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Novel synthesis of diethyl carbonate over palladium/MCM-41 catalysts

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The catalytic activities of palladium supported on Si-MCM-41 and Ti-MCM-41 catalysts have been studied in the reactions of $CO + C_2H_5ONO$. It reveals that copper and titanium used as additives are able to increase the yields of DEC and DEO. The additive copper is favorable to DEO formation, while the additive titanium is favorable to DEC formation.

Keywords: palladium supported MCM-41 catalysts, carbonylation, diethyl carbonate

1. Introduction

Diethyl carbonate (DEC) is widely used for organic synthesis because of having an active methylene group in its molecule. However, it is traditionally manufactured from phosgene and ethanol. The drawbacks of such a process include HCl corrosion, safety hazards and serious environmental problems due to the use of phosgene as a reactant. Therefore, we attempted to develop a new route which is similar to the synthesis of diethyl oxalate (DEO), in which DEC is generated as a by-product [1]. So far clean technology for synthesis of DEC using palladium catalysts has not been reported. We developed a new route in which the oxidative carbonylation of ethanol to diethyl carbonate in the vapor phase was carried out according to the following reaction equations:

$$2C_2H_5OH + 2NO + \tfrac{1}{2}O_2 \rightarrow 2C_2H_5ONO + H_2O \quad (1)$$

$$CO + 2C_2H_5ONO \rightarrow CO(OC_2H_5)_2 + 2NO \quad (2)$$

Mobil researchers have invented MCM-41 type mesoporous molecular sieves possessing a hexagonal array of uniform mesoporous, high thermal stability, high BET surface area and large pore volume [2]. These peculiarities are all very important for its potential utilization as a support of the catalysts in the above oxidative carbonylation reaction. MCM-41 molecular sieves as the supports for efficient catalysts in various catalytic reactions have been reviewed [3,4]. However, no literature is found so far on investigations of the catalytic behavior of MCM-41 and Ti-MCM-41 molecular sieves as the supports for efficient catalysts in the reaction of oxidative carbonylation of ethanol to diethyl carbonate in the vapor phase. Si-MCM-41 and Ti-MCM-41 mesoporous molecular sieves are utilized as the supports for preparing supported palladium catalysts. The purpose of this study is to explore effective catalysts for DEC production in $CO + C_2H_5ONO$ reactions.

2. Experimental

2.1. Catalyst preparation

The supports of Si-MCM-41 (SiM) and Ti-MCM-41 (TiM, $Ti:Si = 1:30$) mesoporous molecular sieves were synthesized according to the procedure given in [5,6]. The properties of these two support materials are as follows: SiM possesses BET surface areas 1009 m^2/g and pore size 2.6 nm, TiM has BET surface area 910 m^2/g and pore size 2.0 nm. Both supports are used as powder. The supported palladium catalysts were prepared by incipient-wetness impregnation with a solution of $PdCl_2$ (0.012 g-Pd/ml) and $CuCl_2{\cdot}2H_2O$ solution (0.003 g-Cu/ml). A solution of $(C_4H_9O)_4Ti$ (0.002 g-Ti/ml) was used as the source of Ti. The palladium loading in the catalysts was maintained at 1.5 wt%. The catalysts were dried at 130 °C overnight.

2.2. Formation of ethyl nitrite

Gas mixtures of 10% O_2/He (6 ml/min) and 20% NO/He (21 ml/min) were introduced into the vessel containing 50 ml ethanol to generate ethyl nitrite (C_2H_5ONO). Ethyl nitrite was produced at 35 °C according to reaction (1). There was no catalyst present in the formation of ethyl nitrite.

2.3. Catalytic performance

The measurements of catalytic activity were carried out in a continuous-flow reaction system with a fixed-bed microreactor. The palladium catalyst was pretreated under flowing hydrogen at atmospheric pressure and 300 °C for 4 h. Then the temperature was decreased to 100 °C for starting the reaction. The reactant gases of 20% CO/He and ethyl nitrite were led into the catalyst bed. The measurements of catalytic activity in the reaction of CO +

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C_2H_5ONO were performed with a catalyst loading of ca. 50 mg at a temperature range of 80–120 °C. The space velocity is 5000–6000 h^{-1}.

Analysis of outlet gases of before and after reaction was performed with a gas chromatograph (HP5890) equipped with FID and a PEG-20M capillary column. The formation rates of the products were expressed by TOF.

2.4. Chemisorption measurements

Hydrogen chemisorption studies were carried out using an OMNISORP(TM) 100CX VER 1G apparatus. Samples (ca. 0.1–0.3 g) were set in a flow-through cell for pretreatment (H_2, 300 °C, 3 h), outgassing and subsequent hydrogen chemisorption measurements. Metallic dispersions and metallic surface area were calculated from hydrogen adsorption isotherms by assuming that one hydrogen atom adsorbs on each surface metal atom. Therefore, the turnover frequency number (TOF) can be calculated according to the well-known definition.

2.5. X-ray powder diffraction

The X-ray diffraction (XRD) patterns were recorded with a Siemens 5000 X-ray powder diffractometer, using Ni-filtered Cu Kα radiation; it was operated at 40 kV and 30 mA.

3. Results and discussion

3.1. XRD patterns

The XRD patterns of Si-MCM-41 and Ti-MCM-41 are shown in figure 1. The typical hexagonal lattice for Si-MCM-41 can be verified by the observation of a strong peak at very low angle ($2\theta \approx 2.3°$) and the other relative peaks at comparatively high angles. Ti-MCM-41 displays considerable broadening peaks compared with Si-MCM-41, indicating the decrease in crystalline contents.

3.2. Dispersion and surface area

A comparison of the metallic dispersion and metallic surface area over six catalysts is given in table 1. It can be

Table 1
A comparison of metal dispersion and metallic surface area.

Catalyst	H/M (%)	Surface area (m^2/g)
1.5 wt% Pd/SiM	7.0	31.4
1.5 wt% Pd–0.5 wt% Cu/SiM	6.5	27.8
1.5 wt% Pd–0.5 wt% Ti/SiM	7.8	34.5
1.5 wt% Pd/TiM	5.0	23.4
1.5 wt% Pd–0.5 wt% Cu/TiM	3.7	16.7
1.5 wt% Pd–0.5 wt% Ti/TiM	4.0	17.9

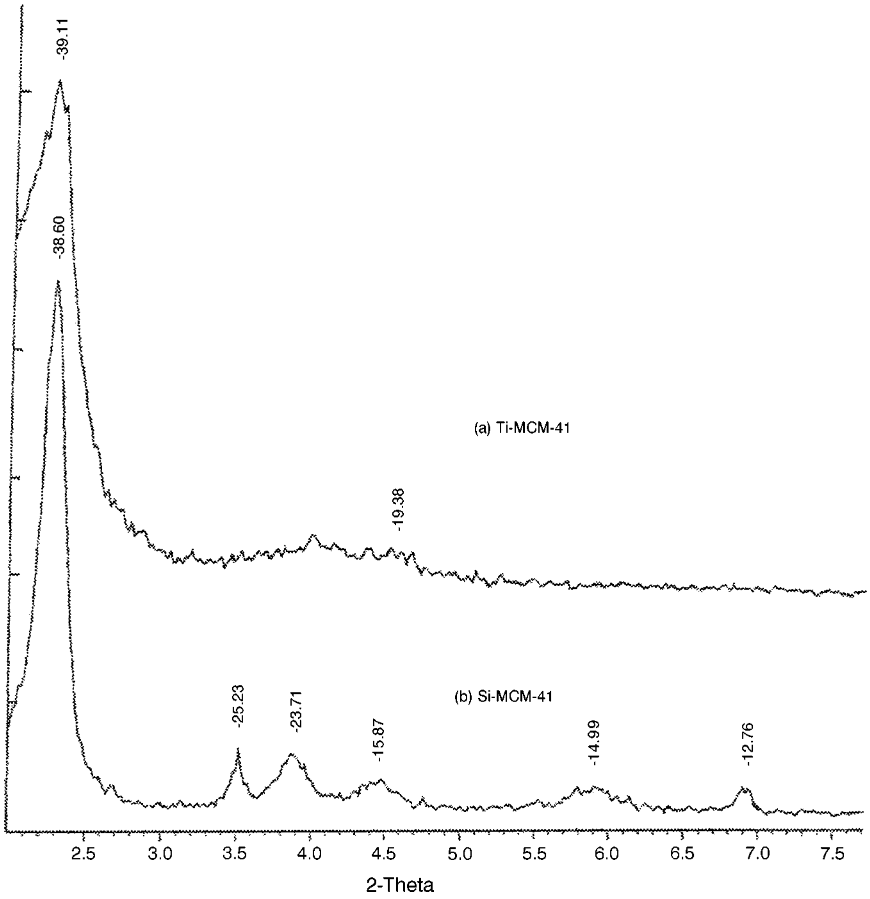

Figure 1. XRD patterns of Si-MCM-41 and Ti-MCM-41.

Table 2
Catalytic performances of Pd, Pd–Cu and Pd–Ti doped on Si-MCM-41.

Catalyst	Temp. (°C)	$\mathrm{TOF}_{\mathrm{DEC}}$ (h^{-1})	$\mathrm{TOF}_{\mathrm{DEO}}$ (h^{-1})
1.5 wt% Pd/SiM	80	135.9	266.3
	90	271.4	402.5
	100	281.8	332.9
	105	305.6	240.5
1.5 wt% Pd–0.5 wt% Cu/SiM	80	89.5	124.5
	90	188.0	396.3
	100	315.1	501.2
	105	448.6	731.7
	110	650.1	758.0
1.5 wt% Pd–0.5 wt% Ti/SiM	80	155.9	116.9
	90	206.5	158.7
	100	338.5	205.3
	105	463.8	270.7
	110	493.8	366.7

Table 3
Catalytic performance of Pd, Pd–Cu and Pd–Ti doped on Ti-MCM-41.

Catalyst	Temp. (°C)	$\mathrm{TOF}_{\mathrm{DEC}}$ (h^{-1})	$\mathrm{TOF}_{\mathrm{DEO}}$ (h^{-1})
1.5 wt% Pd/TiM	80	51.9	–
	90	239.7	–
	100	177.6	–
	110	155.6	–
	115	127.5	–
1.5 wt% Pd–0.5 wt% Cu/TiM	80	259.3	–
	90	440.3	91.6
	100	404.8	–
	105	278.6	–
	110	211.6	–
1.5 wt% Pd–0.5 wt% Ti/TiM	80	37.6	–
	90	74.2	152.7
	100	163.7	119.8
	110	344.8	426.8
	115	566.0	746.4

seen therein that the metal dispersion and metallic surface area over the support Ti-MCM-41 were less than those on the support Si-MCM-41.

3.3. Catalytic performance of the catalyst supported on SiM

A comparison of catalytic performances over three catalysts, 1.5 wt% Pd/SiM, 1.5 wt% Pd–0.5 wt% Cu/SiM and 1.5 wt% Pd–0.5 wt% Ti/SiM, are given in table 2. It can be seen therein that these catalysts demonstrate relatively high reactivity in both DEC and DEO formation in the reactions of $\mathrm{CO} + \mathrm{C_2H_5ONO}$. The 1.5 wt% Pd–0.5 wt% Cu/SiM catalyst exhibited much higher catalytic activities than the 1.5 wt% Pd/SiM catalyst for both DEC and DEO formation rates at reaction temperature above 100 °C. Unfortunately the selectivity of the products was favorable to DEO formation. Over the 1.5 wt% Pd–0.5 wt% Ti/SiM catalyst, however, the catalytic activity of DEC formation was considerably higher than for DEO formation. This result indicates that the additive does play a crucial role in the catalytic behavior in the $\mathrm{CO} + \mathrm{C_2H_5ONO}$ reaction.

3.4. Catalytic performance of the catalyst supported on TiM

Table 3 presents the catalytic performances over the other three catalysts, 1.5 wt% Pd/TiM, 1.5 wt% Pd–0.5 wt% Cu/TiM and 1.5 wt% Pd–0.5 wt% Ti/TiM, for the above reaction under the same reaction conditions. Both 1.5 wt% Pd/TiM and 1.5 wt% Pd–0.5 wt% Cu/TiM catalysts demonstrated high selectivity for DEC formation compared with the catalysts supported on SiM, indicating the presence of a support effect. The catalyst 1.5 wt% Pd–0.5 wt% Ti/TiM demonstrated considerably higher activity for both DEC and DEO formation compared with the catalysts 1.5 wt% Pd/TiM and 1.5 wt% Pd–0.5 wt% Cu/TiM. However, the selectivity of DEC is gradually decreased upon elevating the reaction temperature above 100 °C, which reveals a selectivity shift from DEC to DEO formation with increasing temperature. Despite this disadvantage, these new mesoporous molecular sieves open new possibilities to carry out the oxidative carbonylation of ethanol to produce diethyl carbonate with high selectivity.

3.5. Support effect

The above experimental results reveal that the catalytic behaviors of the catalysts obviously rely on the property of the support. It is interesting to notice in tables 2 and 3 that the catalyst 1.5 wt% Pd–0.5 wt% Ti/SiM is favorable for producing DEC, while DEO is the dominating product over the catalyst 1.5 wt% Pd–0.5 wt% Ti/TiM. Two catalysts, 1.5 wt% Pd/SiM and 1.5 wt% Pd–0.5 wt% Cu/SiM, are favorable to form DEO; however, almost 100% DEC selectivity was obtained over the catalysts 1.5 wt% Pd/TiM and 1.5 wt% Pd–0.5 wt% Cu/TiM. It is really valuable to notice that the isomorphous substitution of Si by Ti in MCM-41 support seems dramatically favorable to DEC formation, implying the presence of an obvious support effect in the reaction of $\mathrm{CO} + \mathrm{C_2H_5ONO}$.

4. Conclusions

In the reaction of $\mathrm{CO} + \mathrm{C_2H_5ONO}$ the catalysts supported on SiM demonstrated higher catalytic activities than the catalysts supported on TiM. It indicates the properties of the support do play a crucial role in the catalytic performance. Two additives, copper and titanium, exhibit different functions on the catalytic behavior: in the case of SiM as the support the additive Cu is favorable to DEO formation, while the additive Ti is towards DEC formation. In the case of TiM as support, however, the two additives show the opposite direction. Further study is needed for exploring the catalytic function of additives as well as the support effect in the novel synthesis route of diethyl carbonate.

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