls that are C-end-adsorbed on Na⁺ and K⁺, and to those O-end-adsorbed on Na⁺, respectively.^[13] Three main categories of carbonyls on Pd particles can thus be identified (Figure S3).^[8] (i) Linear carbonyls (top site) usually appear in the stretching region at approximately 2130–2000 cm⁻¹; bands at approximately 2070 cm⁻¹ and 2028 cm⁻¹ are assigned to CO adsorbed on terrace and edges or corners of particles, respectively.^[14] (ii) Two-fold bridged carbonyls are defined by a v(CO) in the interval at approximately 2000–1850 cm⁻¹; bands at 1990 cm^{-1} and 1950 cm^{-1} , 1910 cm^{-1} represent CO adsorbed on the {100} and {111} faces of Pd crystals, respectively (Figure 1 (f)).^[14b] (iii) Three-fold bridged carbonyls (hollow site), are characterized by a C-O stretching mode in the region at approximately 1920–1800 cm⁻¹.^[8, 11] As shown in Figure 4, the bands of the linear carbonyls adsorbed on the corners of Pd particles (\approx 2026 cm⁻¹) redshift first and then blueshift as the K/Pd atomic ratio increases. The bands of the carbonyls linearly adsorbed on terrace sites (\approx 2070 cm⁻¹) and those of 2and 3-fold bridged carbonyls did not seem to be affected by



changes in the metal K/Pd atom ratio. Another noteworthy feature is that augmenting the potassium loading of the catalyst caused a volcano-shaped CO adsorption peak (Figure 4b and c).

The phenomena seen in Figure 4 are the result of the variations in the interaction intensity of Pd–CO. After decorating the catalyst with potassium, the electron density of the Pd active surface sites is enhanced, this is well evidenced by the results of XPS (Figure 2). The increased electron density of Pd species can enhance back-donation from Pd to antibonding orbitals of CO, which weakens the C–O bond and thus induces a bathochromic shift of the vibration band (Figure 4b).^[8] If excess potassium species are added, the electron density of Pd is enhanced even further. The exorbitant electron density decreases the electron donation from the highest occupied molecular orbital (HOMO) of CO to the metal (σ -bond) to hinder the adsorption of molecular CO,^[11] resulting in the blueshifting of the band of the linearly adsorbed CO and the disruption of CO adsorption on the surface.

Additionally, in Figure 5 the relationships between the areas of CO adsorption peaks in Figure 4 and the catalytic performances is shown. The TOF of DMC presents a \cap -shape with the peak areas of 2- and 3-fold bridged carbonyls, whereas it monotonically increases with the peak area of linear carbonyls adsorbed on the corner site of Pd clusters. The case of the dominant adsorption of linear carbonyls is unusual for carbonylation reactions.^[15] It can be inferred that the linear carbonyls adsorbed on the corner sites of Pd particles are more active participators for this carbonylation reaction thanks to some interaction with the alkali metal cations than the 2- and 3-fold bridged carbonyls. Cairon et al. studied adsorption of CO on NaY and indicated that alkali metal cations interact with CO through the C end and/or O end, in the form of M⁺...CO and/ or M⁺...OC adducts.^[13] Accordingly, the combination of potassium and palladium species is speculated to be responsible for the efficient activation of linearly adsorbed CO molecule. The appearance of Pd–CO···Na⁺/K⁺ (\approx 1766/1740 cm⁻¹) peaks in the spectra in Figure 4(d) may be a good indication of the synergy between Pd and potassium species.^[14b]





To examine in more detail about the interaction among potassium ions, Pd species, and CO molecule, we performed DFT calculations by using the DMol3 code from Materials Studio $3.0.^{[16]}$ A Pd₁₃ cluster is selected as the active-site model of this carbonylation reaction (Figure 6 c). The well described 16 tetrahedral (T) cluster including two six-ring and three four-ring structures is chosen as the Y-type zeolite support model (Figure 6b). (The computational details, selection of active sites, and support models are given in the Experimental Section). The charge imbalance owing to the presence of aluminum in this 16-T cluster model of zeolite framework is compensated by sodium cations.



Figure 6. Results from DFT calculations: a) Optimized structure of Pd cluster embedded in the supercage of Y-type zeolite. b) Schematic view of the 16T cluster model for the Y-type zeolite. c) The optimized structure of Pd/Y catalyst (the single Pd atom was used to balance the charge in the Y-type zeolite structure with Si/Al = 2.2).

The Si/Al ratio (2.2) and the number and locations of chargebalancing cations are in accordance with experimental findings. The sodium cations are located in the supercage: (1) at the center of sodalite but displaced into the supercage; (2) at the center of hexagonal prisms but migrated into the supercage.^[17] The positions of sodium cations after optimization are shown in Figure S2. The potassium-doped catalysts are formed by gradually replacing the Na atom with the K atom, as illustrated in Figure S2 d–f.

A charge analysis was first performed for all optimized structures, which is listed in Table 2. The charges of Pd atoms are positive in Pd/Y catalyst. As the doping amount of alkali metal (Na and/or K) increases, the negative charges on Pd atoms gradually increase, especially for Pd atom numbers 2, 3, 4, 5 and 13. As these Pd atoms located on the top layer of cluster (seen in Figure S2) are relatively closer to alkali metal, the doped alkali metal atoms mainly influence their electron density. The enhanced negative charges on Pd verify that alkali metal atoms donate electrons to Pd, which is consistent with the XPS results. Additionally, it is clearly seen that the number of negative charges on Pd atoms increases stepwise if the sodium atoms are progressively substituted by potassium atoms (Table 2), which suggests that the influence of potassium on the electron density of Pd atoms is much larger than that of sodium. This observation provides some insight into the interpretation of the promotion behavior of potassiumdoped Pd/NaY catalyst.

To clarify the influences of enhanced electronic density of Pd on reactivity, the properties of CO adsorption/desorption on model catalysts were further studied in depth. According to



Entry ^[a]	Pd ^[b]	2 Na	3 Na	K 2 Na	2 K Na	3 K				
1	0.116	0.012	-0.059	-0.030	-0.016	-0.008				
2	0.025	-0.093	-0.191	-0.192	-0.186	-0.210				
3	0.007	-0.020	-0.046	-0.061	-0.066	-0.071				
4	0.010	0.002	-0.010	-0.025	-0.026	-0.034				
5	0.015	0.001	-0.016	-0.031	-0.034	-0.033				
6	0.061	0.071	0.023	-0.004	-0.021	-0.005				
7	0.154	0.176	0.169	0.158	0.165	0.158				
8	0.173	0.095	0.018	0.004	-0.004	0.001				
9	0.119	0.112	0.097	0.085	0.080	0.082				
10	0.166	0.137	0.129	0.107	0.100	0.099				
11	0.165	0.150	0.142	0.129	0.123	0.121				
12	0.214	0.263	0.272	0.301	0.293	0.296				
13	0.370	0.034	0.003	-0.009	-0.003	-0.020				
[a] The n lysts (Fig lysts of F	[a] The number represents the number of Pd atoms in the model cata- lysts (Figure 6c). [b] Pd, 2Na, 3Na, K2Na, 2KNa, and 3K denote the cata- lysts of Pd/Y, Pd/2NaY, Pd/3NaY, Pd/K2NaY, and Pd/3KY, re-									

the charge distribution of Pd atoms and the principles of electrostatic attraction, Atom numbers 2, 3, and 13 were chosen as the adsorption sites of CO molecule. Owing to the three different adsorption manners of the CO molecule, we investigated the cases: top-site (linear adsorption), bridge-site, and hollow site adsorption for each model catalyst. The optimized structures are illustrated in Figure S3. In Table 3 and Figure 7, the adsorption properties of CO on undoped and doped model catalysts are illustrated. The desorption energy of CO molecules (E_{des}) for Pd/Y model catalyst is 1.58 eV consistent with

spectively. 2 and 3 denote the number of alkali metal atom in catalyst.

the data reported in the literature.^[18] If Na and/or K atoms are readed to Pd/Y model catalyst, the E_{des} of the CO molecule displays a volcano shape, which implies that the interaction K strength between Pd and CO increases first and then decreases. The impact of doping K atoms on E_{des} is larger than that of p



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Figure 7. Changes of the CO bond order given as the concentration of alkali cations on the model catalysts. Pd, 2 Na, 3 Na, K 2 Na, 2 K Na, and 3 K represent the model catalyst of Pd/Y, Pd/2 NaY, Pd/3 NaY, Pd/K Na Y, Pd/2 K NaY, and Pd/3 KY, respectively. 2 and 3 denotes the number of alkali metal atoms in the model catalyst.

doping Na atoms. These observations echo the results of CO TPD. With increasing alkali metal level, the bond order of adsorbed CO clearly decreases in comparison with undoped Pd/Y catalyst. These results indicate that CO is more strongly activated by additional doped alkali metal. The data of Pd–C bond parameters also indirectly reflects the activation of CO. It is noteworthy that the bond order of CO diminishes even more when Na atoms are gradually replaced by K atoms, but it will rebound after complete replacement with K atoms (Table 3 and Figure 7). These findings suggest that the introduction of K atom more facilitate the activation of CO than the addition of Na to Pd/Y model catalyst, which is a strong evidence of K promotion effect in catalytic activities.

Model catalysts	Adsorption	CPd 2 ^[a]		C–Pd 3		C–Pd 13		C0		Desorption
	manner	BL ^[b]	BO ^[c]	BL	BO	BL	BO	BL	BO	Energy[d] [ev
	top	1.884	1.28	-	_	-	-	1.154	2.21	
Pd/Y	bridge	1.995	0.79	2.000	0.76	-	-	1.177	2.02	1.58
	hollow	2.069	0.56	2.063	0.59	2.080	0.56	1.191	1.90	
	top	1.846	1.36	-		-	-	1.161	2.13	
Pd/2 NaY	bridge	1.978	0.75	1.999	0.78	-	-	1.176	2.02	1.63
	hollow	2.094	0.52	2.062	0.60	2.074	0.60	1.188	1.88	
	top	1.840	1.54	-	-	-	-	1.182	1.86	
Pd/3 NaY	bridge	1.991	0.78	2.010	0.80	-	-	1.181	1.95	2.23
	hollow	2.084	0.53	2.073	0.61	2.074	0.59	1.197	1.83	
	top	1.838	1.57	-	-	-	-	1.183	1.84	
Pd/K2NaY	bridge	1.998	0.79	2.007	0.80	-	-	1.180	1.98	2.25
	hollow	2.064	0.56	2.091	0.58	2.068	0.62	1.200	1.82	
	top	1.837	1.58	-	-	-	-	1.186	1.82	
Pd/2KNaY	bridge	1.996	0.80	2.013	0.79	-	-	1.183	1.97	2.29
	hollow	2.069	0.56	2.103	0.57	2.065	0.64	1.200	1.82	
	top	1.833	1.56	-	-	-	-	1.181	1.89	
Pd/3 KY	bridge	1.978	0.81	1.999	0.80	-	-	1.181	1.95	2.12
	hollow	2.056	0.58	2.109	0.57	2.063	0.64	1.206	1.78	

[a] C–Pd2 represents the bond between C atom and Pd atom No. 2. [b] BL indicates bond length. [c] BO indicates bond order. [d] CO desorption energy calculated by the following equation: $E_{des} = E(cat.) + E(CO) - E(cat.-CO)$, where E(cat.-CO), E(cat.), and E(CO) are the total energies of each structure.



Furthermore, the bond length and bond order of top-site-adsorbed CO display \cap - and U-shape, respectively. However, the data are irregular for CO adsorption on bridge-site and hollow-site.

The U-shape of CO bond order for top sites as a function of the potassium concentration implies that the activation extent of CO first increases and then decreases. In other words, the activation of CO is related to the concentration of potassium atoms. Doped certain amount of potassium can enhance the activation of CO, but excessive doping will lead to an opposite result. These results correlate well with the trends observed in activity data and characterization analyses (Figure 3 and 4).

Moreover, it is surprising to find that the bond orders of CO adsorbed on top sites for alkali metal doped model catalysts are atypically low (Figure 7), which distinguishes the case of undoped Pd/Y model catalyst. This unusual situation suggests that top-site-adsorbed CO molecules are much more activated than bridge- and hollow-site-adsorbed ones, coinciding with the prevailing linear carbonyls in Figure 4. Under the above analyses, it is reasoned that the exceptional situation of dwindling bond order for linear carbonyls is a cooperative consequence of Pd species and alkali metal. To further confirm this idea, a topological study on the electronic charge density distribution was conducted using the atoms in molecules (AIM) analysis.^[19] As shown in Figure 8 and S4, a bond critical point (BCP) is found between sodium/potassium and the O atom of linear CO. For all CO linear adsorption structures, the local topological properties (in a.u.) of the electronic charge density distribution and the Laplacian of electron density are shown in the Supporting Information, Table S1 and Figure S4. The positive values of $\bigtriangledown^2 \rho_{\rm b}$ for this BCP indicate that the interatomic



Figure 8. Molecular graphs for CO linearly adsorbed on a) Pd/3NaY, b) Pd/ K2NaY, c) Pd/2KNaY and d) Pd/3KY catalysts. Large circles correspond to the nuclei. Lines connecting the nuclei indicate bond paths. Small dots on lines are the BCP.

interaction between O and Na/K species are closed-shell (electrostatic) interactions.^[20] Potassium cations display the properties of Lewis acids in this case based on the definition of Lewis acids. According to the above experimental (Figure 4d) and theoretical analyses (Figure 8 and Figure S4), it can be concluded that the structure of Pd–CO···Na⁺/K⁺ indeed exists in K-promoted Pd/NaY catalysts during activation of CO molecule. As such, the activation of linearly adsorbed CO molecule is not only ascribed to its interaction with Pd species but also to the interaction with potassium cations as Lewis acid sites in zeolite. This observed synergy between Pd and alkali metal is absent for linearly adsorbed carbonyls on terrace sites as well as for CO bound to bridge and hollow sites, reflected in the irregularity of bond orders (Figure 7).

The CO molecule is activated and thus energetically participates in the carbonylation reaction. In turn, the apparent activation energies (E_a) of MN carbonylation reaction should be reduced. To test this value, each catalyst was evaluated at different temperatures (373 K, 383 K, and 393 K). The logarithm of STY was correlated with the reciprocal of temperature to calculate E_a based on Arrhenius equation. The E_a (Table 1) for doped samples is, as expected, lower than that of the undoped sample.^[5b] It is therefore concluded that adding a certain amount of potassium facilitates the activation of CO and, consequently, the rate of the carbonylation reaction.

Conclusions

We have successfully enhanced the catalytic performance of Pd/NaY catalyst for the carbonylation reaction of methyl nitrite by adding potassium dopants to the zeolite structure. The origin of the outstanding reactivity was unraveled through a combination of experimental characterizations and DFT calculations. Doping the structure with potassium enhanced the electron density of Pd species in the catalyst, leading to an improvement in the activation of CO. Moreover, the potassium cations, presenting the nature of Lewis acid sites in zeolite, interacted with the O atom of CO linearly adsorbed onto the corner site of the Pd cluster, further activating the adsorbed CO entities. These two activation ways work together to allow CO to easily participate in the carbonylation reaction, in turn, promote the synthesis of dimethyl carbonate. This paper demonstrated a synergy effect between potassium and Pd active species in the carbonylation of methyl nitrate to dimethyl carbonate in detail. Understanding this cooperativity is conducive to comprehending the mechanism for this carbonylation reaction, and consequently to aiding in the design and optimization of catalysts.

Experimental Section

Preparation of catalysts

NaY zeolite was first calcined at 550 °C for 5 h in air at a ramp rate of 2 °C min⁻¹. The K-doped NaY support (KNaY) was prepared by a conventional liquid-phase ion-exchange technique. NaY zeolite powder was dispersed into a previously prepared KCl solution and then stirred vigorously for 12 h at 80 °C. To remove excess chloride



ions, the exchanged samples were thoroughly washed with deionized water, dried at 110 °C for 2 h, and calcined at 550 °C for 5 h. The process of loading Pd active component was similar. Notably, the Pd(NH₃)₄Cl₂ solution (0.01 M) was added dropwise to KNaY slurry at 80 °C and then magnetically stirred for 8 h. The calcination procedure was performed at 200 °C for 4 h at a ramp rate of 0.5 °Cmin⁻¹ in a muffle furnace. The samples were designated by the label Pd/KNaY(*i*) with *i* representing the molar ratio of potassium and palladium. The loadings of Pd and the K/Pd molar ratios were analyzed by inductively coupled plasma optical emission spectroscopy (ICP–OES). The details of catalysts characterization method (BET, XRD, CO TPD, XPS, ICP and CO IR) and the catalytic activity test are described in the Supporting Information.

Details of DFT calculations

DFT calculations were performed using DMol3 code from Materials Studio 3.0 with the exchange and correlation energy functional expressed in the Perdew–Wang (PW91) generalized gradient approximation (GGA).^[21] A double numerical plus polarization (DNP) basis set was used throughout the calculation. The convergence criteria were set to be 2×10^{-5} Ha, 0.004 HaÅ⁻¹, and 0.005 Å for energy, force, and displacement convergence, respectively. A self-consistent field (SCF) density convergence with a threshold value of 1×10^{-5} Ha was specified. All wave function (wfn) files used in this work were generated by gaussian03 software.^[22] The topological graphs were plotted by Multiwfn software.^[23]

Initially exchanged Pd(NH₃)₄²⁺ ions were gradually reduced by CO, migrated, agglomerated and eventually formed Pd clusters during the carbonylation reaction.^[4] Using studies about the formation of Pd particles in NaY and the pore size (13 Å) of FAU zeolite as guides, Pd₁₃ cluster (8.5 Å) was selected as the carbonylation active site model.^[24] Additionally, owing to steric effects (Figure 6a), the locations of Pd cluster and charge-balanced cations,^[17a,25] a well described 16 tetrahedral (T) cluster consisting of two 6-ring and three 4-ring structures was used as the model of Y-type zeolite. All dangling bonds were saturated with hydrogen atoms and the terminal H atoms were oriented in the direction of next tetrahedral atom.

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Keywords: carbonylation \cdot density functional calculations \cdot doping \cdot palladium \cdot potassium

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