DOI: 10.1002/cctc.201300170



# Synthesis of Dimethyl Carbonate through Vapor-Phase Carbonylation Catalyzed by Pd-Doped Zeolites: Interaction of Lewis Acidic Sites and Pd Species

Yuanyuan Dong, Shouying Huang, Shengping Wang, Yujun Zhao, Jinlong Gong, and Xinbin  $Ma^{*[a]}$ 

Palladium on solid acidic supports has been used as a catalyst in various industrial processes<sup>[1]</sup> and is becoming increasingly important in modern organic reactions. It has been reported that the catalytic performances of these Pd-based catalysts are strongly affected by the support materials and additives, with particular emphasis on the nature of the acidic sites.<sup>[2]</sup> For instance, in nucleophilic reactions catalyzed by transition metals, the reaction rate was improved<sup>[2b]</sup> and higher conversions and selectivities were achieved<sup>[2f]</sup> by the introduction of Lewis acidic sites; for alkane hydroconversion reactions, the enhanced catalytic performance was attributed to an increase in the Lewis acidity of the supports.<sup>[2c]</sup>

In green chemistry terms, dialkyl carbonates have obtained widespread attention in industry because of their excellent physical and chemical properties.<sup>[3]</sup> Vapor-phase carbonylation

of alkyl nitrite over supported Pd-based catalysts is considered to be a promising route to produce dialkyl carbonates.[3c,4] Pddoped zeolites, prepared by a conventional ion-exchange (CIE) technique with aqueous solutions of  $Pd(NH_3)_4^{2+}$  ions, exhibit better catalytic performances and higher stability in this process.<sup>[3c, 5]</sup> It was reported that the activities of the catalysts were influenced by several factors, including the local environment and concentration of Pd<sup>[5,6]</sup> and the type of acidic sites of the zeolite support.[3c] It is widely accepted that Brønsted acids, formed in the preparation of Pd-doped zeolite catalysts, could accelerate the decomposition of alkyl nitrite, which would lead to poor activities.<sup>[3c,5]</sup> Thus, Brønsted acids were avoided to the greatest extent. The effect of Lewis acidic sites on the vapor-phase carbonylation of alkyl nitrite has not been clarified. Therefore, this paper attempts to address the specific role of Lewis acids in Pd/zeolite-catalyzed vapor-phase carbonylation reactions.

The nature of Lewis acidic sites in zeolites strongly depends on the composition of the zeolite framework (e.g.,  $SiO_2/Al_2O_3$ ratio).<sup>[7]</sup> Therefore, we first prepared Pd-doped zeolites with various  $SiO_2/Al_2O_3$  molar ratios (i.e., tuning surface acidity) by employing the CIE method. The Pd-doped zeolites were then tested in the vapor-phase carbonylation of methyl nitrite (MN) to dimethyl carbonate (DMC), which we used as a probe reaction. Among microporous materials, Faujasite (FAU) zeolites have been frequently employed as supports for vapor-phase



Figure 1. FTIR spectra of pyridine adsorbed on FAU (a) and Pd/FAU (b) with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios.

carbonylation reactions owing to their unique characteristics such as a wide range of  $SiO_2/Al_2O_3$  ratios, relatively large pore diameter, and uniform 3D channel structure.<sup>[5]</sup> The acidic properties of FAU zeolites and Pd/FAU catalysts with different  $SiO_2/Al_2O_3$  ratios (2.5, 5.5, 10, and 14) were determined by pyridine adsorption infrared (IR) spectroscopy. Figure 1 depicts the spectra in the frequency range from 1300 to 1700 cm<sup>-1</sup>. The band at approximately 1542 cm<sup>-1</sup> is ascribed to the C–C stretching vibration of the pyridinium ion on the Brønsted sites. The bands at approximately 1454 and 1442 cm<sup>-1</sup> are attributed to the C–C stretching vibration of the pyridine com-



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plex on the coordinately unsaturated Al<sup>3+</sup> ions<sup>[8]</sup> and the pyridine molecules coordinated to the Na<sup>+</sup> ions,<sup>[9]</sup> respectively. In zeolites, except for extra-framework species such as coordinately unsaturated  $\ensuremath{\mathsf{AI}^{3\,+}}$ ions acting as Lewis acids,<sup>[10]</sup> the charge-balancing cations that act as electron acceptors can also be considered as Lewis acids.[11] In Figure 1a, the intensity of the bands representing the Lewis acidic sites (  $\approx\!1442$ and 1454 cm<sup>-1</sup>) of the FAU zeolites displays the shape of a volcano with increasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. For supported Pd catalysts, changes in the Lewis acidic sites



**Figure 2.** The relationship between Lewis acidic sites and catalytic activities of the Pd/FAU catalysts with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. Reaction conditions: T=383 K, P=0.2 MPa, gas hourly space velocity (GHSV)=8000 h<sup>-1</sup>, CO/MN/N<sub>2</sub>=3.3:20:76.7 (vol.%).

still follow this trend, as indicated in Figure 1 b. The concentration of the Brønsted and Lewis acidic sites<sup>[12]</sup> in the Pd/FAU catalysts obtained from the intensity of the corresponding bands is listed in Table 1. Additionally, in Figure 1 a, FAU zeolites with

Table 1. Amount of acidic sites and the loading of Pd in the Pd/FAU catalysts.				
Catalyst	$PyH^{+[a]}$	PyL <sup>(b)</sup>	Pd <sup>[c]</sup>	
	[mmol g <sup>-1</sup> ]	[mmol g <sup>-1</sup> ]	[wt%]	
Pd/FAU(2.5)	$\begin{array}{c} 0.09 \pm 0.02 \\ 0.08 \pm 0.02 \\ 0.41 \pm 0.02 \\ 0.35 \pm 0.02 \end{array}$	$0.28 \pm 0.02$	0.84	
Pd/FAU(5.5)		$0.57 \pm 0.01$	0.85	
Pd/FAU(10)		$0.13 \pm 0.02$	0.83	
Pd/FAU(14)		$0.10 \pm 0.02$	0.83	
[a] Pyridinium ion on Brønsted sites. [b] Pyridine complex on Lewis sites. [c] Loading of Pd was determined by ICP				

high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios were produced by hydrothermal de-aluminization of FAU(5.5) zeolites, which is widely believed to form extra-framework aluminum species ( $\approx 1454 \text{ cm}^{-1}$ )<sup>[13]</sup> and a large amount of Brønsted sites.<sup>[14]</sup> This is evidenced by the results in Figure S1 (Supporting Information), which shows the <sup>27</sup>Al MAS NMR spectra of FAU zeolites with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios.

Moreover, upon loading 1 wt% of Pd (the optimum Pd loading for this type of reaction<sup>[5]</sup>) to the FAU supports, the bands at approximately 1542 and 1454 cm<sup>-1</sup> appeared in the samples with low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios and increased with increasing ratios of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Sato et al.<sup>[15]</sup> reported that NH<sub>4</sub><sup>+</sup> exchanged with Na<sup>+</sup> to form Brønsted sites and that the zeolite framework partial de-aluminization occurred during the ion-exchange process.

The catalytic properties of the Pd/FAU catalysts with different  $SiO_2/Al_2O_3$  ratios were examined under the same reaction conditions<sup>[5]</sup> in a continuous fixed-bed microreactor. For a given loading of Pd (Table 1), the Pd/FAU catalysts with different  $SiO_2/Al_2O_3$  ratios exhibited different catalytic activities.

We further correlated the catalytic activities with the Lewis sites of the catalysts (Figure 2). The turnover frequencies (TOFs, calculated on the basis of CO conversion per mole Pd per hour) increased linearly as the amount of Lewis acidic sites in the Pd/FAU catalysts was increased (Figure 2a). The selectivity for DMC on the basis of MN followed the same trend, as Figure 2b indicates. Moreover, a control experiment indicated that the FAU zeolite itself is inactive in this reaction (Figure S2, Supporting Information). Accordingly, we can deduce that the Lewis acidic sites in the catalysts promoted the vapor-phase carbonylation reactions. However, it is noteworthy that the Pd/ FAU catalysts with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios possess a large amount of Brønsted acidic sites, which could result in the excessive decomposition of alkyl nitrite, which would lead to a sharp decrease in activity.<sup>[3c]</sup> Thus, the influence of Brønsted acidic sites cannot be ruled out as a reason for the low activities of the Pd/FAU catalysts with high ratios of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. To exclude the effects of the Brønsted acidic sites and to further verify the unique role of the Lewis acidic sites, we designed experiments to either eliminate the Brønsted acidic sites or to keep the amount of Brønsted acidic sites consistent.

As Figure 1 a shows, the FAU(5.5) zeolite has only Lewis-type acidic sites. Additionally, Pd/FAU(5.5) showed the best performance in the vapor-phase carbonylation of MN (Figure 2). Therefore, we passivated the surface acidity of the FAU(5.5) zeolite by deposition of a thin silica layer,<sup>[16]</sup> resulting from hydrolysis of tetraethoxysilane (TEOS), to modify the amount of Lewis acidic sites. Upon treatment with TEOS, the FAU(5.5) zeolites were subjected to conventional ion exchange with aqueous solutions of Pd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> ions, the so-called Pd/iT-FAU(5.5) samples (*i* indicates the amount of TEOS per gram of zeolite). It was shown that the acidity distribution of the FAU zeolites was homogeneous.<sup>[17]</sup> Part of the Lewis acidic sites could be coated with thin silica layers by chemical liquid deposition (CLD) of TEOS.<sup>[16a]</sup> Thus, we investigated the influence of Lewis acidity through quantification of the Lewis acidic sites.

After treatment with TEOS, no obvious differences were observed in the physical properties of the FAU zeolites. In com-

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parison with the FAU(5.5) zeolite, the pore-size distribution curves and the N<sub>2</sub> adsorptiondesorption curves of the ITzeolites remained FAU(5.5) almost the same (Figure S3, Supporting Information), and this indicates that the treatment had a negligible impact on the textural properties. In addition, the XRD patterns of the FAU(5.5) zeolite and the *i*T-FAU(5.5) zeolite were identical (Figure S4, Supporting Information). These results imply that the thin layer of silica formed in the hydrolysis process of TEOS uniformly covzeolite surface. ered the Changes in the Lewis acidic sites



Figure 3. FTIR spectra of pyridine adsorbed on *i*T-FAU (a) and Pd/*i*T-FAU (b) with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=5.5.

were determined by pyridine adsorption IR spectroscopy (Figure 3). With an increase in the amount of TEOS, the peak intensity of the Lewis acid ( $\approx 1442 \text{ cm}^{-1}$ ) in the FAU zeolites (Figure 3 a) first decreased, owing to the fact that a portion of the Lewis acidic sites was covered with a silica layer resulting from hydrolysis of TEOS,<sup>[18]</sup> and then increased, which can be ascribed to the formation of tricoordinate silicon acting as a Lewis acidic site.<sup>[17]</sup> The change in the amount of Lewis acidic sites in the Pd/*I*-FAU catalysts follows the same trend, as indicated in Figure 3b. Table 2 summarizes the amount of acidic sites in the Pd/*I*-FAU catalysts obtained from the intensity of

the corresponding bands in the IR spectra. Furthermore, the Brønsted sites and the non-framework aluminum species appeared in the spectra of the Pd//T-FAU(5.5) catalysts as a result of  $NH_4^+$  exchange with  $Na^+$  and de-aluminization of the zeolite framework in the ion-exchange process, respectively.<sup>[15]</sup>

The Pd/*i*T-FAU(5.5) catalysts, all having the same Pd content, were evaluated under the same reaction conditions. Figure 4 depicts the relationship between catalytic performance and Lewis acidic sites of the Pd/*i*T-FAU catalysts. The TOF is linearly related to the amount of Lewis acidic sites in the Pd/*i*T-FAU catalysts

Table 2. Amount of acidic sites and the Pd loading of the Pd//T-FAU(5.5) catalysts.				
Catalyst	PyH <sup>+[a]</sup> [mmol g <sup>-1</sup> ]	PyL <sup>(b)</sup> [mmol g <sup>-1</sup> ]	Pd <sup>[c]</sup> [wt %]	
Pd/FAU(5.5) Pd/0.2T-FAU(5.5) Pd/0.4T-FAU(5.5) Pd/0.6T-FAU(5.5)	$\begin{array}{c} 0.08 \pm 0.02 \\ 0.09 \pm 0.02 \\ 0.08 \pm 0.02 \\ 0.09 \pm 0.01 \end{array}$	$\begin{array}{c} 0.56 \pm 0.02 \\ 0.22 \pm 0.02 \\ 0.29 \pm 0.02 \\ 0.35 \pm 0.01 \end{array}$	0.85 0.85 0.83 0.84	
[a] Pyridinium ion on Brønsted sites. [b] Pyridine complex on Lewis sites. [c] Loading of Pd was determined by ICP				



**Figure 4.** The relationship between Lewis acidic sites and catalytic activities of the Pd//T-FAU(5.5) catalysts. Reaction conditions: T = 383 K, P = 0.2 MPa, GHSV = 8000 h<sup>-1</sup>, CO/MN/N<sub>2</sub> = 3.3:20:76.7 (vol.%).

(Figure 4a). CO conversion increased first and then remained constant, and the same trend was observed for DMC selectivity (Figure 4b). This phenomenon differs from the result shown in Figure 2b. The DMC selectivity was affected by both the Brønsted and Lewis acidic sites for the Pd/FAU catalysts with different  $SiO_2/Al_2O_3$  ratios, whereas it was affected only by the Lewis acidic sites for the TEOS-treated catalysts. These results

further confirm the crucial role of Lewis acids in determining catalytic activity.

It was clarified that the electronic state of a noble metal could be modified by the support materials.<sup>[2a]</sup> Coq et al.<sup>[19]</sup> reported that Pd sites became electron deficient as a result of Lewis acidity. For the vapor-phase carbonylation reaction to DMC, Pd<sup>II</sup> species are considered to be the active species.<sup>[1,5]</sup>

During the reaction, the Pd<sup>II</sup> species could be reduced by CO, which would result in lower activity. In our experiments, with the same loading of Pd, catalysts with larger amounts of Lewis acidic sites showed better catalytic properties, which may mean that the percentage of Pd<sup>II</sup> species in the catalysts was greater. Therefore, we employed X-ray photoelectron spectroscopy (XPS) to test the chemical states of Pd in the catalysts after the same reaction time (7 h). The results are shown in Figure S5 (Supporting Information). Some significant differences are observed in the XPS spectra. Upon treatment of TEOS, the peaks representing the Pd $^{\delta_+}$  species (Pd 3d<sub>5/2</sub>=337.2 eV)<sup>[5]</sup> were unclear relative to the peak of Pd metal (Pd  $3d_{5/2} =$ 335.3 eV) and the area percentage declined. This result is in accord with changes in the Lewis acidic sites and catalytic activities. Thus, we believe that the Lewis acidic sites, which are electron acceptors in this system, maintain the Pd species in an electron-deficient state, which in turn promotes the synthesis of dialkyl carbonates.

In conclusion, we have determined the crucial role of Lewis acidic sites in the vapor-phase carbonylation of methyl nitrite over Pd/FAU catalysts. For a given loading of the Pd catalyst, the greater the amount of Lewis acidic sites, the better the catalysts performed, because of the larger percentage of active Pd<sup> $\delta$ +</sup> species in the catalysts. Clarification of the effects of Lewis acidic sites on Pd-doped zeolite catalyzed carbonylation reactions could contribute to the understanding of the mechanism for such reactions and help in the design and optimization of catalysts.

## **Experimental Section**

#### **Catalysts preparation**

The FAU zeolites were firstly calcined at 773 K for 4 h in air at  $2 \text{ Kmin}^{-1}$ . All of the Pd/FAU catalysts were prepared by conventional ion exchange, which was performed by the dropwise addition of a dilute solution (0.01 M) of Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> to a FAU slurry at 353 K over 6 h. The Pd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>-exchanged samples were thoroughly washed with deionized water to eliminate chloride ions. The samples were then dried at 383 K for 2 h and subsequently calcined at 473 K for 4 h at 0.5 Kmin<sup>-1</sup> in muffle. These obtained catalysts are termed Pd/FAU(*x*) (*x* indicates the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio). The loading of Pd was analyzed by inductively coupled plasma (ICP).

#### **Passivation with TEOS**

The FAU(5.5) zeolites were treated with tetraethoxysilane (TEOS) to passivate the external surfaces of the zeolites. The FAU zeolites were firstly absorbed with enough water. TEOS [0.2, 0.4, 0.6 gg<sup>-1</sup> of FAU(5.5) zeolite] was added to the suspension of the FAU(5.5) zeolite in *n*-hexane (25 mL), and the mixture was then stirred for 5 h in an airtight container at 298 K. After deposition, the solvent was removed by evaporation, and the remaining powder (*i*T-FAU) was calcined in air for 2 h at 773 K (heating rate: 2 Kmin<sup>-1</sup>).

### Acknowledgements

Financial support from the National Natural Science Foundation of China (20936003), Program for New Century Excellent Talents in University (NCET-10-0611), and the Program of Introducing Talents of Discipline to Universities (B06006) is gratefully acknowledged.

**Keywords:** carbonylation • dimethyl carbonate • Lewis acids • palladium • zeolites

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Received: May 5, 2013 Published online on June 11, 2013