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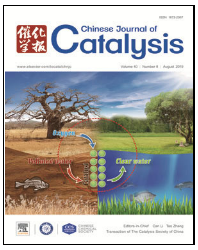

Communication

Amine formylation with CO_2 and H_2 catalyzed by heterogeneous Pd/PAL catalyst

Xingchao Dai [a,d], Bin Wang [b], Aiqin Wang [c], Feng Shi [a,*]

[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China

[b] Key Laboratory for Utility of Environment-Friendly Composite Materials and Biomass in University of Gansu Province, College of Chemical Engineering, Northwest Minzu University, Lanzhou 730030, Gansu, China

[c] Key Laboratory of Clay Mineral Applied Research of Gansu Province, Center of Eco-materials and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China

[d] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

For the first time, Pd supported on natural palygorskite was developed for amine formylation with CO_2 and H_2. Both secondary and primary amines with diverse structures could be converted into the desired formamides at < 100 °C, and good to excellent yields were obtained.

CO_2 emission reduction and resource utilization are one of the major challenges in the 21st century due to an energy crisis in the foreseeable future and increasing environmental pressure [1]. As an economic, safe, and sustainable C_1 resource, the transformation of CO_2 to high value-added products through modern technology has attracted significant attention [2–9]. However, the highly symmetrical molecular structure of CO_2 and the high oxidation state of the carbon atom are responsible for its extremely stable chemical properties, making the activation and conversion of CO_2 difficult under mild conditions. Typically, the conversion of CO_2 involves three steps: adsorption, activation, and directed transformation. Therefore, an ideal catalytic material for CO_2 transformation should exhibit multifunctional characteristics and be able to adsorb, activate, and selectively convert CO_2 to the desired product. Introducing an organic ligand containing active elements is a common means of achieving the transformation [3]. By targeted interaction with the active metal center [10–16], the ligand could suppress or increase the ability of the active metal center in certain aspects to finally achieve the accurate mediation of the catalytic performance. Although good results have been achieved by the above methods, the high cost and complicated synthetic pro-

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[*] Corresponding author. Tel: +86-931-4968142; Fax: +86-931-8277088; E-mail: fshi@licp.cas.cn

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cesses of the organic ligands are undesirable from the standpoint of industrial application. Therefore, exploring new multifunctional materials with excellent catalytic performances in CO_2 resource utilization is important.

Pd has been proven to be active in the reductive formylation of CO_2 with H_2 as the reducing agent [17–25], and two examples of homogeneous catalytic systems [24,25] and seven examples of heterogeneous versions [17–23] have been reported thus far. In these systems, good product yields were obtained when aliphatic secondary amines were used as the starting materials, while only low to moderate product yields were obtained in the case of aliphatic primary amines [22,23]. Recently, Liu and Han et al. [17–19] showed that Mg-Al layered double hydroxide (Mg-Al LDH) and N-doped carbon (NC) supported Pd (Pd/LDH and Pd/NC) as well as mesoporous imine-based organic polymer coordinated Pd (Imine-POP@Pd) were active for the amine formylation with CO_2 and H_2, although a high reaction temperature (140 °C) and/or CO_2 pressure (3 MPa), as well as high Pd loading (8.1 wt%) were required. Based on the continuous efforts focused on the transformation of CO_2 [26,27], our group [20] demonstrated that the hydroxyl group-regulated nano-Pd/C catalyst could catalyze the N-formylation of amines with CO_2 and H_2, although the reaction conditions were still relatively harsh and the procedure for preparing the carbon support was complicated. Therefore, developing a general heterogeneous catalyst for the amine formylation with CO_2 and H_2 is still of significance.

Palygorskite (PAL), also known as attapulgite (APT), is a naturally available, one-dimensional nanoscale hydrated magnesium aluminum silicate clay mineral with abundant zeolite-like channels, a high surface area, and moderate cation exchange capacity [28]. Besides, PAL possesses multiple types of acid and basic active sites due to the existence of interlayer water molecules, surface adsorbed oxygen, and hydroxyl groups, as well as some cations, such as Si, Al, and Mg. Therefore, PAL could provide a reaction environment containing multiple functional sites and be a promising catalyst support candidate for the preparation of multifunctional catalytic materials. Herein, we present the first example of PAL supported heterogeneous Pd catalysts for the general and efficient amine formylation with CO_2 and H_2, under mild reaction conditions (Fig. 1). Both secondary and primary amines can be converted into the corresponding formamides with good to excellent yields, at < 100 °C with 1 MPa CO_2.

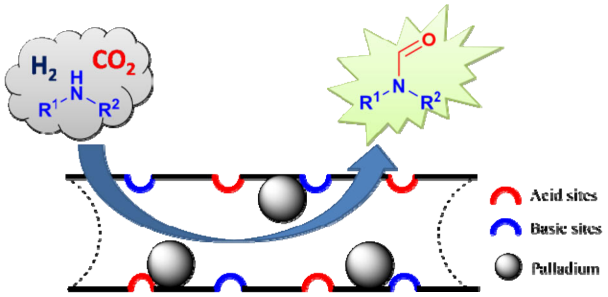
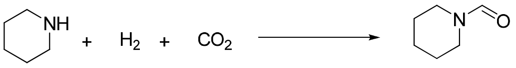


Fig. 1. N-formylation of amine with CO_2 and H_2 catalyzed by Pd/PAL catalyst via the synergistic effect of multiple functional sites.

Initially, a series of supported Pd-based catalysts with different supports were prepared by the reductive deposition method, in which the metal Pd was reduced and deposited on or in the PAL support with H_2PdCl_4 as a metal precursor and hydrazine hydrate as the reducing agent (see Supporting Information). The catalysts were characterized by different analytical techniques and tested for formamide synthesis by the reaction of piperidine with CO_2 and H_2 (Table 1). Obviously, PAL was better as a catalyst support than other inorganic oxides (entries 1–8), and 24% yield of piperidine-1-carbaldehyde was obtained in the presence of Pd/PAL catalyst (entry 1). Considering the unique structure and cation exchange capacity of PAL, we speculated that the excellent catalytic performance of the Pd/PAL catalyst might have originated from the synergistic effect of the intrinsic acid and basic sites in the PAL support and the metal Pd species inside the PAL support. Basically, the introduction of Pd species inside the PAL support might be favorable for the formation of the desired formamide. To verify the assumption, a Pd/PAL-12 catalyst was prepared by extending the ion exchanging time to 12 h. As expected, the Pd/PAL-12 catalyst exhibited excellent catalytic performance and the formamide yield was increased to 35% (entry 9). Subsequently, the effect of base additives was studied, and different bases such as KOH, NaOH, K_2CO_3, Na_2CO_3, and NaF were tested and their effects were compared (Entries 10–14). Consequently, K_2CO_3 was proven to be the most suitable base and 60% yield of piperidine-1-carbaldehyde could be obtained by introducing 50 mol% K_2CO_3 (entry 12). Relatively low yields were observed for other bases (entries 10, 11, and 13). By extending the reaction time to 24 h, the yield of piperi-

Table 1

Catalyst screening and reaction condition optimization[a].



Entry	Catalyst	Solvent	Base	*t*/h	Yield[b] (%)
1	Pd/PAL	MeOH	—	5	24
2	Pd/Al_2O_3	MeOH	—	5	15
3	Pd/SiO_2	MeOH	—	5	14
4	Pd/MgO	MeOH	—	5	22
5	$Pd/MgAlO_x$	MeOH	—	5	15
6	$Pd/MgSiO_x$	MeOH	—	5	15
7	$Pd/AlSiO_x$	MeOH	—	5	5
8	$Pd/MgAlSiO_x$	MeOH	—	5	22
9	Pd/PAL-12	MeOH	—	5	35
10	Pd/PAL-12	MeOH	KOH	5	47
11	Pd/PAL-12	MeOH	NaOH	5	24
12	Pd/PAL-12	MeOH	K_2CO_3	5	60
13	Pd/PAL-12	MeOH	$NaCO_3$	5	51
14	Pd/PAL-12	MeOH	NaF	5	35
15	Pd/PAL-12	MeOH	K_2CO_3	24	90
16	PAL	MeOH	K_2CO_3	5	—
17[c]	Pd^0	MeOH	K_2CO_3	5	—
18[d]	Pd/C	MeOH	K_2CO_3	5	26

[a] Reaction conditions: 1 mmol piperidine, 100 mg catalyst, 3 MPa H_2, 1 MPa CO_2, 50 mol% base, 3 mL solvent, 96 °C (reaction temperature). [b] Yields were determined by GC-FID with biphenyl as an external standard. [c] Pd^0 (0.38 mg, prepared by the same procedure used for the Pd/PAL catalyst) was used as the catalyst. [d] Commercial 5 wt% Pd/C (8 mg, obtained from Lanzhou Zhongke Kaidi Chemical New Technology Co., Ltd.) was used as the catalyst.

Table 2
Properties of the prepared catalysts.

Entry	Catalyst	Pd [a] (wt%)	SA [b] ($m^2 g^{-1}$)	PV [c] ($10^{-2}/cm^3 g^{-1}$)	APR [d] (nm)
1	Pd/PAL-12	0.38	149	62.2	8.4
2	Pd/PAL	0.33	171	69.1	8.1
3	Pd/MgO	0.36	31	12.8	8.2
4	Pd/Al_2O_3	0.34	144	42.2	5.9
5	Pd/SiO_2	0.38	414	97.3	4.7
6	Pd/$MgAlO_x$	0.40	174	43.9	5.1
7	Pd/$MgSiO_x$	0.37	245	17.6	1.4
8	Pd/$AlSiO_x$	0.39	24	2.5	2.1
9	Pd/$MgAlSiO_x$	0.35	44	5.6	2.5

[a] Determined by ICP-AES. [b] BET surface area. [c] Total pore volume. [d] Average pore radius.

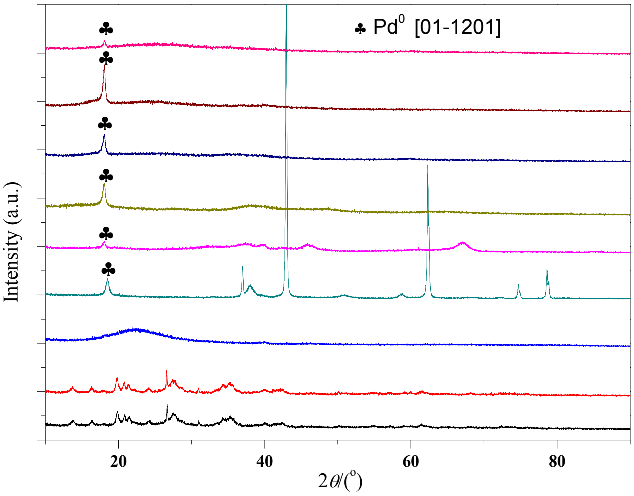


Fig. 2. XRD diffraction patterns of the prepared catalysts. The catalyst samples are Pd/PAL-12, Pd/PAL, Pd/SiO_2, Pd/MgO, Pd/Al_2O_3, Pd/$MgAlO_x$, Pd/$MgSiO_x$, Pd/$AlSiO_x$, and Pd/$MgAlSiO_x$ in ascending order, respectively.

dine-1-carbaldehyde could be increased to 90% (entry 15). The formamide product was not observed when the bare PAL support or metallic Pd^0 was applied, which implied that the supported Pd^0 was active for the N-formylation of amine with CO_2 and H_2 (entries 16 and 17). As a weak acidic gas, CO_2 was easily adsorbed on basic sites, while basic amine was easily adsorbed on acid sites [29,30]. Considering the existence of multiple functional acid and basic sites on and in the PAL, the support might be mainly responsible for the adsorption of amine and CO_2. When commercial Pd/C was applied under identical reaction conditions, a low yield of formamide was obtained (entry 18).

To explore the correlation between the structure and activity, the prepared catalysts were extensively characterized. The N_2 adsorption-desorption analysis revealed that the BET surface area of the active Pd/PAL-12 catalyst was smaller than that of Pd/PAL (Table 2, entries 1 and 2), which suggested that more metal Pd migrated into the support, leading to the blockage of some pores. The Pd/SiO_2 catalyst had the largest BET surface area (entry 5), and the smallest BET surface area was obtained in the case of Pd/$AlSiO_x$ (entry 8). Notably, the active catalyst, Pd/PAL-12, exhibited the highest average pore radius (8.4 nm, Table 2, entry 1 and Fig. S1), suggesting that the large pore size might be favorable for the formation of the desired product. The Pd contents of the prepared catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and it varied in the range of 0.33 wt%–0.40 wt% (Table 2).

The powder X-ray diffraction (XRD) patterns are shown in Fig. 2. Only the major reflections of the supports were observed in the Pd/PAL-12, Pd/PAL, and Pd/SiO_2 catalysts; no signal indicative of the Pd species was observed, which suggested that the Pd species might be highly dispersed or amorphous. Contrary to the above cases, an obvious diffraction peak at ~18° was observed for all other catalysts, which could be attributed to the formation of metallic Pd species [31]. The Pd particles were not observed in the transmission electron microscopy (TEM) and high resolution (HR)-TEM images of Pd/PAL-12, which might be due to the low metal loading or the formation of Pd species with very small size inside the support (Figs. S2a–b). A similar phenomenon was observed in the TEM image of the used Pd/PAL-12 catalyst (Figs. S2s–t) and no obvious differences were observed upon comparing the fresh and used samples.

The surface properties of the catalysts were determined by X-ray photoelectron energy spectroscopy (XPS). The deconvolution of the Pd 3*d* spectrum for the Pd/PAL-12 catalyst revealed two components with binding energies (BEs) at approximately 335.6 and 338 eV (Fig. 3), which were similar to those for the metallic Pd [32]. The second component with a BE of 338 eV could be ascribed to the peak for Mg KL3 auger, which could be confirmed by comparing the XPS spectra of all other Mg-containing catalysts (Fig. S3). In similarity to the case with the Pd/PAL-12 catalyst, a typical metallic Pd BE could be observed in the XPS spectra of other catalysts (Fig. S3). In other words, Pd on the surface of all catalysts existed in its metallic Pd^0 form. Thus, it is difficult to explain the difference in catalytic performances only by the state of the surface Pd. The above

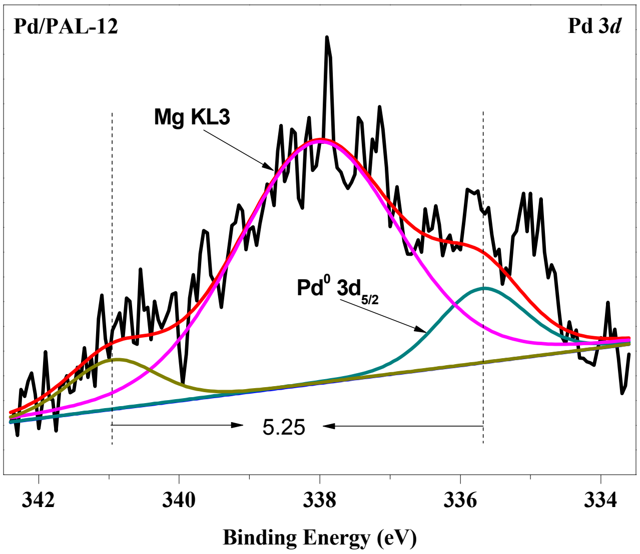


Fig. 3. XPS spectra of the Pd/PAL-12 catalyst.

Table 3
The surface and bulk atomic ratio of the catalysts.

Catalyst	$S_{Pd/Mg}$ (10^{-3})	$B_{Pd/Mg}$ (10^{-3})	$S_{Pd/Al}$ (10^{-3})	$B_{Pd/Al}$ (10^{-3})	$S_{Pd/Si}$ (10^{-3})	$B_{Pd/Si}$ (10^{-3})
Pd/PAL-12	6.78	20.73	43.83	15.66	7.17	4.11
Pd/PAL	7.99	18.00	73.75	13.60	9.62	3.57
Pd/MgO	5.16	1.36	—	—	—	—
Pd/Al_2O_3	—	—	6.24	1.64	—	—
Pd/SiO_2	—	—	—	—	8.95	2.15
Pd/$MgAlO_x$	7.88	3.43	7.16	3.43	—	—
Pd/$MgSiO_x$	15.26	3.49	—	—	34.73	3.49
Pd/$AlSiO_x$	—	—	266.08	4.09	70.41	4.08
Pd/$MgAlSiO_x$	37.23	6.41	534.50	9.61	64.49	3.20

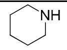
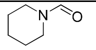
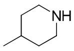
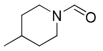
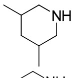
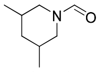
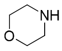
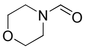
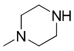
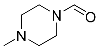
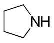
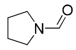
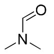
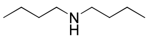
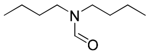
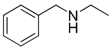
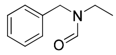
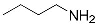
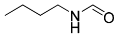
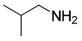
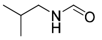
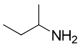
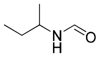
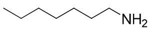
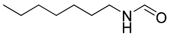
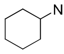
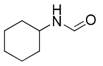
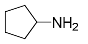
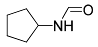
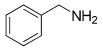
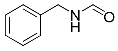
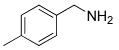
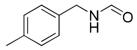
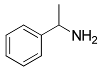
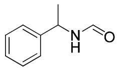
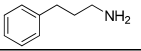
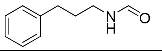
S: The surface atomic ratio. B: The bulk atomic ratio.

speculation that some Pd might migrate into the support, might be the reason for the relatively high activity with PAL as support. Therefore, the amount of Pd in the support was evaluated by comparing the surface and bulk Pd/M (M = Mg, Al or Si) ratio of the catalysts (Table 3). Noticeably, the surface Pd/Mg ratio in the Pd/PAL-12 catalyst was much lower than that in the bulk, which meant that most of the Pd migrated into the support. This is in good agreement with the results for N_2 adsorption-desorption analysis. A similar phenomenon was observed for Pd/PAL, although it was found that the amount of Pd inside the support should be less than that in the case of the Pd/PAL-12 catalyst by comparing the two surfaces and bulk Pd/Mg ratio, which might be the reason that the Pd/PAL catalyst exhibited lower catalytic activity than that of the Pd/PAL-12 catalyst. For the other Mg-containing catalysts such as Pd/MgO, Pd/$MgAlO_x$, Pd/$MgSiO_x$, and Pd/$MgAlSiO_x$, more Pd species were observed in the supports.

Summarizing the above discussions, the excellent catalytic performance of the Pd/PAL-12 catalyst could be attributed to the relatively high amount of metal Pd that migrated into the PAL support. The PAL support has a unique chain-layer structure and contains multiple acid and basic sites. If the metal Pd migrates into the support, it can easily interact with more acid and basic sites in comparison to the surface metal Pd. Moreover, the local environment consisting of multiple functional sites, including metal Pd, acid, and basic sites provides favorable reaction conditions for the adsorption and activation of amine, CO_2, and H_2.

Next, the scope and limitations of the Pd/PAL-12 catalyst were explored with the reaction of different amines and CO_2/H_2 (Table 4). Cyclic secondary amines could be converted into the desired formamides in excellent yields. For example, 90%–99% yields were obtained when piperidine and its derivatives were used as the substrates (entries 1–3). Similar results were obtained in the cases of morpholine, 1-methylpiperazine, and pyrrolidine (entries 4–6). The Pd/PAL-12 catalyst is also active for the reaction of normal secondary amine and CO_2/H_2. An important industrial molecule, i.e., DMF, could be obtained in 86% yield when dimethylamine aqueous solution was used as the starting material (entry 7). A nearly identical result was obtained for dibutylamine (entry 8). The tolerance for N-benzylethanamine was also good and could be converted into the corresponding formamide in 83% yield (entry 9). Besides, primary amines with diverse structures also proved to be active substrates and could easily react with CO_2/H_2 to synthesize the desired formamides. When butan-1-amine, 2-methylpropan-1-amine, butan-2-amine, and heptan-1-amine were used as the substrates (entries 10–13), 83%–96% yields were obtained. Cyclohexanamine and cyclopentanamine were converted into the corresponding formamides in 88% and 76% yields, respectively (entries 14 and 15). When benzylamine and 4-methyl-benzylamine were applied as the starting materials, 81-86% yields of the desired products were obtained (entries 16 and 17). Notably, good yield was obtained in the case of 1-phenylethanamine (entry 18). Typically, a 90% yield of the corresponding formamide was obtained when 3-phenylpropan-1-amine reacted with CO_2/H_2 (entry 19).

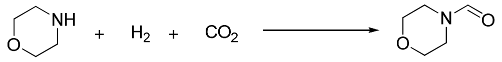
Table 4
Results for N-formylation of different amines[a].

Entry	Substrate	Product	Yield[b] (%)
1			90/85[c]/84[d]
2			99
3			95
4			99
5			98
6			90
7			86
8			85
9			83
10			88
11			96
12			83
13			95
14			88
15			76
16			81
17			86
18			78
19			90

[a] Reaction conditions: 1 mmol amines, Pd/PAL-12 (0.37 wt% Pd, 0.35 mol% Pd), 3 MPa H_2, 1 MPa CO_2, 3 mL MeOH, 96 °C (reaction temperature). [b] The product yields were determined by GC-FID with biphenyl as an external standard. [c] The catalyst was used at the 2nd run. [d] The catalyst was used at the 3rd run.

Finally, the reusability of Pd/PAL-12 catalyst was tested for the reaction of piperidine with CO_2/H_2 (Table 4, Entry 1). After each reaction, the catalyst was recovered by simple centrifugation, washed, dried, and reused without further treatment. The catalyst could be recycled for 3 runs without obvious deactiva-

Table 5
Comparison of the performances of the heterogeneous Pd catalysts reported in literature and in this study.



Entry	Catalyst	Pd loading (wt%)	CO_2/H_2 (MPa)	Base	T/°C	t/h	Yield (%)	Ref.
1	Pd/PAL-12	0.38	1/3	K_2CO_3 50%	96	24	99	This work
2	Pd/Al_2O_3-NR	0.53	1/2	—	130	24	96	[23]
3	Pd-Au/PANI-CNT	1.6	3.5/3.5	—	125	48	95.2	[22]
4	Pd/NC	2	3/4	—	130	24	93	[19]
5	mine-POP-Pd	8.1	3/3	K_3PO_4 30%	100	24	97	[17]

tion and 84% product yield could be still maintained at the 3rd run. Further Pd leaching test was performed to demonstrate the stability and heterogeneity of the catalyst. After reacting for 5 h, the catalyst was removed, and the filtrate was analyzed by ICP-AES. As a result, no Pd was detected in the filtrate and the formamide product was not generated after removing the catalyst, which further confirmed the stability of the catalyst during the reaction and the supported Pd as the active species.

To assess our catalytic system, the catalytic performance of the Pd/PAL-12 catalyst for the N-formylation of amine with CO_2 and H_2 was compared with that of the supported Pd-based catalysts reported in the literature. Considering the wide use of morpholine as a typical starting material, the N-formylation of morpholine was used as the model reaction to evaluate the catalytic performance of the different catalysts (Table 5). The results showed that our catalyst system had the lowest Pd loading and reaction temperature, but the highest yield of formamide for the same reaction time, although a catalytic amount of base was required, which confirmed that our catalyst was more active.

To gain insights into the reaction mechanism, we traced the reaction of piperidine and CO_2 by GC-MS. The analysis results of the reaction mixtures revealed the formation of methyl formate. Based on the results and early reports [18], a possible reaction mechanism was proposed. First, CO_2 and H_2 are adsorbed and activated by the Pd/PAL catalyst, followed by the reaction with methanol as the reaction medium to *in situ* generate $HCOOCH_3$ intermediate with the aid of K_2CO_3. Subsequently, the generated $HCOOCH_3$ reacts with piperidine to form the targeted product.

In summary, a general and efficient supported Pd catalyst was developed for amine formylation with CO_2 and H_2. The catalyst was prepared by a simple reductive deposition method with the natural palygorskite containing multiple functional sites as support. Utilizing this catalyst, N-formylation of a series of secondary and primary amines with CO_2 and H_2 could be performed under mild conditions and good to excellent yields were obtained. The analysis by a combination of characterization techniques revealed that most of the Pd in the active Pd/PAL-12 catalyst migrated into the PAL support, and the interaction of Pd and acid/basic sites inside the support was the key to synthesizing the desired formamides. The study of the reaction mechanism revealed that the amine formylation might proceed via methyl formate intermediate pathway.

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Graphical Abstract

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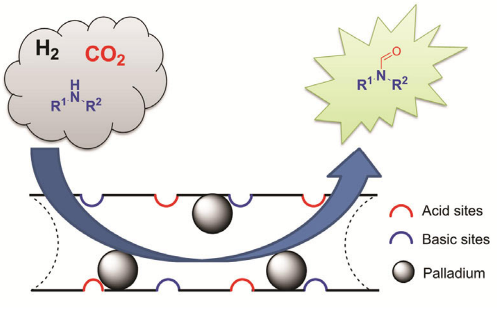
Amine formylation with CO_2 and H_2 catalyzed by heterogeneous Pd/PAL catalyst

Xingchao Dai, Bin Wang, Aiqin Wang, Feng Shi*
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences; Northwest Minzu University; University of Chinese Academy of Sciences



Heterogeneous Pd catalyst with the natural palygorskite as support could effectively catalyze amine formylation with CO_2 and H_2 *via* the synergistic effect of multiple functional sites.

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Pd/PAL催化二氧化碳、氢气和胺反应合成甲酰胺

代兴超[a,d]，王斌[b]，王爱勤[c]，石峰[a,*]
[a]中国科学院兰州化学物理研究所羰基合成与选择氧化国家重点实验室，甘肃兰州730000
[b]西北民族大学化工学院甘肃省高校环境友好复合材料及生物质利用省级重点实验室，甘肃兰州730030
[c]中国科学院兰州化学物理研究所环境材料与生态化学研究发展中心甘肃省粘土矿物应用研究重点实验室，甘肃兰州730000
[d]中国科学院大学，北京100049

摘要: CO_2高效活化和定向转化合成高附加值化学品是催化化学领域的重要研究课题. 然而, 由于CO_2分子具有高度对称结构和高的碳原子氧化态, 其在温和条件下的活化和转化仍然是一个挑战. 众所周知, CO_2的有效吸附和活化是其转化利用的前提. 因此, 一种理想的CO_2催化转化材料应该具有吸附、活化和选择性转化CO_2的多功能特性. 据报道, 金属Pd能够催化CO_2/H_2和胺反应合成甲酰胺. 但是已有的催化体系通常只对脂肪族仲胺显示出高的活性, 当脂肪族伯胺用作反应底物时仅低到中等的产物收率. 最近, Liu和Han等报道负载型的Pd催化剂Imine-POP@Pd、Pd/LDH和Pd/NC能够催化CO_2和脂肪族伯胺反应合成甲酰胺. 但是这些催化体系要求高的反应温度(140 °C)、CO_2压力(3 MPa)和Pd担载量(8.1 wt%). 我们小组最近发现富羟基官能团碳担载的纳米Pd能够有效催化CO_2/H_2和胺反应合成甲酰胺, 但是反应条件仍然比较苛刻且碳载体制备过程复杂.

凹凸棒石是一种天然的一维纳米水合镁铝硅酸盐粘土矿物, 不仅具有独特的链层状结构, 而且含有丰富的纳米孔道和多种酸碱位点. 因此, 凹凸棒石有可能提供多种活性位点协同作用的反应环境, 用作CO_2活化转化多功能催化材料合成的潜在载体. 本论文首次以凹凸棒石为催化剂载体制备了负载型多相Pd/PAL催化剂, 并将其应用于CO_2的还原胺化反应. 在低于100 °C、1 MPa CO_2条件下, 实现了一系列不同结构仲胺和伯胺到目标产物甲酰胺的转化, 并获得了较好的产物收率. 催化剂重复使用性研究结果表明, 催化剂Pd/PAL在反应过程中较为稳定. BET、XRD和XPS表征揭示, 部分负载的金属Pd进入到了载体内部, 其与载体内部酸碱位点的协同作用可能是催化剂Pd/PAL能够高效催化CO_2/H_2和胺反应合成甲酰胺的重要原因. 控制实验和反应机理研究表明, 甲酸甲酯是甲酰胺形成的可能中间体.

关键词: 甲酰化; 二氧化碳; 胺; 多相钯催化剂; 甲酰胺

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*通讯联系人. 电话: (0931)4968142; 传真: (0931)8277088; 电子信箱: fshi@licp.cas.cn

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