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Nanostructured CeO$_2$ Promoted Pd /α-Alumina Diethyl Oxalate Catalyst with High Activity and Stability

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A Pd/α-Al$_2$O$_3$ nanocatalyst was synthesized and investigated as a catalyst for CO oxidative coupling to diethyl oxalate and CeO$_2$ was used as a promoter as well. With the highest activity and stability found so far, great CO conversion and diethyl oxalate selectivity were achieved due to the addition of CeO$_2$.

Ethylene glycol (EG) is a crucial raw chemical with a global demand of around 25 million tons each year, which is mostly produced through traditional petrochemical technology.[1, 2] However, the cost of this production is relatively high due to the continuously increasing price of natural gas and crude oil, and dwindling sources of petroleum. Furthermore, strong acids or alkalis such as sulphuric acid or sodium hydroxide have to be used through the traditional method, which causes severe corrosion to the equipment and environmental problems.[3] Therefore, a green route which is independent of petroleum while achieves high yield of EG is in demand and of great significance.

Coal is the most abundant energy reserve in the world that some people like because of their needs while others hate due to the various emissions resulting from its combustion.[4] To reduce CO$_2$ emission and produce high-value fuels and chemicals from coal, coal gasification and liquefaction technologies have attracted increasing interest during the past few decades.[5-8] Coal to ethylene glycol, as a potentially green and economic coal liquefaction technology, has been attracting extensive attention in both academic and business circles in the past decades.[9-12] Although it is challenging to achieve high industrial production levels, due primarily to achieving good performance of the catalysts, this technology has been scaled-up to industrial levels of production in China and Europe. Until now, China has leaded the word in this area and has successfully built the world's first annual 200 thousand ton coal to ethylene glycol production plant in 2009.[13]

Syngas to ethylene glycol process contains several steps. The step of CO oxidative coupling to di-alkyl oxalate is the critical one since di-alkyl oxalate is needed for production of EG with hydrogenation. Two major chemical reactions are involved with the overall CO oxidative coupling step, CO coupling and RONO regeneration, as shown in R1 and R2 respectively. R in both R1 and R2 could be methyl, ethyl or butyl groups. R1 needs catalyst while R2 does not. Esterification between oxalic acid and alcohol has been employed as a traditional way of synthesizing oxalic ester. However, this method has several problems, such as severe pollution, high energy consumption and high capital costs. Therefore, oxidative coupling CO with alkyl nitrite for formation of oxalic ester is gaining increasing interest.[3, 14-20]

$$2\,CO + 2RONO \rightarrow (COOR)2 + 2NO \qquad (R1)$$

$$2ROH + 2NO + \frac{1}{2}O2 \rightarrow 2RONO + H2O \qquad (R2)$$

Various supported palladium catalysts for gas-phase synthesis of dimethyl oxalate (DMO) or diethyl oxalate (DEO) have been investigated, and the results have demonstrated that higher conversion and selectivity are realized on Pd/α-Al$_2$O$_3$ compared to Pd on active carbon or γ-Al$_2$O$_3$.[21, 22] However, the relatively high Pd loading (around 2 wt %) is always an issue for industrial application of CO oxidative coupling to DMO which greatly increases the cost of production. Therefore, the design of low Pd loaded catalysts with high performance is important to industry. A Pd/α-Al$_2$O$_3$ nanocatalyst with ultra-low Pd loading that exhibits high activity and stability for CO oxidative coupling to DMO was developed recently.[23] This catalyst was prepared by a Cu^{2+} assisted in situ reduction method at room temperature, which significantly increased the dispersion and the specific surface area of active component Pd, and also decreased the ensemble size of Pd nanoparticles dispersed over the Pd/α-Al$_2$O$_3$. To further enhance the activity and stability of Pd/α-Al$_2$O$_3$, several metals such as Fe,[24, 25] Ni, and Ce were reported as promoters to enhance the dispersion of Pd on the support or decrease the Pd particles size.[24-27] CeO$_2$ was reported as a promoter for Pd/α-Al$_2$O$_3$ catalyst.[28] However, the activity of the CeO$_2$ promoted catalyst was only evaluated up to 100 min.

Although methyl nitrite has been maturely used, especially in China, for the industrial synthesis of DMO, it is controlled in the US due to its highly flammable, explosive, and toxic properties.

Ethyl nitrite, however, is a safe and non-explosive alkyl nitrite that also can be used for CO oxidative coupling reaction.[18, 20, 29-32] Therefore, to find a good catalyst with low Pd loading and high catalytic activity for CO oxidative coupling to DEO is of great significance. Herein, we report a Pd-CeO_2 α-Al_2O_3 nanocatalyst with 0.8% Pd (Wt%) loading and 0.2 Wt% CeO_2 as a catalyst for CO oxidative coupling to DEO. We present the preparation and characterization of two catalysts with and without CeO_2 as a promoter. The comparison of catalytic activities between the two catalysts is discussed and the interaction among Pd, ceria and the support leading to the activity differences is also presented.

The textural characteristics of Pd-CeO_2/α-Al_2O_3 catalyst were investigated by transmission electronic microscopy (TEM) (Fig. 1), scanning transmission electronic microscopy (STEM) and scanning electronic microscopy (SEM) (Fig. S5). TEM images presented in Fig. 1a and c clearly show that the Pd nanoparticles of Pd-CeO_2/α-Al_2O_3 are dispersed on the α-Al_2O_3 relatively uniformly while the dispersion of Pd nanoparticles of Pd/α-Al_2O_3 is poor. Moreover, the results in Fig. 1b and d show that the average Pd nanoparticles size of the Pd-CeO_2/α-Al_2O_3 catalyst is 13.2 nm which is smaller than that of the Pd/α-Al_2O_3 catalyst (17.3 nm). The Pd nanoparticles size distribution of the Pd-CeO_2/α-Al_2O_3 catalyst is narrower than that of the Pd/α-Al_2O_3 catalyst as well. CeO_2 was difficult to detect by TEM which may be due to its low loading concentration. However, the red circles in Fig. S 5a indicate the dispersion of CeO_2 on the α-Al_2O_3 support, which is confirmed by energy dispersive X-ray (EDX) spectra. The dispersion of CeO_2 particles was not as good as Pd particles. Small portion of the added CeO_2 aggregated into the large particles while most of it which played the promoter role existed in the form of small nanoparticles that hardly detectable with SEM or TEM. In summary of the results from TEM and SEM, it can be concluded that the promoter CeO_2 not only promotes the dispersion of Pd on the support, but also decreases the nanoparticle size of Pd.

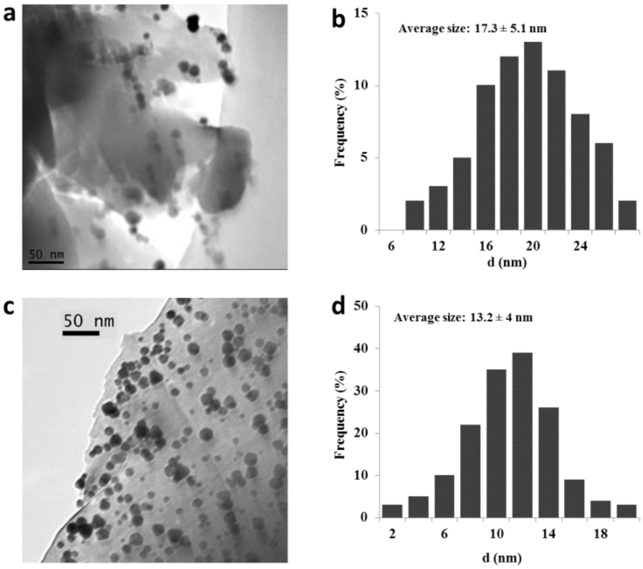

Fig. 1 TEM (a) and size distribution (b) of catalyst Pd/α-Al_2O_3; TEM (c) and size distribution (d) of catalyst Pd-CeO_2/α-Al2O_3.

The two catalysts, Pd/α-Al_2O_3 and Pd-CeO_2/α-Al_2O_3, were analyzed with X-ray photoelectron spectroscopy (XPS) (Pd 3d) before and after the reaction with CO and EN at 140 ℃ (Fig S3). Although there were small differences between Pd/α-Al_2O_3 and Pd-CeO_2/α-Al_2O_3, the obtained Pd $3d_{3/2}$ and Pd $3d_{5/2}$ values for both Pd (0) and Pd (II) were consistent with the published literatures.[33-35] In Fig. 2a and c, both the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of catalysts Pd/α-Al_2O_3 and Pd-CeO_2/α-Al_2O_3 are around 335 and 340 eV, respectively, which indicates that the oxidation state of Pd in the catalysts is Pd(0). However, after reaction, two new peaks appeared in both of the catalysts (Fig. S3 c and d), which are assigned to Pd(II),[35] indicating that some Pd(0) in the two catalysts was oxidized to Pd(II) by ethyl nitrite to form an intermediate, $CH_3CH_2O-Pd(II)-O CH_2CH_3$.[13] The peaks area of the Pd(II) in Fig. S3d is much bigger than the peaks area in Fig. S3b, which indicates that more intermediate was generated on the surface of Pd-CeO_2/α-Al_2O_3 catalyst, and therefore Pd-CeO_2/α-Al_2O_3 may have higher catalytic activity with the addition of CeO_2. Furthermore, the percentage of the Pd on both catalysts was calculated using the peaks area of the XPS and the Pd-CeO_2/α-Al_2O_3 catalyst showed higher Pd concentration (0.92%) than that of the Pd /α-Al_2O_3 catalyst (0.81%) , which suggests that the promoter CeO_2 can also enhance the Pd loading concentration on the support.[21] X-ray diffraction (XRD) (Fig. S4) was also attempted to further confirm the XPS results. However, no detectable CeO_2 or Pd peak was found which may be due to their low concentrations and the high dispersion of Pd.[28]

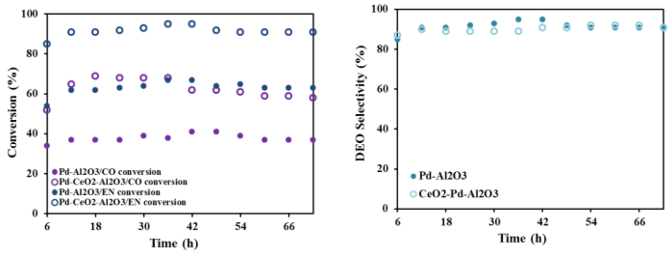

Fig. 2 Conversion of CO (blue lines) and EN (red lines) of CO oxidative coupling to DEO with different catalysts within 72 h (a) and DEO selectivity of CO oxidative coupling to DEO with different catalysts within 72 h (b).

Table 1 CO oxidative coupling to DEO with different catalysts.[a]

Catalysts	Pd content (wt%)	Ce content (wt%)	Conversion[b] (%)	Selectivity (%)	STY (g L^{-1} h^{-1})
Pd/α-Al_2O_3	0.8	_	39	95	195
Pd-CeO_2/α-Al_2O_3	0.8	0.15	65	93	318
CeO_2/α-Al_2O_3	_	0.2	_	_	_

[a] Reaction conditions: 3.5 g of catalyst, 1200 h^{-1} of gas hourly space velocity (GHSV), reactants volume ratio CO/EN is 1.2. 0.1 Mpa, 140 ℃. [b] Conversion of CO.

The catalytic performances of the two catalysts were evaluated under the same conditions. With the addition of CeO_2, the conversion of CO and EN was increased from 39% to 65% and 64% to 92%, respectively (Fig. 2a), which is 50% moreconversion for both of the reactants. The STY of DEO with Pd-CeO_2/α-Al_2O_3 was also greatly increased, which is 60% higher than that of Pd/α-Al_2O_3 at 140 ℃ (Table 1). Meanwhile, the selectivity of DEO with these two catalysts was almost the same (92-95%). Since there was no catalytic activity found for the catalyst CeO_2/α-Al_2O_3, the CeO_2 must play an important role as a promoter and the interaction of CeO_2 with Pd was responsible for the high activity and selectivity in CO oxidative coupling to DEO. Most of all, the catalytic activity of catalyst Pd-CeO_2/α-Al_2O_3 can be maintained for at least 72 h (Fig. 2b), which lays a good foundation for a further long-term stability test.

Fig. 3 illustrates the in situ DR-FTIR spectra for the reaction of CO with ethyl nitrite to DEO. The band at 1768 cm^{-1} is attributed to the C=O stretching vibrations of the DEO product. It is obvious to note that the intensity of the band at 1768 cm^{-1} in the spectrum of Fig. 3b is stronger than that in the spectrum of Fig. 3a and from the integration results of the two peaks (Fig. S6), the peak area of Pd-CeO_2/α-Al_2O_3 catalyst is 20% bigger than that of the catalyst without CeO_2, which demonstrates the superior catalytic activity of Pd-CeO_2/α-Al2O_3 relative to Pd /α-Al2O_3, consistent with the results of catalytic activity evaluation, TEM, and XPS results.

The effect of temperature on both EN and CO conversion where Pd-CeO_2/Al_2O_3 was used as the catalyst for CO oxidative coupling to DEO reaction was also evaluated (Fig. S7). The conversions of EN and CO increased by 20% when the temperature increased from 120 ℃ to 140 ℃, while the selectivity of DEO had little change until the temperature reached to 180 ℃. Both the CO conversion and DEO selectivity decreased at 180 ℃ due to the decomposition of the EN. Therefore, the future plan for this project is optimizing the Pd-CeO_2/Al_2O_3 catalyst to achieve a lower reaction temperature while maintaining high DEO selectivity.

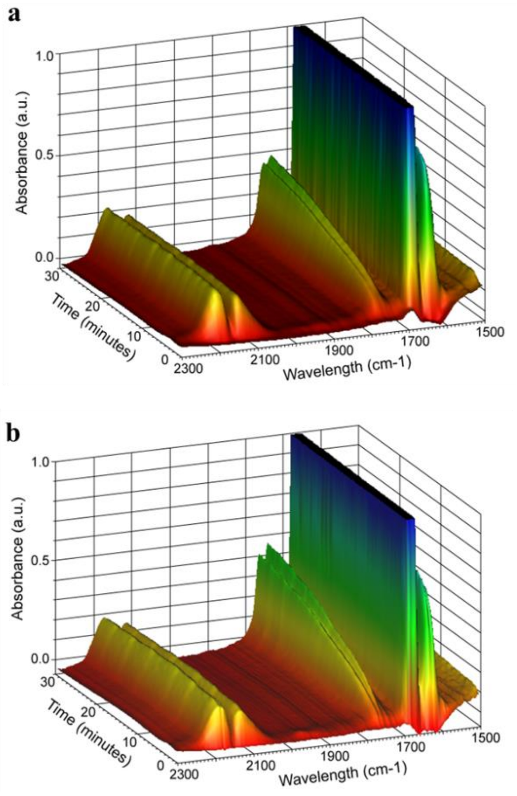

Fig. 3 In situ FTIR sepctra for the CO oxidative coupling to DEO reaction with Pd/α-Al_2O_3 (a) and Pd-CeO_2/α-Al_2O_3 (b).

In summary, a low Pd loading Pd/Al_2O_3 nanocatalyst with 0.8% Pd (Wt%) loading and an average Pd size of 13.2 nm was synthesized for CO oxidative coupling to DEO. After the introduction of 0.2 Wt% CeO_2, Pd-CeO_2/Al_2O_3 catalyst showed remarkably higher catalytic activity compared with the catalyst without CeO_2. The CO conversion was increased by 50% (from 39% to 62%) with the DEO selectivity higher than 90% when the CeO_2 was used as a promoter and, importantly, the high activity and selectivity could be maintained up to 72 h without visible decrease. TEM results showed clearly that CeO_2 not only improved the dispersion of palladium on the surface of the support but also decreased the palladium size as well, thus resulting in the excellent catalytic activity. In consideration of the facile synthesis and low Pd loading of this catalyst as well as the risky factors of methyl nitrite, this highly efficient and stable nanocatalyst may have a promising industrial application, especially in the US, of coal to ethylene glycol.

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Notes and references

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A Pd-CeO_2/α-Al_2O_3 nanocatalyst was used as CO oxidative coupling to diethyl oxalate catalyst with the CO conversion significantly increased.