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1       **Mechanical pressure-mediated Pd active sites formation in NaY**  
2       **zeolite catalysts for indirect oxidative carbonylation of methanol to**  
3       **dimethyl carbonate**

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19

1 **Abstract**

2       The structural transformation of metal-containing zeolite catalysts subjected to  
3 mechanical compression is often disregarded in the preparation of catalysts. Herein,  
4 the impact of the mechanical compression on the catalytic active sites of Pd/NaY  
5 catalysts responsible for the indirect oxidative carbonylation of methanol to dimethyl  
6 carbonate (DMC) has been disclosed. The DMC selectivity of the catalysts was found  
7 to strongly depend on the mechanical-pressure applied, as the mechanical pressure  
8 controlled the ratio of Pd<sup>(2+δ)+</sup> and Pd<sup>δ+</sup> species (0 < δ ≤ 2) in the catalysts. The  
9 mono-dispersed Pd clusters (1.3 nm) in the Pd/NaY catalyst were obtained under  
10 mechanical treatment of 300 MPa. This catalyst showed high CO conversion of 89%  
11 and DMC selectivity of 83%, that maintained for at least 150 h. Combining  
12 experimental and density functional theory studies, we revealed that the Pd<sup>δ+</sup> rather  
13 than the Pd<sup>(2+δ)+</sup> species enhanced the adsorption of CO and CH<sub>3</sub>ONO reactants and  
14 inhibited the decomposition of CH<sub>3</sub>ONO reactant into byproducts, and thus enhanced  
15 the DMC selectivity. The mechanical pressure applied had a noticeable effect on the  
16 structural features of the metal-containing zeolite catalysts, but despite its importance,  
17 this aspect has been poorly considered in the field of heterogenous catalysis.

18

19 **Keywords:** Mechanical pressure; Active site; Palladium; NaY; Carbonylation;  
20 Dimethyl carbonate

## 1 **1. Introduction**

2 In commercial applications, heterogenous catalysts are seldom utilized in a  
3 powder form, and thus the catalyst shaping is indispensable to be implemented in  
4 industrial reactors [1–3]. Several shaping methods are used, among which the most  
5 important are extrusion, spray drying, tableting and granulation [4,5]. Among these  
6 methods, the tableting method produces the most regularly shaped bodies such as  
7 pellets and cylinders, which often have high mechanical strength [6,7]. However, the  
8 tableting process is often conducted by trial-and-error approach [8]. The tableting  
9 method is often proprietary, and the related patents provided a range of shaping  
10 conditions and rarely disclosed any details [9,10]. In most cases, there is a huge  
11 difference in the performance of catalysts in powder and the shaped forms [11].  
12 Therefore, understanding the chemical and structural features of catalysts behind  
13 tableting process is desirable for both fundamental research and commercial  
14 applications.

15 High-pressure inorganic chemistry is one of the “Top Ten Emerging Technologies  
16 in Chemistry 2020” reported by the International Union of Pure and Applied  
17 Chemistry (IUPAC). Previous high-pressure studies of zeolites revealed unusual  
18 structural and chemical changes [12–14]. Several zeolites were amorphized under  
19 high pressure, i.e., pressure-induced full or partial amorphization reverting back to the  
20 original crystalline structure upon decompression [15,16]. The partly disordered  
21 structure resulted from the local collapse and distortion of zeolite framework, which

1 was closely related to the properties of charge-balancing cations in the zeolites [17].  
2 Lee et al. reported that high pressure of 1.9 GPa led to the irreversible migration and  
3 rearrangement of charge-balancing cations, i.e., pressure-induced migration, and to  
4 the formation of super-hydrated zeolite with a doubled water content described as  
5 pressure-induced hydration [18]. They also suggested that the structural changes of  
6 zeolites under high pressure were mediated by the charge-balancing cations and their  
7 coordination environment, which could drive the changes in the  
8 order-disorder/disorder-order transitions and framework distortion [19]. Jordá et al.  
9 demonstrated that ITQ-29 zeolite with LTA topology was transformed into a new  
10 ITQ-50 zeolite under a high pressure of 3.2 GPa [20]. The behavior of  
11 metal-containing zeolite catalysts under high pressure has not been systematically  
12 investigated. It is worthwhile to study whether the catalytic performance of  
13 metal-containing zeolite catalysts is dependent on the mechanical pressure, and if so,  
14 to what extent.

15 Green and sustainable manufacture of valuable commercial chemicals based on  
16 C1 chemistry via one-carbon feedstocks from abundant carbon resources such as  
17 shale gas and coal, is an emerging alternative to the petroleum routes [21–23].  
18 Dimethyl carbonate (DMC) is a green, versatile compound which can be used as a  
19 methylating and methoxycarbonylating agent, fuel additive, electrolyte liquid carrier  
20 for lithium-ion batteries, as well as for polycarbonate and isocyanate syntheses  
21 [24,25]. The traditional production of DMC ((CH<sub>3</sub>O)<sub>2</sub>CO) involves the utilization of a

1 toxic feedstock, phosgene ( $\text{COCl}_2$ ) [26]. In the past decade, extensive studies have  
2 been carried out to develop environmentally sustainable and efficient processes for  
3 DMC production including the transesterification of methanol ( $\text{CH}_3\text{OH}$ ) with  
4 ethylene/propylene carbonate, the direct synthesis from carbon dioxide ( $\text{CO}_2$ ) and  
5  $\text{CH}_3\text{OH}$ , the alcoholysis of urea, and direct/indirect oxidative carbonylation of  
6  $\text{CH}_3\text{OH}$  [27–29]. Among these methods, the indirect oxidative carbonylation of  
7 methanol to DMC has gained substantial interest due to the cheap raw materials, mild  
8 operation conditions and high atom efficiency [30]. This process involves two  
9 separate reactions presented in Scheme S1 in Supporting Information (SI): (1)  
10 Pd-catalyzed oxidative carbonylation to DMC:  $\text{CO} + 2\text{CH}_3\text{ONO} \rightarrow (\text{CH}_3\text{O})_2\text{CO}$   
11  $+ 2\text{NO}$ , and (2) non-catalytic methyl nitrite ( $\text{CH}_3\text{ONO}$ ) regeneration with recycled NO:  
12  $2\text{CH}_3\text{OH} + 2\text{NO} + 1/2\text{O}_2 \rightarrow 2\text{CH}_3\text{ONO} + \text{H}_2\text{O}$ . The overall reaction ( $\text{CO} + 2\text{CH}_3\text{OH}$   
13  $+ 1/2\text{O}_2 \rightarrow (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O}$ ) is a green and efficient process converting C1  
14 feedstocks (CO and  $\text{CH}_3\text{OH}$ ) to C2 product.

15 The gas-phase indirect oxidative carbonylation of methanol to DMC has been  
16 industrially implemented by Ube Industries, Ltd., Japan, using a  $\text{PdCl}_2$ /active-carbon  
17 catalyst [31,32]. However, chlorine such as hydrogen chloride ( $100 \mu\text{L L}^{-1}$ ) must be  
18 added into the reactants to prevent the Pd sintering and maintain the activity of  
19 chlorine-containing catalyst [32,33]. There is an incentive to eliminate chlorine from  
20 this process to reduce costs associated with equipment corrosion, chlorine  
21 regeneration and generation, product purification and emissions. Consequently, the

1 development of chlorine-free, high-performance Pd catalysts is highly desirable for  
2 the DMC synthesis. Various chlorine-free Pd catalysts have been investigated, and the  
3 most appropriate catalyst support was NaY zeolite in comparison to NaX,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  
4  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, silica, and MgO [31,34,35]. Guo et al. revealed that the copper promoter  
5 could improve the Pd dispersion and maintain the Pd<sup>2+</sup> active sites on the Pd/NaY  
6 catalyst [36]. Dong et al. reported that potassium-doped Pd/NaY catalyst enhanced the  
7 activation of CO reactant by forming a Pd-CO...K<sup>+</sup> structure [37]. They also revealed  
8 that Lewis acidity of the Pd/NaY catalyst favored the DMC formation, while Brønsted  
9 acidity could accelerate the undesired decomposition of CH<sub>3</sub>ONO reactant into  
10 methyl formate and dimethoxymethane byproducts [34]. Tan et al. found that the  
11 catalytic activity of the Pd/NaY catalyst was related to the high oxidation state of Pd  
12 species, which could be tuned by the organic ligands [38]. They also demonstrated, by  
13 performing density functional theory (DFT) calculations, that the  
14 mononuclear-isolated Pd<sup>2+</sup> centers are critical for high DMC selectivity while the  
15 aggregation of Pd species was responsible for the formation of dimethyl oxalate  
16 byproduct [35]. The possible mechanism of the reaction followed oxidative addition  
17 and reductive elimination, and consisted of (1) oxidization of Pd<sup>0</sup> species by methyl  
18 nitrite (CH<sub>3</sub>ONO) reactant to generate NO-Pd<sup>2+</sup>-OCH<sub>3</sub>, (2) insertion of adsorbed CO  
19 into NO-Pd<sup>2+</sup>-OCH<sub>3</sub> to form NO-Pd<sup>2+</sup>-COOCH<sub>3</sub>, and (3) the reaction between  
20 NO-Pd<sup>2+</sup>-COOCH<sub>3</sub> and NO-Pd<sup>2+</sup>-OCH<sub>3</sub> to yield DMC [33,39]. The Pd<sup>2+</sup> species are  
21 generally considered to be the active sites for the formation of DMC [30,33,35]. In

1 view of the redox cycle of active sites, the function of Pd<sup>0</sup> species is still under  
2 discussion. Yamamoto et al. reported that Pd/NaY catalyst showed a delayed  
3 deactivation and decreased by about 50% after 300 h test [40]. Tan et al. found that  
4 Pd/NaY catalyst with mononuclear-isolated Pd<sup>2+</sup> centers was stable for at least 100 h  
5 [35], but the selectivity of inevitable byproducts such as methyl formate and  
6 dimethoxymethane was not disclosed. Recently, we reported on the preparation of  
7 stable Pd/EMT catalyst tested for 130 h. We found that the EMT zeolite framework  
8 could inhibit the palladium sintering and maintain the Pd<sup>2+</sup> active sites [41]. The  
9 chlorine-free Pd-based catalysts are still under development, and the bottleneck for  
10 their industrialization is the lack of sufficiently active and stable catalysts.

11 Herein, we presented the mechanical pressure-mediated preparation of  
12 Pd-containing NaY zeolite catalyst (Pd/NaY) by a tableting method. The Pd/NaY  
13 catalyst was tested in the reaction of indirect oxidative carbonylation of methanol to  
14 DMC. The structural changes that took place during the mechanical compression of  
15 the Pd/NaY catalyst and their effects on the catalytic performance in the DMC  
16 synthesis were disclosed.

## 17 **2. Experimental**

### 18 *2.1. Catalyst preparation*

19 NaY zeolite was kindly supplied by Daqing Chemical Research Center, China.  
20 Prior to the ion exchange, the NaY zeolite was pre-activated at 550 °C for 2 h under



1 static air. In a typical process, 16.7 mg palladium chloride ( $\text{PdCl}_2$ , Sinopharm  
2 Chemical Reagent Co., Ltd., China) was dissolved in 1.2 mL,  $0.94 \text{ mol L}^{-1}$  ammonia  
3 ( $\text{NH}_3$ ) solution to form a clear palladium ammonia complex ( $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ ) solution.  
4 The  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$  solution was added dropwise into the activated NaY zeolite slurry  
5 containing 1.0 g zeolite and 100.0 g deionized water. The resulting suspension was  
6 stirred at room temperature ( $25 \text{ }^\circ\text{C}$ ) for 12 h and subsequently was heated at  $80 \text{ }^\circ\text{C}$  to  
7 evaporate the excess ammonia until the pH value of the suspension decreased to  
8 7.0–7.2 [35,36]. Then the solid was collected by vacuum filtration and washed  
9 thoroughly with deionized water. After drying at  $80 \text{ }^\circ\text{C}$  for 6 h, the sample was  
10 calcined at  $200 \text{ }^\circ\text{C}$  for 2 h under static air. The as-prepared Pd/NaY catalyst had a  
11 Si/Al molar ratio of 2.8 and a Pd loading of 1.0 wt%, corresponding to roughly 1.2 Pd  
12 atoms per unit cell, which was determined by inductively coupled plasma-atomic  
13 emission spectroscopy (ICP-AES).

14 As known, the shaping pressure applied for commercial catalysts is in the range of  
15 100–1000 MPa using the tableting process [9]. To study the effect of the mechanical  
16 pressure, the as-prepared Pd/NaY catalyst was subjected to treatment under pressure  
17 in the range of 60–600 MPa (Fig. S1). After the mechanical compression, the samples  
18 were crushed and sieved into 60–80 mesh. The as-obtained catalysts in pellet form  
19 were denoted as Pd/NaY- $x$ , where  $x$  corresponds to the mechanical pressure (an  
20 example, the catalyst shaped at 300 MPa was named as Pd/NaY-300).

## 1 2.2. Characterizations

2 Transmission electron microscopy (TEM) images of the catalysts were recorded  
3 using a JEOL JEM-2100 TEM instrument. High-angle annular dark-field scanning  
4 transmission electron microscopy (HAADF-STEM) images were taken on a JEOL  
5 JEM-2100F STEM instrument. The chemical composition of the samples was  
6 determined by an energy dispersive X-ray spectrometer (EDS). Scanning electron  
7 microscopy (SEM) images were acquired on a JEOL JSM-7900F SEM instrument.  
8 The Pd loading and Si/Al molar ratio of the samples were measured by inductively  
9 coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo IRIS Intrepid  
10 II XSP. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on an  
11 Escalab 250xi spectrometer with an Al K $\alpha$  radiation. All binding energies were  
12 referenced to the C 1s peak at 284.6 eV. The solid-state  $^{29}\text{Si}$  cross-polarization  
13 magic-angle spinning nuclear magnetic resonance (CP MAS NMR), and single pulse  
14  $^{29}\text{Si}$  MAS NMR spectra were measured on a Bruker Avance 400 spectrometer. The  
15 chemical shifts were referenced to the kaolin ( $-91$  ppm).

16 X-ray diffraction (XRD) patterns of the catalysts were obtained using a Bruker D8  
17 Advance diffractometer with a Cu K $\alpha$  radiation. The relative crystallinity of the  
18 samples was determined by measuring the sum of eight Bragg peak areas, namely  
19 (331), (511), (440), (533), (642), (822), (555) and (664), and related to the peaks area  
20 of the reference sample [42]. The Pd/NaY powder catalyst before the mechanical  
21 compression was taken as a reference assigning 100% of crystallinity. After

1 subtracting the background and  $k\alpha_2$  line broadening from the obtained patterns, the  
2 average crystallite sizes were estimated using the Scherrer equation [43].

3 The unit cell parameter ( $\alpha$ ) of the samples was determined from the (555)  
4 reflection, using pure silicon as an internal standard [42]. The framework Si/Al molar  
5 ratio of the samples was estimated from the unit cell parameter ( $\alpha$ ) by the following  
6 equation [42]:

$$\text{Si/Al ratio} = \frac{25.858 - \alpha}{\alpha - 24.191}$$

7 Textural features of the samples were analyzed by  $N_2$  physisorption isotherms  
8 measured at  $-196$  °C using a Quantachrome Autosorb-IQ3 instrument. The specific  
9 surface area was calculated using the Brunauer-Emmett-Teller (BET) method; the  
10 pore size distribution was determined by the DFT model from the adsorption branch  
11 of the  $N_2$  sorption isotherms.

12 *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)  
13 experiments with a carbon monoxide (CO) probe molecule were performed in a  
14 Harrick Scientific HVC-DRP-4 cell fitted with ZnSe windows using a Bruker Vertex  
15 70 spectrometer, equipped with a mercury-cadmium-telluride (MCT) detector. The  
16 sample temperature was monitored by a K-type thermocouple welded onto the top  
17 center of the cell. Typically, about 0.002 g sample without diluents was pre-treated in  
18  $N_2$  flow ( $80 \text{ mL min}^{-1}$ ) at  $200$  °C for 1 h, and then cooled down to  $30$  °C for taking a  
19 background spectrum. The adsorption of CO was conducted at  $30$  °C using a gas  
20 mixture of 10 vol% CO in  $N_2$ . After that, the sample was purged thoroughly with pure

1 N<sub>2</sub> and then the DRIFTS spectra were recorded at 30 °C and 50 °C. Each spectrum  
2 was obtained using the Kubelka-Munk mode from 4000 cm<sup>-1</sup> to 600 cm<sup>-1</sup> (4 cm<sup>-1</sup>  
3 resolution and 32 scans).

### 4 2.3. Reactivity tests

5 The schematic diagram of the setup used for the catalytic test is presented in  
6 Scheme S2 (Supporting Information, SI). The indirect oxidative carbonylation of  
7 methanol to DMC was performed in a continuous-flow-type fixed-bed microreactor  
8 (quartz tube, 8 mm i.d.) under 0.1 MPa. Quartz wool was placed below the catalyst  
9 bed to hold the catalyst. The reaction temperature was maintained using a tube  
10 furnace equipped with a temperature-programed controller and a K-type  
11 thermocouple. The reactant of methyl nitrite (CH<sub>3</sub>ONO) was prepared through an  
12 esterification reaction ( $2\text{NaNO}_2 + 2\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 \rightarrow 2\text{CH}_3\text{ONO} \uparrow + \text{Na}_2\text{SO}_4 +$   
13  $2\text{H}_2\text{O}$ ) in the laboratory. The methyl nitrite gas was collected into a steel cylinder and  
14 then mixed with 99.99 vol% N<sub>2</sub> to form a gas mixture of CH<sub>3</sub>ONO/N<sub>2</sub> (1/4, mole).  
15 The 99.99 vol% N<sub>2</sub>, gas mixtures of CO/N<sub>2</sub> (1/9, mole) and CH<sub>3</sub>ONO/N<sub>2</sub> (1/4, mole)  
16 were fed via three calibrated mass flow meters, respectively. The gas hourly space  
17 velocity (GHSV) and reaction temperature were varied in the range of 4000–800000  
18 mL g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup> and 100–120 °C, respectively. Analysis of product stream was conducted  
19 using an online gas chromatography (Agilent 7890B). A thermal conductivity detector  
20 (TCD, 2.5-m molecular sieve 5A and 1.0-m HayeSep Q packed columns, Agilent) was

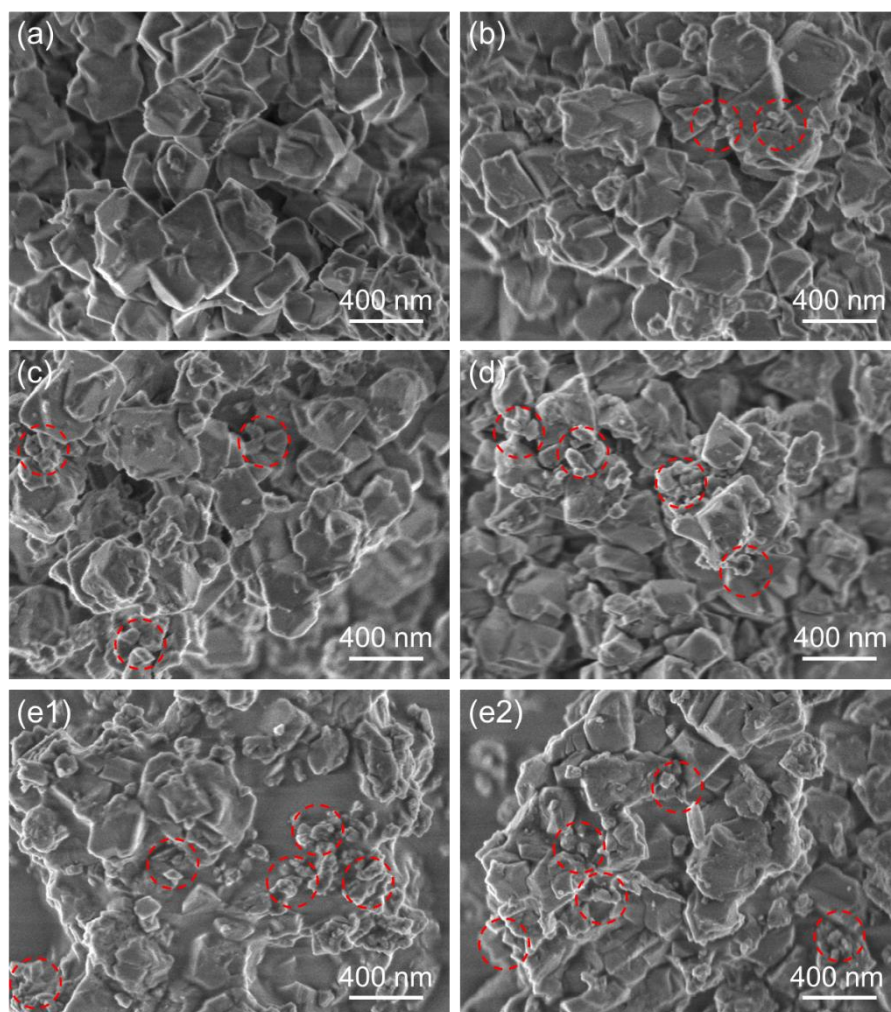
1 used to measure the CO and N<sub>2</sub>. A flame ionization detector (FID, 30-m HP-Innowax  
2 capillary column, Agilent) was employed to detect the CH<sub>3</sub>ONO, DMC,  
3 dimethoxymethane and methyl formate. The kinetic experiments, and the calculations  
4 of the turnover frequency (TOF), Thiele modulus, effectiveness factor, CH<sub>3</sub>ONO  
5 conversion, CO conversion, DMC, dimethoxymethane and methyl formate selectivity  
6 were presented in SI.

### 7 **3. Results and discussion**

#### 8 *3.1. General properties of Pd/NaY catalysts prepared under treatment with different* 9 *mechanical pressures*

10 The morphologies of the Pd/NaY catalysts prepared under treatment with different  
11 mechanical pressures are presented in Fig. 1. The Pd/NaY-60 catalyst consisted of  
12 aggregated crystals with a size of 300–500 nm (Fig. 1a). With increasing the  
13 mechanical pressure from 60 MPa to 150 MPa, the mechanical compression led to the  
14 fragmentation of several zeolite crystals, and consequently, sporadic small crystals  
15 were found on the Pd/NaY-150 catalyst as marked with red circles in Fig. 1b. With  
16 further increasing the mechanical pressure, more and more primary zeolite crystals  
17 were fragmented into small pieces as observed by SEM (Fig. 1c–e). In line with the  
18 SEM, the TEM pictures revealed the gradual decrease of average crystal size from  
19 370 nm to 180 nm with enhancing the mechanical pressure (Table 1). Even though the  
20 Scherrer equation is not highly accurate when the crystal size is larger than 100 nm  
21 [44], the crystal size estimated based on the XRD study showed a similar trend to the

1 TEM observation (Table 1).



2

3 **Fig. 1.** SEM images of the Pd/NaY catalysts prepared under treatment with different  
4 mechanical pressures: (a) Pd/NaY-60, (b) Pd/NaY-150, (c) Pd/NaY-300, (d)  
5 Pd/NaY-450 and (e1,e2) Pd/NaY-600. The fragmentations of zeolite crystals were  
6 marked with red circles.

7

8

9

10

1

2 **Table 1** Physicochemical properties of Pd/NaY catalysts prepared under treatment  
 3 with different mechanical pressures and their catalytic performance in the indirect  
 4 oxidative carbonylation of methanol to DMC.

Catalyst	$S_{\text{BET}}$	$V_{\text{micro}}$	Size,	Size,	$\alpha$	Si/Al,	Si/Al,	$E_a$	TOF
	( $\text{m}^2$	( $\text{cm}^3 \text{g}^{-1}$ ) <sup>a</sup>	XRD	TEM	(nm) <sup>d</sup>	XRD <sup>d</sup>	XPS <sup>e</sup>	(kJ	( $\text{s}^{-1}$ ) <sup>g</sup>
	$\text{g}^{-1}$ ) <sup>a</sup>		(nm) <sup>b</sup>	(nm) <sup>c</sup>				$\text{mol}^{-1}$ ) <sup>f</sup>	
Pd/NaY-60	893	0.32	89	370	2.463	2.8	2.8	67	0.25
Pd/NaY-150	853	0.31	84	300	2.463	2.8	2.8	67	0.22
Pd/NaY-300	841	0.30	79	270	2.464	2.7	2.7	67	0.13
Pd/NaY-450	800	0.28	64	200	2.464	2.7	2.7	58	0.11
Pd/NaY-600	732	0.26	54	180	2.464	2.7	2.7	55	0.08

5 <sup>a</sup> BET surface area, and the micropore volume determined by the *t*-plot method.

6 <sup>b</sup> Size calculated using the Scherrer equation.

7 <sup>c</sup> Size evaluated by TEM analysis.

8 <sup>d</sup> Unit cell parameter ( $\alpha$ ) determined from the (555) reflection, and the framework

9 Si/Al molar ratio estimated from the unit cell parameter ( $\alpha$ ).

10 <sup>e</sup> Si/Al molar ratio determined from the XPS spectra.

11 <sup>f</sup> Apparent activation energy ( $E_a$ ) calculated from the Arrhenius plots (Fig. S2).

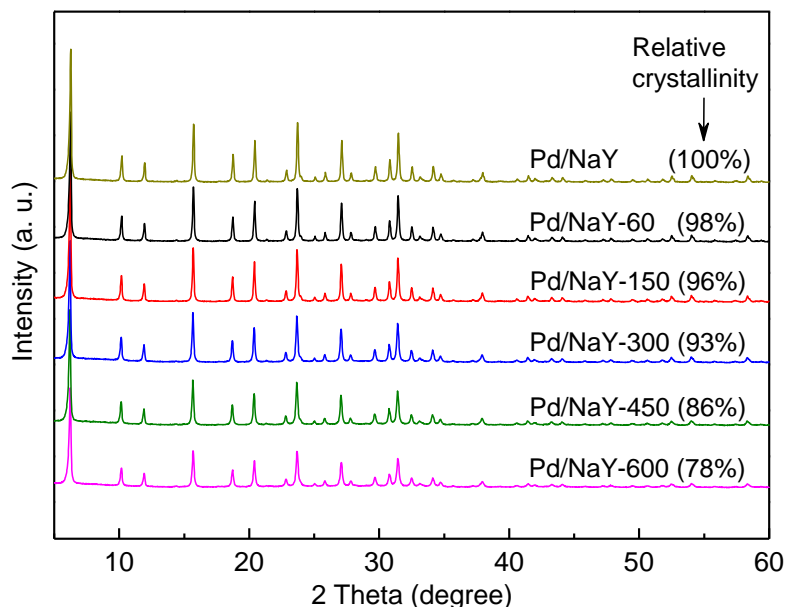
12 <sup>g</sup> TOF based on the CO conversion and surface Pd atoms calculated by decreasing the

13 CO conversion below 10 % with GHSV of 800000  $\text{mL g}_{\text{cat.}}^{-1} \text{h}^{-1}$  at 110 °C.

1

2       With increasing the mechanical pressure from 60 MPa to 300 MPa, the catalysts  
3 still had a high crystallinity (93%–98%), indicating that the mechanical compression  
4 caused a negligible damage of the zeolite framework (Fig. 2). However, the relative  
5 crystallinity was only 78% with further increasing the mechanical pressure up to 600  
6 MPa (Fig. 2). The obvious decrease in crystallinity was attributed to the  
7 pressure-induced amorphization [15,16], suggesting that more framework defects and  
8 amorphous aluminosilicate parts were formed in the Pd/NaY-450 and Pd/NaY-600  
9 catalysts. These five catalysts showed almost the same unit cell parameter of  
10 2.463–2.464 nm calculated using the silicon internal standard method (Table 1) [42].  
11 The Si/Al molar ratios measured by XRD and XPS were determined to be 2.7–2.8 on  
12 all five catalysts (Table 1), which was consistent with that of 2.8 measured by  
13 ICP-AES on the Pd/NaY catalyst before the shaping. In addition, the Bragg peaks of  
14 PdO (JCPDS 88-2434) and Pd<sup>0</sup> (JCPDS 01-1201) were not observed on all five  
15 catalysts (Fig. S3), which might be due to the high Pd dispersion and/or low Pd  
16 loading.





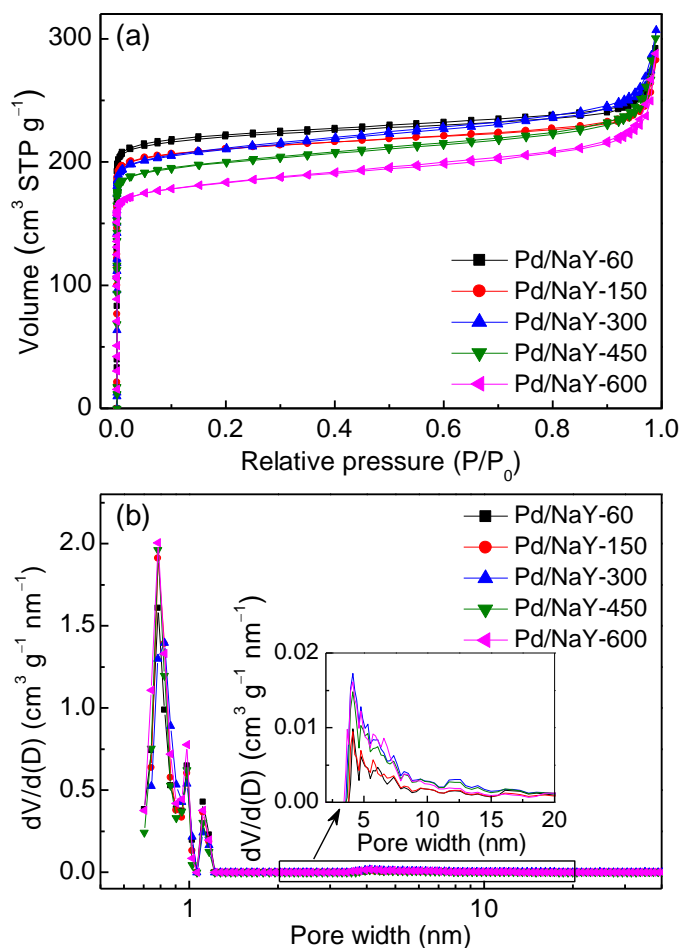
1

2 **Fig. 2.** XRD patterns of the Pd/NaY catalysts with the corresponding degree of  
 3 crystallinity (%) prepared under treatment with different mechanical pressures.

4

5 The N<sub>2</sub> adsorption isotherms of all five catalysts exhibited the typical profile of  
 6 microporous material (type I) with a high adsorption capacity at low P/P<sub>0</sub> (Fig. 3a)  
 7 [45]. All five catalysts showed similar pore size distribution consisting of micropores  
 8 of about 0.74 nm corresponding to the FAU-type zeolite, and mesopores of 4.1 nm  
 9 originated from the aggregation of zeolite crystals (Fig. 3b) [46]. This suggested that  
 10 the mechanical compression had a negligible effect on the pore size distribution of the  
 11 catalysts. As shown in Table 1, the Pd/NaY-60, -150 and -300 catalysts presented  
 12 similar surface area of 841–893 m<sup>2</sup> g<sup>-1</sup> and micropore volume of 0.30–0.32 cm<sup>3</sup> g<sup>-1</sup>.  
 13 When the mechanical pressure increases to 600 MPa, the surface area and volume of  
 14 the Pd/NaY-600 catalyst decreased to 732 m<sup>2</sup> g<sup>-1</sup> and 0.26 cm<sup>3</sup> g<sup>-1</sup>, respectively. This  
 15 indicated the formation of abundant framework defects and amorphous

1 aluminosilicate areas on the Pd/NaY-600 catalyst, which was consistent with the SEM  
2 and XRD results (Figs. 1–3 and Table 1).

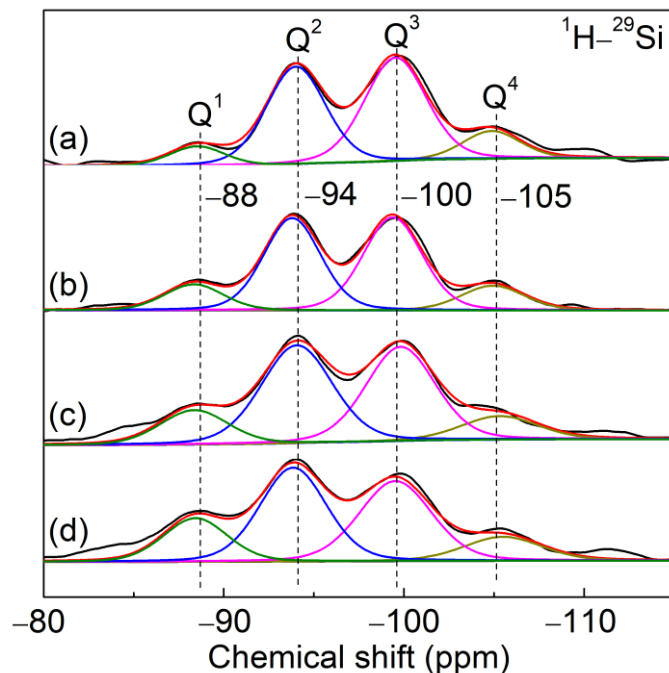


3  
4 **Fig. 3.** (a) N<sub>2</sub> sorption isotherms and (b) pore size distribution of the Pd/NaY catalysts  
5 prepared under treatment with different mechanical pressures. Pore size distribution  
6 was determined by the DFT model.

7

8 The <sup>29</sup>Si CP MAS NMR spectra of the catalysts prepared under different shaping  
9 pressures were recorded to examine the structural deformation, and the results are  
10 shown in Fig. 4. The spectra of all samples contained four resonance peaks at -88,  
11 -94, -100 and -105 ppm corresponding to Q<sup>1</sup>, Q<sup>2</sup>, Q<sup>3</sup> and Q<sup>4</sup> species, respectively

1 [47,48]. The resonance peak at  $-88$  ppm of the Pd/NaY-600 catalyst appeared with  
2 enhanced intensity in the  $^{29}\text{Si}$  CP MAS NMR spectrum in comparison to the  $^{29}\text{Si}$   
3 MAS NMR (Fig. S4). The existence of H–Si dipolar interaction due to the presence of  
4 framework defects (silanols) in the  $Q^1$  species is indicated [49–51]. As shown in Table  
5 2, the fraction of  $Q^1$  species was gradually increased from 7.2% to 16.7% with  
6 increasing the shaping pressure applied to the catalysts from 60 MPa to 600 MPa.  
7 This confirmed that more framework defects ( $Q^1$  species) in the catalysts were formed  
8 under treatment at high shaping pressure, which was consistent with the XRD and  $\text{N}_2$   
9 sorption results.



10

11 **Fig. 4.** Solid-state  $^{29}\text{Si}$  CP MAS NMR spectra of the Pd/NaY catalysts prepared under  
12 treatment with different mechanical pressures: (a) Pd/NaY-60, (b) Pd/NaY-150, (c)  
13 Pd/NaY-300 and (d) Pd/NaY-600.

14

1

2

3

4 **Table 2** Fraction of Si species of the Pd/NaY catalysts prepared under treatment with  
 5 different mechanical pressures determined by solid-state  $^{29}\text{Si}$  CP MAS NMR  
 6 spectroscopic study.<sup>a</sup>

Catalyst	Q <sup>1</sup> (-88 ppm)	Q <sup>2</sup> (-94 ppm)	Q <sup>3</sup> (-100 ppm)	Q <sup>4</sup> (-105 ppm)
Pd/NaY-60	7.2%	38.9%	43.1%	10.8%
Pd/NaY-150	11.0%	38.0%	39.7%	11.3%
Pd/NaY-300	13.3%	39.5%	37.0%	10.2%
Pd/NaY-600	16.7%	37.4%	34.7%	11.2%

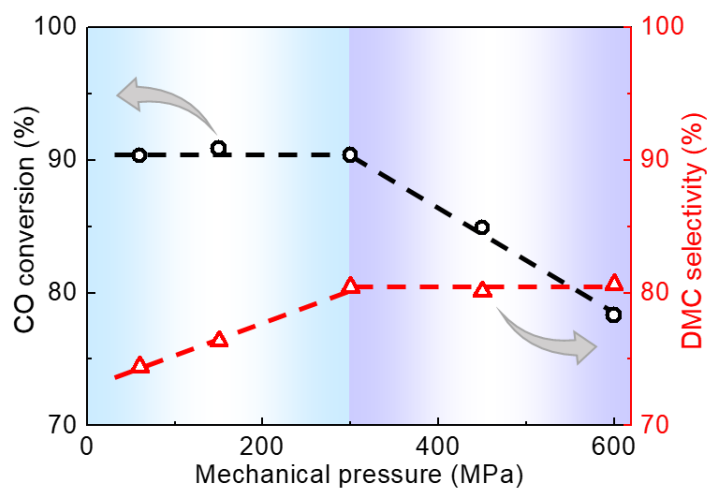
7 <sup>a</sup> Fraction of Si species determined based on the peak areas in the solid-state  $^{29}\text{Si}$  CP  
 8 MAS NMR spectra presented in Fig. 4.

9

10 *3.2. Catalytic performance of Pd/NaY catalysts prepared under treatment with*  
 11 *different mechanical pressures*

12 The catalytic activities of the series of Pd/NaY catalysts in the indirect oxidative  
 13 carbonylation of methanol to DMC are presented in Fig. 5. When the mechanical  
 14 pressure was less than 300 MPa, the CO conversion of about 90.4% was preserved  
 15 while the DMC selectivity increased progressively from 74.4% to 80.4%. At the

1 mechanical pressure larger than 300 MPa, the CO conversion declined from 90.4% to  
2 78.3% while the DMC selectivity of about 80% was preserved. In addition, the DMC  
3 selectivity using the Pd/NaY-60, -150, -300, -450 and -600 catalysts gradually  
4 increased, while the selectivity of methyl formate, dimethoxymethane byproducts  
5 progressively decreased with prolonging the reaction time from 1 h to 6 h (Fig. S5).  
6 For example, the selectivities of DMC, methyl formate and dimethoxymethane were  
7 75.7%, 13.7% and 10.6% after 1 h catalytic test, respectively. After 6 h, the  
8 selectivities of DMC, methyl formate and dimethoxymethane using the Pd/NaY-300  
9 catalyst were 80.4%, 10.9% and 8.6%, respectively (Fig. S5). The increase of DMC  
10 selectivity with prolonging the reaction time would be discussed in posterior XPS  
11 analysis.



12  
13 **Fig. 5.** CO conversion (black circles) and DMC selectivity (red triangles) for the  
14 indirect oxidative carbonylation of methanol to DMC on the Pd/NaY catalysts  
15 prepared under treatment with different mechanical pressures (60, 150, 300, 450 and  
16 600 MPa). Reaction conditions: 0.1000 g catalyst; feed gas, CO/CH<sub>3</sub>ONO/N<sub>2</sub> =

1 1/6/33 (mole); GHSV = 8000 mL  $\text{g}_{\text{cat.}}^{-1} \text{h}^{-1}$ ; reaction temperature = 110 °C; feed  
2 pressure = 0.1 MPa. The data were collected after 6 h catalytic test (each point was an  
3 average value of three measurements).

4

5

6 To study both internal and external diffusion, the kinetic experiments were  
7 conducted, and the results are shown in Fig. S6 and Table S1. The GHSV was in the  
8 range of 4000–24000 mL  $\text{g}_{\text{cat.}}^{-1} \text{h}^{-1}$  for the Pd/NaY-300 catalyst with different  
9 amounts of 0.1000 g and 0.1600 g; a similar CO conversion under the same GHSV  
10 was measured (Fig. S6). This suggested that the external diffusion effect could be  
11 neglected with a GHSV larger than 4000 mL  $\text{g}_{\text{cat.}}^{-1} \text{h}^{-1}$  [52,53]. The Thiele modulus  
12 was determined to be 0.156, 0.126, 0.113, 0.086 and 0.075 for the Pd/NaY-60, -150,  
13 -300, -450 and -600 catalysts, respectively (Table S1 and details are provided in SI).  
14 All the effectiveness factors approached the value of 1 and thus the DMC synthesis  
15 could be regarded as surface-limited reaction (Table S1) [54,55]. In addition, a  
16 thermocouple was placed in the middle of the catalyst bed for monitoring the reaction  
17 temperature during the catalytic tests, and no temperature rise (< 1 °C) was detected  
18 between the catalyst bed and the reactor during the kinetic experiments. Therefore, the  
19 heat and mass transfer should have a negligible effect on the reaction rate.

20 The apparent activation energies for the indirect oxidative carbonylation of  
21 methanol to DMC were measured in the temperature range of 100–120 °C with an

1 interval of 5 °C. As presented in Table 1, these five Pd/NaY catalysts showed  
2 comparable apparent activation energies of 55–67 kJ mol<sup>-1</sup> under the same reaction  
3 conditions (Fig. S2). This indicated that the dominant reaction pathway and the rate  
4 control step were identical for these catalysts [56,57]. Furthermore, the CO  
5 conversion was decreased below 10% at 110 °C and GHSV of 800000 mL g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>  
6 (details provided in SI). The intrinsic activity, i.e. the TOF decreased from 0.25 s<sup>-1</sup> to  
7 0.08 s<sup>-1</sup>, with increasing the shaping pressure from 60 MPa to 600 MPa (Table 1).  
8 This was possibly related to the amorphization of zeolite support after the mechanical  
9 treatment.

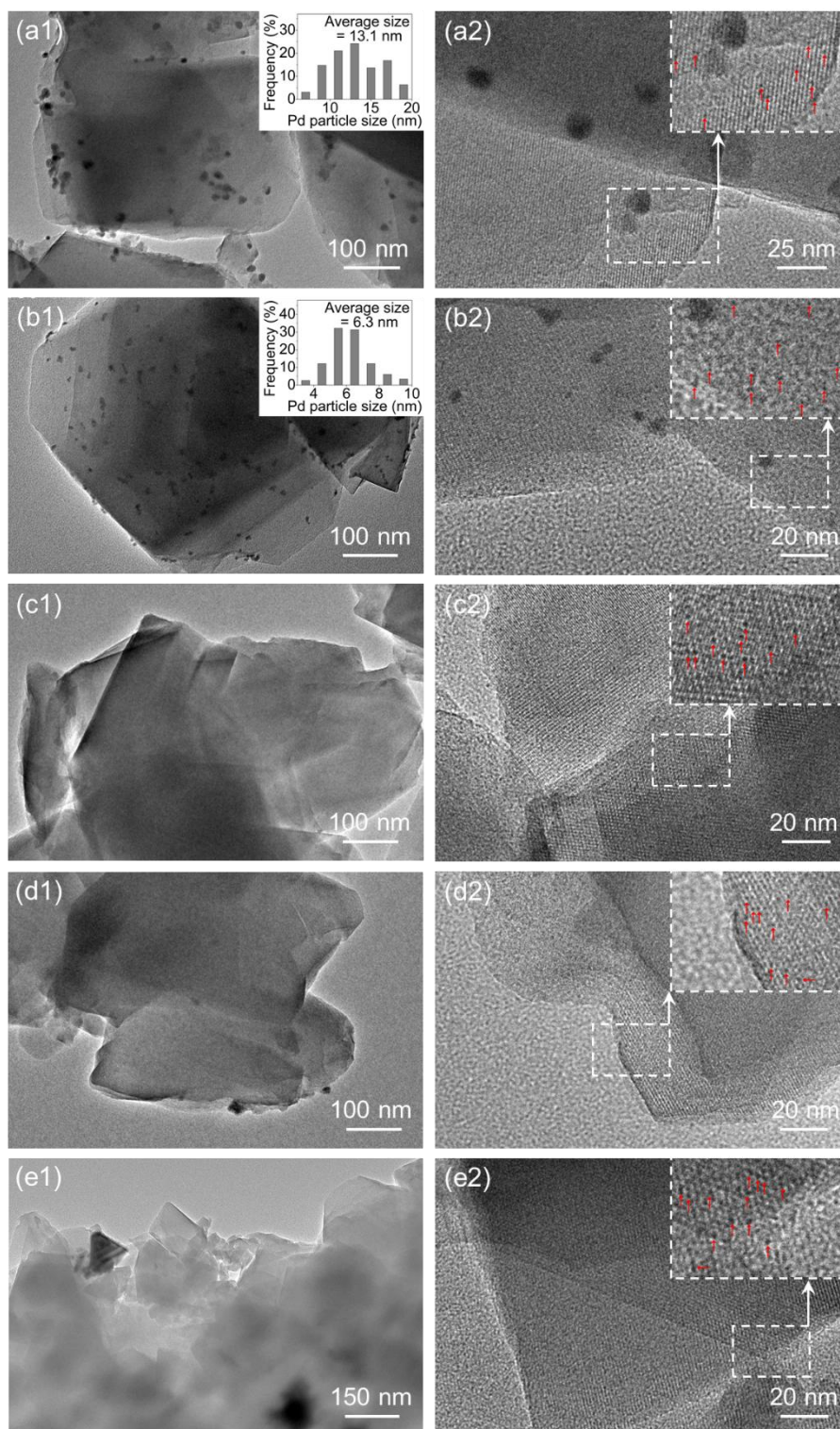
### 10 3.3. Understanding the formation of mechanical pressure-mediated active sites in 11 Pd/NaY catalysts

12 TEM study of the used Pd/NaY catalysts prepared under treatment with different  
13 mechanical pressures was conducted to evaluate the size and distribution of palladium.  
14 As described previously, the Pd/NaY catalyst was prepared by an ion-exchange  
15 method with Pd precursor of Pd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>; and the low-temperature calcination at 200  
16 °C caused the Pd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> to lose partially the NH<sub>3</sub> ligands and to generate the  
17 Pd(NH<sub>3</sub>)<sub>n</sub><sup>2+</sup> (n < 2) sites on the catalyst [41]. Neither Pd clusters (below 2 nm) nor  
18 nanoparticles were observed on the fresh Pd/NaY-60 catalyst before the catalytic test  
19 (Fig. S7). While the used Pd/NaY-60 catalyst after 6 h test contained a mixture of both  
20 small Pd clusters (about 1 nm) and large Pd nanoparticles (Fig. 6a1,a2). The average

1 size of the Pd nanoparticles was estimated to be 13.1 nm based on measuring about  
2 200 nanoparticles (*inset* of Fig. 6a1). The TEM images of fresh and used Pd/NaY-60  
3 catalysts indicated that the large Pd nanoparticles were formed because of the  
4 catalytic test. This was in line with the previous observation revealing the palladium  
5 sintering on the Pd/NaY catalyst after the catalytic test [41]. The used Pd/NaY-150  
6 catalyst contained Pd nanoparticles of 6.3 nm that were remarkably smaller than the  
7 counterparts on the Pd/NaY-60 catalyst (Fig. 6a1,b1). Interestingly, no big Pd  
8 nanoparticles were detected on the used Pd/NaY-300 catalyst and only  
9 mono-dispersed Pd clusters of about 1 nm confined within the zeolite framework were  
10 identified (Fig. 6c1,c2). The used Pd/NaY-450 was similar to the used Pd/NaY-300  
11 catalyst with the exception that sporadic large Pd nanoparticles of about 20 nm could  
12 be seen in the TEM pictures (Fig. 6c1,d1). Bigger Pd particles up to 110 nm were  
13 detected on the used Pd/NaY-600 catalyst (Fig. 6e1). The XRD pattern of this sample  
14 contained the Bragg peaks corresponding to the metallic Pd<sup>0</sup>(111) and Pd<sup>0</sup>(200)  
15 (JCPDS 01-1201) with a non-homogeneous dispersion (Fig. S3). As stated above, the  
16 mechanical compression resulted in the formation of framework defects, such as  
17 collapse of micropore, framework distortions, fragmentation of primary zeolite  
18 crystals, and even amorphization of zeolites (Table 1) [16,19]. With increasing the  
19 mechanical pressure from 60 MPa to 300 MPa, the average size of the Pd  
20 nanoparticles decreased from 13.1 nm to 6.3 nm, but only mono-dispersed Pd clusters  
21 (about 1 nm) were detected on the Pd/NaY-300 catalyst (Fig. 6a1–c1,a2–c2). It was



1 thus reasonable to infer that the framework defects possibly played an important role  
2 in hindering the aggregation of Pd clusters. This was in line with the report disclosing  
3 that the zeolite defects served as hosting place for the Pd species, thus separating them  
4 from each other and preventing their growth [58–60]. At the mechanical pressure  
5 larger than 300 MPa, more amorphous aluminosilicate areas were formed, and thus  
6 possibly led to sintering of the Pd and formation of bigger metal particles (Fig. 6e1)  
7 [35,58].

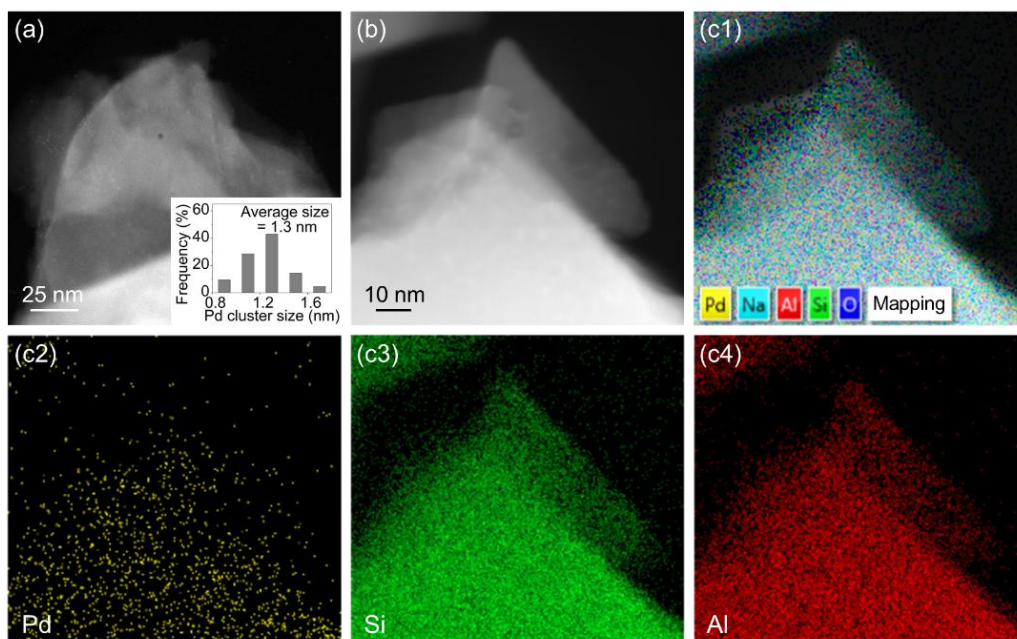


1  
2 **Fig. 6.** TEM images of the used catalysts after 6 h catalytic test: (a1,a2) Pd/NaY-60,  
3 (b1,b2) Pd/NaY-150, (c1,c2) Pd/NaY-300, (d1,d2) Pd/NaY-450 and (e1,e2)  
4 Pd/NaY-600. *Inset* of (a1) and (b1): size distribution of Pd nanoparticles determined  
5 by measuring about 200 nanoparticles. *Inset* of (a2), (b2), (c2), (d2) and (e2): enlarged

1 area of the catalysts and Pd clusters marked by red arrows.

2

3 Consistent with the TEM observation, the HAADF-STEM images of the used  
4 Pd/NaY-300 catalyst further confirmed the presence of mono-dispersed Pd clusters  
5 (Figs. 6c1,c2 and 7). The average size of the Pd clusters was determined to be 1.3 nm  
6 based on measuring about 200 clusters (*inset* of Fig. 7a). The HAADF-STEM-EDS  
7 elemental mapping showed that the Pd was homogeneously distributed on the used  
8 Pd/NaY-300 catalyst.



9

10 **Fig. 7.** (a) HAADF-STEM image and the size distribution of Pd (*inset*), (b)

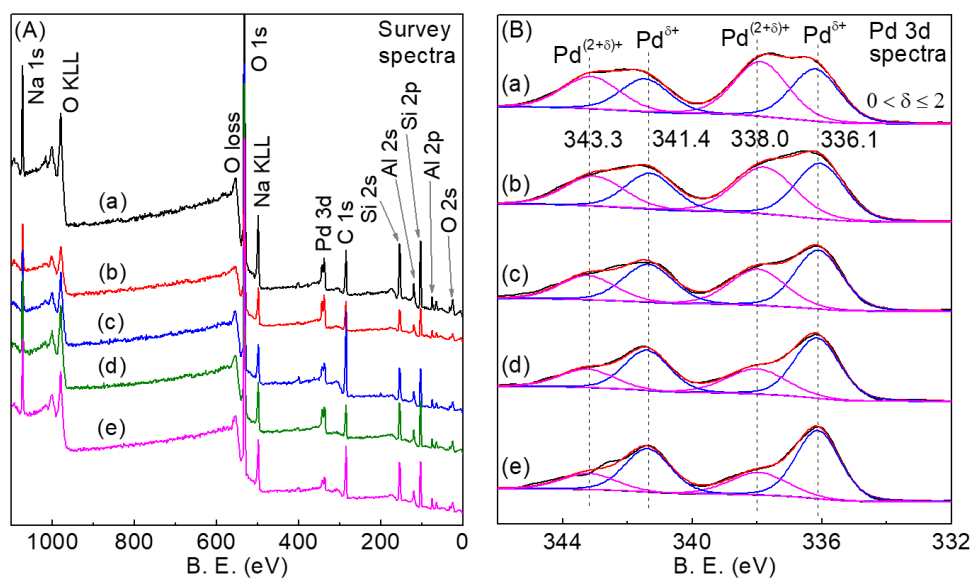
11 HAADF-STEM image and (c1–c4) the corresponding HAADF-STEM-EDS  
12 elemental mapping of the used Pd/NaY-300 catalyst after 6 h catalytic test. The size  
13 distribution of Pd determined by measuring about 200 clusters.

14

15 As stated above, the Pd<sup>2+</sup> species were generally believed to be the active sites for

1 the formation of DMC [35,39]. Therefore, XPS study was performed to check the  
2 effect of mechanical pressure on the electronic properties of Pd species. As shown in  
3 Fig. 8A, the XPS spectra confirmed the presence of Pd, Si, Al, Na, O and C elements  
4 on all five catalysts. The Pd 3d regions of these catalysts exhibited the  $3d_{5/2}$  and  $3d_{3/2}$   
5 peaks with a spin-orbit splitting of 5.3 eV; only the Pd  $3d_{5/2}$  peak was discussed  
6 herein (Fig. 8). Generally,  $Pd^0$  was characterized by a Pd  $3d_{5/2}$  peak at 334.8–335.6 eV,  
7 and it shifted to higher binding energy with the increase of palladium oxidation state.  
8 The peaks detected at 336.4–337.3 eV and 338.0–338.9 eV corresponded to the  $Pd^{2+}$   
9 and  $Pd^{4+}$  species, respectively [57,61–64]. Consequently, the peaks at 336.1 eV and  
10 338.0 eV were assigned to  $Pd^{\delta+}$  and  $Pd^{(2+\delta)+}$  species ( $0 < \delta \leq 2$ ) on all five catalysts  
11 (Fig. 8B); similar observations had been reported previously [65,66]. The XPS peak  
12 area ratio corresponding to the  $Pd^{(2+\delta)+}/Pd^{\delta+}$  species for these five catalysts decreased  
13 remarkably from 1.16 to 0.45 with increasing the mechanical pressure from 60 MPa  
14 to 600 MPa applied to the catalysts (Table 3). Generally, the charge of Pd species  
15 increases with decreasing the particle size based on the intrinsic size effect [61,67].  
16 Herein, the average Pd charge monotonically decreased with increasing the  
17 mechanical pressure (Table 3), while the Pd particle size distribution showed a  
18 volcano-like behavior according to the TEM observations (Fig. 6). The lack of  
19 correlation between the Pd particle size and the charge could be explained as follows:  
20 (1) The  $Pd^{(2+\delta)+}$  species possibly result from the Pd clusters and nanoparticles charged  
21 by the zeolite framework through the formation of Pd–O ionic bonds [35,40] and (2)

1 Lewis acid sites of zeolite support are considered to be electron acceptors and thus  
 2 make the Pd species lose the electrons [34]. The increase of the mechanical pressure  
 3 caused the formation of more framework defects and partial amorphization, which  
 4 inhibited the formation of the Pd<sup>(2+δ)+</sup> species and thus decreased the Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup>  
 5 ratio [68].



6  
 7 **Fig. 8.** (A) XPS spectra and (B) Pd 3d spectra of used catalysts after 6 h catalytic test:  
 8 (a) Pd/NaY-60, (b) Pd/NaY-150, (c) Pd/NaY-300, (d) Pd/NaY-450 and (e)  
 9 Pd/NaY-600.

10  
 11 **Table 3** Peak areas of Pd<sup>δ+</sup> ( $0 < \delta \leq 2$ ), Pd<sup>(2+δ)+</sup>, and Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> area ratio of used  
 12 catalysts after 1 h and 6 h catalytic tests determined by XPS.<sup>a</sup>

Catalyst	Time	Area of Pd <sup>δ+</sup>	Area of Pd <sup>(2+δ)+</sup>	Pd <sup>(2+δ)+</sup> /Pd <sup>δ+</sup> ratio
Pd/NaY-60	1 h	5744	10037	1.75
Pd/NaY-150	1 h	8660	11574	1.34

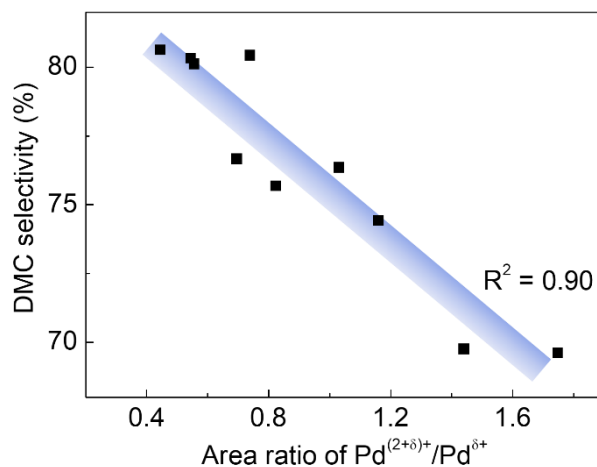
Pd/NaY-300	1 h	9110	7506	0.82
Pd/NaY-450	1 h	8448	5877	0.70
Pd/NaY-600	1 h	9678	5269	0.54
Pd/NaY-60	6 h	7761	8982	1.16
Pd/NaY-150	6 h	8428	8693	1.03
Pd/NaY-300	6 h	8728	6453	0.74
Pd/NaY-450	6 h	8409	4672	0.56
Pd/NaY-600	6 h	10281	4578	0.45

1 <sup>a</sup> Peak areas of Pd<sup>(2+δ)+</sup> at 338.0 eV and Pd<sup>δ+</sup> at 336.1 eV based on XPS spectra of the  
2 used catalysts after 1 h (Fig. S8) and 6 h (Fig. 8) tests.

3

4 The XPS results and catalytic performance of these five catalysts after 6 h  
5 catalytic test showed that the area ratio of Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> decreased gradually, while the  
6 DMC selectivity increased with raising the mechanical pressure from 60 MPa to 600  
7 MPa (Figs. 5 and 8, Table 3). As stated above, the DMC selectivity also increased on  
8 each catalyst with extending the reaction time from 1 h to 6 h (Fig. S5). The  
9 Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> area ratios of catalysts Pd/NaY-60, -150, -300, -450 and -600 after 6 h  
10 test were smaller than the ones measured after 1 h (Table 3). The relationship between  
11 the Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio and DMC selectivity on these five catalysts after 1 h and 6 h  
12 catalytic tests was shown in Fig. 9. A linear relationship with a correlation coefficient  
13  $R^2 = 0.9$  between the DMC selectivity and the Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio was observed (Fig.

1 9). This indicated that the  $\text{Pd}^{(2+\delta)+}/\text{Pd}^{\delta+}$  ratio played a critical role in the DMC  
2 selectivity which would be further discussed in posterior Section 3.4.



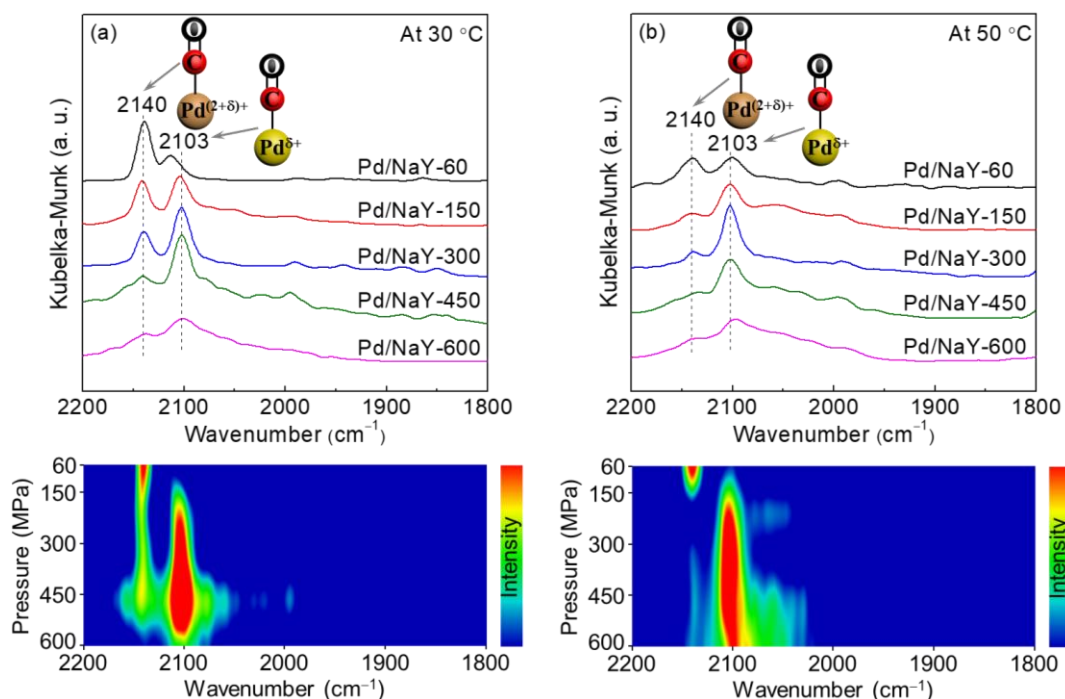
3  
4 **Fig. 9.** The relationship between the area ratio of  $\text{Pd}^{(2+\delta)+}/\text{Pd}^{\delta+}$  and DMC selectivity of  
5 the used catalysts (Pd/NaY-60, -150, -300, -450 and -600) after 1 h and 6 h catalytic  
6 tests ( $\text{Pd}^{(2+\delta)+}/\text{Pd}^{\delta+}$  ratio shown in Table 3).

7  
8 Combining the TEM and XPS results, it could be concluded that the highly  
9 dispersed Pd species contributed to the high CO conversion, while the low  
10  $\text{Pd}^{(2+\delta)+}/\text{Pd}^{\delta+}$  ratio led to the high DMC selectivity for the indirect oxidative  
11 carbonylation of methanol to DMC.

12 3.4. Correlation between the  $\text{Pd}^{(2+\delta)+}/\text{Pd}^{\delta+}$  ratio and DMC selectivity: Enhanced  
13 adsorption of reactants

14 Carbon monoxide is not only a common probe molecule but also the reactant for  
15 the DMC synthesis. The DRIFTS spectra of CO adsorbed on the used Pd/NaY  
16 catalysts were presented in Fig. 10. The band at  $2103\text{ cm}^{-1}$  was assigned to the linear

1 CO adsorption over  $\text{Pd}^{\delta+}$  species ( $0 < \delta \leq 2$ ), and the band at  $2140 \text{ cm}^{-1}$  corresponded  
 2 to the linear CO adsorption on  $\text{Pd}^{(2+\delta)+}$  species [69,70]. With increasing the  
 3 mechanical pressure of the catalysts from 60 MPa to 600 MPa, the band  
 4 corresponding to  $\text{Pd}^{(2+\delta)+}$  species declined while the band related with  $\text{Pd}^{\delta+}$  species  
 5 gradually increased (Fig. 10a). This was consistent with the evolution of the  
 6  $\text{Pd}^{(2+\delta)+}/\text{Pd}^{\delta+}$  ratio determined by XPS (Fig. 8 and Table 3). When the temperature of  
 7 the DRIFTS reaction cell was increased from  $30 \text{ }^\circ\text{C}$  to  $50 \text{ }^\circ\text{C}$ , the band corresponding  
 8 to  $\text{Pd}^{(2+\delta)+}$  species decreased noticeably while the intensity of the band corresponding  
 9 to  $\text{Pd}^{\delta+}$  species was well preserved. This suggested that CO adsorption on the  $\text{Pd}^{(2+\delta)+}$   
 10 species was weaker than on the  $\text{Pd}^{\delta+}$  species, which was due to the weak  $\pi$   
 11 back-donation [57]. This finding further indicated that the change of the  $\text{Pd}^{(2+\delta)+}/\text{Pd}^{\delta+}$   
 12 ratio could affect the adsorption of CO reactant on these catalysts.



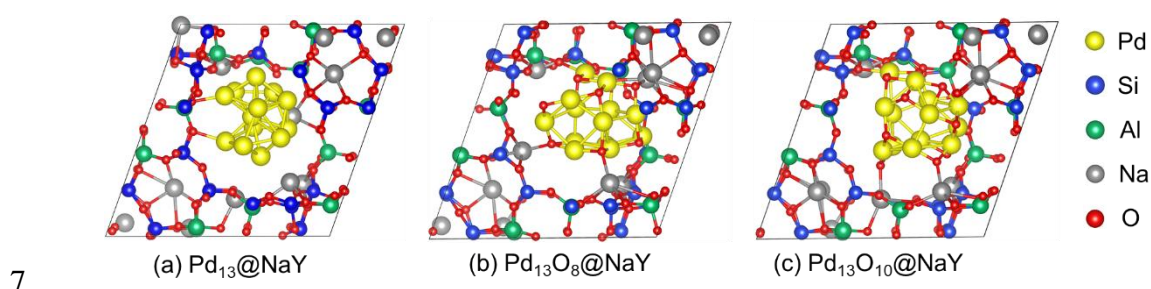
13  
 14 **Fig. 10.** DRIFTS spectra of CO adsorbed on the used Pd/NaY-60, -150, -300, -450



1 and -600 catalysts after 6 h catalytic test at (a) 30 °C and (b) 50 °C. The samples were  
2 pre-treated in N<sub>2</sub> at 200 °C, cooled down to 30 °C, exposed to 10 vol% CO in N<sub>2</sub> and  
3 thoroughly purged with N<sub>2</sub>. After that, the spectra were obtained at 30 °C and 50 °C.

4  
5 In order to further understand the effect of the Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio on the DMC  
6 selectivity, we conducted DFT calculations to probe the adsorption of CO and  
7 CH<sub>3</sub>ONO reactants on the Pd species with different valence states. A primitive cell  
8 (Si<sub>24</sub>Al<sub>24</sub>O<sub>96</sub>) of the faujasite structure with the  $Fd\bar{3}$  space group symmetry was used  
9 to model the NaY zeolite. Based on the Löwenstein rule, we replaced 12 Al atoms by  
10 12 Si atoms to obtain a Si/Al molar ratio of 3.0, which was close to that of the  
11 synthesized Pd/NaY catalyst (Si/Al=2.8, Table 1). Furthermore, 12 Na atoms were  
12 added into the cell based on the reported distribution, i.e., 17% in site I (~2 Na  
13 atoms), 29% in site I' (~4 Na atoms) and 54% in site II (~6 Na atoms) [71,72]. A Pd<sub>13</sub>  
14 cluster reported by a previous study [37] was embedded into the supercage of NaY  
15 (Pd<sub>13</sub>@NaY) to model the synthesized Pd/NaY catalysts and the optimized structure  
16 was shown in Fig. 11a. Since the synthesized Pd/NaY catalysts had mixed valence  
17 states of (2+δ)+ and δ+, we also constructed Pd<sub>13</sub>O<sub>8</sub>@NaY and Pd<sub>13</sub>O<sub>10</sub>@NaY models  
18 by adding eight or ten oxygen atoms onto the Pd<sub>13</sub> cluster of Pd<sub>13</sub>@NaY (Fig. 11). To  
19 locate the stable structures of Pd<sub>13</sub>O<sub>8</sub>@NaY and Pd<sub>13</sub>O<sub>10</sub>@NaY, we carried out a  
20 molecular dynamics (MD) simulation of ~ 25 ps (time step: 1 fs) on each of these two  
21 systems in the canonical (NVT) ensemble with T = 137 °C. For each system,

1 geometry optimizations were performed on the selected low-energy structures  
2 obtained from the MD simulation, and the structure with the lowest energy was  
3 selected for further study. Charge analyses showed that the Pd atoms of Pd<sub>13</sub>@NaY  
4 were partially transformed into Pd<sup>(2+δ)+</sup> species after adding eight or ten oxygen atoms  
5 onto the Pd<sub>13</sub> cluster (Table S2). The Pd<sub>13</sub>O<sub>10</sub>@NaY had the highest Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio,  
6 followed by Pd<sub>13</sub>O<sub>8</sub>@NaY and then Pd<sub>13</sub>@NaY (Table S2).



12 **Fig. 11.** Optimized structures of (a) Pd<sub>13</sub>, (b) Pd<sub>13</sub>O<sub>8</sub>, and (c) Pd<sub>13</sub>O<sub>10</sub> clusters  
13 embedded in the supercage of NaY zeolite. Pd, Si, Al, Na, and O atoms were  
14 presented in yellow, blue, green, grey, and red, respectively.

15 Since the DRIFTS spectra suggested linear adsorption of CO on all five Pd/NaY  
16 catalysts (Fig. 10), only the top-site adsorption was considered in our DFT  
17 calculations. The optimized structures of linear adsorption of CO on the Pd<sub>13</sub>@NaY,  
18 Pd<sub>13</sub>O<sub>8</sub>@NaY, and Pd<sub>13</sub>O<sub>10</sub>@NaY models are presented in Fig. S9. We found that the  
19 CO preferred to be adsorbed on the Pd<sup>δ+</sup> sites in comparison with the Pd<sup>(2+δ)+</sup> sites  
(Table 4). This was mainly due to the stronger π back-donation of Pd<sup>δ+</sup> compared to  
the Pd<sup>(2+δ)+</sup> sites, [57] which was consistent with the DRIFTS results (Fig. 10). The  
most favorable adsorption energy of CO at Pd<sup>δ+</sup> site increased significantly with

1 decreasing the oxygen atoms of the models (1.32 eV for Pd<sub>13</sub>O<sub>10</sub>@NaY → 2.06 eV  
 2 for Pd<sub>13</sub>O<sub>8</sub>@NaY → 2.61 eV for Pd<sub>13</sub>@NaY, Table 4) [73]. In addition, the  
 3 dissociative adsorption of CH<sub>3</sub>ONO on the considered models showed a similar trend  
 4 to the adsorption of the CO reactant. More specifically, the dissociative adsorption  
 5 energies of CH<sub>3</sub>ONO on the Pd<sub>13</sub>O<sub>10</sub>@NaY, Pd<sub>13</sub>O<sub>8</sub>@NaY, and Pd<sub>13</sub>@NaY models  
 6 were 2.06, 2.44, and 2.71 eV, respectively (Fig. S9 and Table S3). Therefore, our DFT  
 7 results suggested that the lower the Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio of the catalyst was, the stronger  
 8 the adsorption of CO and CH<sub>3</sub>ONO reactants were expected.

9

10 **Table 4** Calculated most favorable adsorption of CO at the Pd<sup>δ+</sup> and Pd<sup>(2+δ)+</sup> sites in  
 11 the Pd<sub>13</sub>@NaY, Pd<sub>13</sub>O<sub>8</sub>@NaY, and Pd<sub>13</sub>O<sub>10</sub>@NaY models.

Model	Adsorption mode	Site <sup>a</sup>	Valence state <sup>b</sup>	<i>E<sub>ads</sub></i> (eV) <sup>c</sup>
Pd <sub>13</sub> O <sub>10</sub> @NaY	Linear	Pd-13	δ+	1.32
	Linear	Pd-6	(2+δ)+	0.64
Pd <sub>13</sub> O <sub>8</sub> @NaY	Linear	Pd-3	δ+	2.06
	Linear	Pd-4	(2+δ)+	0.46
Pd <sub>13</sub> @NaY	Linear	Pd-13	δ+	2.61

12 <sup>a</sup> Pd-*x*, where *x* represents the number of Pd atoms in the models (Fig. S9).

13 <sup>b</sup> The valence states of Pd were determined by calculating their Bader charges (see  
 14 Table S2 in SI for details).

15 <sup>c</sup> Calculated adsorption energy (*E<sub>ads</sub>*) of CO.

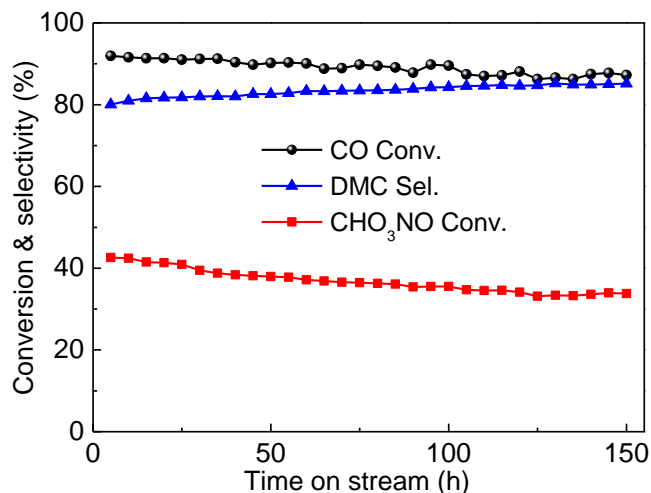
1

2       The calculated high adsorption energies of CO and CH<sub>3</sub>ONO also suggested that  
3 these two reactants could be easily adsorbed on the Pd/NaY catalysts (Tables 3 and S2)  
4 [73]. This indirectly indicated that the Langmuir-Hinshelwood mechanism was  
5 preferred for the DMC synthesis over the Pd/NaY catalysts [40,74]. Since DMC  
6 synthesis and catalytic decomposition of CH<sub>3</sub>ONO reactant were parallel competing  
7 reactions (details provided in SI), the catalytic decomposition of CH<sub>3</sub>ONO was  
8 examined on all five Pd/NaY catalysts at 110 °C using a feed of CH<sub>3</sub>ONO/N<sub>2</sub> = 1/4  
9 (mole). With increasing the shaping pressure from 60 MPa to 600 MPa, the activity of  
10 undesired decomposition of CH<sub>3</sub>ONO reactant gradually decreased from 30.0% to  
11 20.9% (GHSV = 30000 mL g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>) and from 21.7% to 15.2% (GHSV = 90000 mL  
12 g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>) on these five Pd/NaY catalysts, which gave a reverse trend to the DMC  
13 selectivity for the DMC synthesis (Figs. 5 and S10). This suggested that Pd/NaY  
14 catalyst with a low Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio could hinder the undesired decomposition of  
15 CH<sub>3</sub>ONO reactant.

16       In summary, combining the XPS, DRIFTS and DFT results, it could be concluded  
17 that the mechanical pressure tuned the Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio and further adjusted the  
18 adsorption of CO and CH<sub>3</sub>ONO reactants. The increased amount of Pd<sup>δ+</sup> species could  
19 enhance the adsorption of CO and CH<sub>3</sub>ONO reactants and inhibit the undesired  
20 decomposition of CH<sub>3</sub>ONO reactant into byproducts, thereby improving the DMC  
21 selectivity.

### 1 3.5. Stability of the Pd/NaY-300 catalyst

2 A long-term catalytic test was carried out on the best performing Pd/NaY-300  
3 catalyst, and the results are shown in Fig. 12. The catalyst showed a good stability  
4 throughout the 150 h catalytic test, exhibiting CO conversion of  $89 \pm 2\%$ , CH<sub>3</sub>ONO  
5 conversion of  $37 \pm 3\%$ , and DMC selectivity of  $83 \pm 1\%$ . The DMC selectivity  
6 gradually increased with extending the reaction time from 1 h to 150 h (Fig. 12). The  
7 Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> area ratio of the Pd/NaY-300 catalyst after 150 h catalytic test was  
8 determined to be 0.40 by XPS (Fig. S11). According to the nearly linear relationship  
9 between the Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio and DMC selectivity (Fig. 9), the predicted DMC  
10 selectivity was 81%. This further confirmed that the DMC selectivity depended on  
11 Pd<sup>(2+δ)+</sup>/Pd<sup>δ+</sup> ratio. The TEM revealed that the used Pd/NaY-300 catalyst after 150 h  
12 contained a mixture of both abundant Pd clusters of about 1 nm and sporadic Pd  
13 nanoparticles of about 6 nm (Fig. S12). Except sporadic Pd nanoparticles, the TEM  
14 images of the used Pd/NaY-300 catalyst (after 150 h catalytic test) were similar to the  
15 catalyst after 6 h catalytic test (Figs. 6c1,c2 and S12), which indicated the excellent  
16 resistance to Pd sintering. No Bragg peaks corresponding to PdO (JCPDS 88-2434)  
17 and Pd<sup>0</sup> (JCPDS 01-1201) were detected in the XRD pattern of the used Pd/NaY-300  
18 catalyst (Fig. S13).



1

2 **Fig. 12.** Durability performance of the Pd/NaY-300 catalyst in the indirect oxidative  
 3 carbonylation of methanol to DMC measured for 150 h. Reaction conditions: 0.1000 g  
 4 catalyst; feed gas, CO/CH<sub>3</sub>ONO/N<sub>2</sub> = 1/6/33 (mole); GHSV = 8000 mL g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>;  
 5 reaction temperature = 110 °C; feed pressure = 0.1 MPa. Each point was an average  
 6 value of three measurements.

#### 7 4. Conclusions

8 Palladium-containing NaY zeolite catalysts were prepared by mechanical-pressure  
 9 controlled treatment and tested in the indirect oxidative carbonylation of methanol to  
 10 dimethyl carbonate (DMC). The mechanical pressure applied to the Pd/NaY catalysts  
 11 was found to have a pronounced effect on the Pd dispersion and the catalysts stability.  
 12 The Pd clusters with a size of 1.3 nm homogeneously distributed in the NaY zeolite  
 13 were obtained under mechanical-pressure treatment of 300 MPa. This catalyst not  
 14 only showed the high CO conversion of 89% and DMC selectivity of 83%, but also  
 15 was very stable for at least 150 h. The DMC selectivity was closely related to the

1 mechanical pressure applied as it was related with the amount of Pd<sup>(2+δ)+</sup> and Pd<sup>δ+</sup> (0 <  
2 δ ≤ 2) active sites formed in the Pd/NaY catalysts. The *in situ* DRIFTS and DFT  
3 calculations revealed clearly that the Pd<sup>δ+</sup> in contrast to Pd<sup>(2+δ)+</sup> species enhanced the  
4 adsorption of CO and CH<sub>3</sub>ONO reactants and inhibited the undesired decomposition  
5 of CH<sub>3</sub>ONO reactant into byproducts, and thus enhanced the DMC selectivity.

6

### 7 **Declaration of Competing Interest**

8 The authors declare that they have no known competing financial interests or  
9 personal relationships that could have appeared to influence the work reported in this  
10 paper.

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