



Article Synthesis of Dimethyl Carbonate from CO₂ and Methanol over Zr-Based Catalysts with Different Chemical Environments

Linmeng Huo¹, Tian Wang¹, Keng Xuan², Lei Li³, Yanfeng Pu^{1,*}, Chenxin Li¹, Congzhen Qiao¹, Hao Yang¹ and Yan Bai^{1,*}

- ¹ Henan Province Engineering Research Center of Catalytic Reaction, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China; huolmhenan@163.com (L.H.); mtdykxwt@163.com (T.W.); gdhzlcx@163.com (C.L.); qiaocongzhen@henu.edu.cn (C.Q.); hyang@henu.edu.cn (H.Y.)
- ² School of Water Resources & Environmental Engineering, East China University of Technology, Fuzhou 330013, China; xuankeng@ecut.edu.cn
- ³ State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 27# South Taoyuan Road, Taiyuan 030001, China; lilei@sxicc.ac.cn
- * Correspondence: puyf@henu.edu.cn (Y.P.); baiyan@henu.edu.cn (Y.B.)

Abstract: The adsorption and activation of both CO₂ and methanol are mainly affected by the distance of the Lewis acid site, Zr^{4+} , and Lewis base, Zr^{4+}/O^{2-} , of the Zr-based catalysts. In this paper, Zr-incorporated SBA-15 (Zr-SBA-15) and Zr-grafted SBA-15 (Zr/SBA-15) catalysts were prepared with different Zr environments, and were analyzed with N₂ adsorption–desorption isotherms, X-ray diffraction, UV-vis spectra, and XPS. It was proposed that Zr-SBA-15 catalyst with Si-O-Zr-OH and Zr-O-Si-OH structure exhibited non-adjacent sites between Zr^{4+} and Zr^{4+}/O^{2-} , while Zr/SBA-15 catalyst with Zr-O-Zr-OH structure showed neighboring sites between Zr^{4+} and Zr^{4+}/O^{2-} . Furthermore, the Zr/SBA-15 catalyst at the same reaction conditions. For combined in situ infrared and catalytic performance, it was indicated that the methanol and CO₂ could be activated to form DMC, only when the Zr⁴⁺ and Zr⁴⁺/O²⁻ sites existed and were adjacent to each other in the Zr-O-Zr-OH of Zr/SBA-15 catalyst.

Keywords: dimethyl carbonate; in situ FTIR spectra; ZrO₂-grafted SBA-15; Zr-incorporated SBA-15; carbon dioxide

1. Introduction

Dimethyl carbonate (DMC), as a versatile chemical compound, can be used as a green solvent, electrolyte in lithium-ion batteries, and an alternative to some toxic substances such as phosgene, dimethyl sulphate, and alkyl halide for carbonylation and methylation reactions. Furthermore, DMC has been regarded as a fuel additive (alternatives to MTBE) due to its high octane number (105) and oxygen content (53.3%). Presently, the synthesis routes of DMC mainly include methanolysis of phosgene, transesterification of ethylene/propylene carbonate, methanolysis of urea, oxidative carbonylation of methanol, electrochemical route, and direct synthesis from CO_2 and methanol [1–6]. The direct synthesis route of DMC from methanol and CO_2 , avoiding the poisonous reagents such as phosgene and carbon monoxide, is very attractive.

Homogenous catalysts, including metal acetates [7], metal tetra-alkoxides [8], and alkali compounds [9,10], have been adopted in DMC synthesis from CO₂ and methanol, directly, while heterogeneous catalysts such as supported metal catalysts Cu-Ni or Cu-Fe have exhibited better catalytic activity in a fixed-bed reactor. Metal oxides including ZrO_2 , CeO_2 [11–19], H_3PO_4/ZrO_2 [20,21], Al_2O_3/CeO_2 [22], $Ce_xZr_{1-x}O_2$ [23–26], $H_3PW_{12}O_{40}/Ce_xZr_{1-x}O_2$ [27], [EMIM]Br/Ce_{0.5}Zr_{0.5}O_2 [28], $Ce_xZr_{1-x}O_2$ /grapheme [29], and Fe_xZr_{1-x}O_y [30] also showed a definite catalytic activity in a batch reactor. However,



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). methanol conversion and DMC yield are always constrained by the thermodynamic limitations. To overcome the thermodynamic limitations, the removal of water from the reaction medium appears to be of essence. The addition of dehydrating agents and promoters such as nitrile compounds [12,13,17,18], calcium chloride [31], 2,2-dimethoxy propane [16,26], molecular sieves [32,33], ketals [8], aldols [34], and trimethoxymethane (TMM) [28] to the reaction system have been applied in the literature. However, the DMC formation rate is still unacceptable, and theoretical study on the reaction mechanism between methanol and CO_2 is still desired so as to design high-performance catalysts.

Currently, theoretical research about this synthesis route is mainly focused on the amphoteric Zr-OH hydroxyl groups and coordinately unsaturated Zr^{4+}/O^{2-} sites within Zr-based catalysis. In 2001, Bell et al. investigated the mechanism of DMC formation over zirconia [35,36] using in situ infrared spectroscopy, and the results are shown in Scheme 1. In this process, the methanol molecule is activated, giving methoxy species (Zr-OCH₃) on the Zr⁴⁺ sites, and releases the H atom, and then the H atom reacts with the surface OH group to form H_2O . Then, the carbon dioxide molecule reacts with Zr-OCH₃, and a methoxy carbonate anion intermediate occurs. Finally, the intermediate further reacts with the CH₃+ to create DMC. Besides, Tomishige [37] further discovered the neighboring acid-base sites over the tetragonal ZrO₂ surface by TPD of co-adsorbed CO₂ and NH₃, and then established the relationship between the activity and the amounts of acid-base sites. It suggested that the neighboring acid-base sites were the key active sites for DMC formation. Based on the above research, it is natural to wonder if Zr-OH hydroxyl groups and unsaturated Zr^{4+}/O^{2-} Lewis acid/base pairs are both present simultaneously but not adjacent on the catalyst surface, can DMC be produced? As far as we know, research in this area has not been reported previously.



Scheme 1. Synthetic routes for the m-CH₃OC(O)O-Zr(Si) on the Zr/SBA-15 catalyst.

According to the literature, it was suggested that non-adjacent acid-base sites could be obtained on Zr-incorporated SBA-15 materials through hydrothermal synthesis. Chen et al. [38,39] claimed that Zr(IV) could be incorporated in the silica frameworks as isolated Zr species when the Zr/Si molar ratio was less than 0.03. Thunyaratchatanon et al. [40] revealed that Zr species could be incorporated into the silica framework with no agglomeration when the Zr/Si molar ratio was less than 0.07. Previous studies have shown that Zr-SBA-15 with non-adjacent Zr⁴⁺ and Zr⁴⁺/O²⁻ sites in Si-O-Zr-OH or Zr-O-Si-OH could be designed and synthesized successfully with the help of the segregation of silicon atoms in the SBA-15 framework. For comparison, the Zr-grafted SBA-15 materials with a special Zr-O-Zr-OH structure were prepared by growing ZrO₂ monolayers over a mesoporous SBA-15 framework [41–43], which showed neighboring Zr⁴⁺ and Zr⁴⁺/O²⁻ sites, similar to with pure ZrO₂. Based on these results, it is possible to study the effect of the distance between Zr^{4+} and Zr^{4+}/O^{2-} sites on the activity for DMC formation.

In this article, to clarify the effect of the distance between Zr^{4+} and Zr^{4+}/O^{2-} sites on the activity for DMC formation, Zr-incorporated SBA-15 with non-adjacent acid-base sites, Zr-grafted SBA-15 with neighboring acid-base sites, and pure SBA-15 were prepared and used for the DMC synthesis from CO₂ and CH₃OH. The effects of catalyst preparation methods on Zr structure were investigated. Subsequently, the effects of neighboring acidbase sites on the activity for DMC formation were clarified through changing the adsorption sequence of methanol and CO₂ (adsorb methanol first and then CO₂, adsorb CO₂ first and then methanol, adsorb methanol and CO₂ simultaneously). Moreover, a possible reaction mechanism for the DMC synthesis over Zr-based catalysts was also proposed. These results will provide ideas for the design of a high-performance catalyst for the DMC synthesis from CO₂ and methanol.

2. Results and Discussion

2.1. Catalytic Performance

The catalytic performance of Zr-SBA-15, Zr/SBA-15, and SBA-15 catalysts for the DMC synthesis are shown in Table 1. To compare the catalytic activity, the reaction time was set to 1 h to ensure that the reaction was in kinetic range. For all catalysts, no other by-products but DMC appeared in both gas and liquid phase products. Therefore, DMC selectivity was considered to be 100%, and this was consistent with Tomishige's results [37]. It was found that no DMC was detected without catalyst (Table 1, Entry 1). Then, there was also no DMC formation over the pure SBA-15 catalyst (Table 1, Entry 2), implying that this catalyst was inactive for this reaction.

Table 1. The catalytic performance of various catalysts for the DMC synthesis from CO₂ and CH₃OH.

Entry	Catalyst	Zr ^a (mmol)	Reaction Time (h)	Catalyst Weight (g)	DMC Yield (%)	TON ^b	Ref.
1	None	-	1	0	0	0	This work
2	SBA-15	-	1	0.5	0	0	This work
3	Zr/SBA-15-L	0.089	1	0.5	0.012	0.134	This work
4	Zr/SBA-15	0.167	1	0.5	0.029	0.173	This work
5	Zr/SBA-15-H	0.242	1	0.5	0.061	0.252	This work
6	Zr/SBA-15-S	0.321	1	0.5	0.087	0.271	This work
7	Zr/SBA-15	0.167	4	0.5	0.220	1.317	This work
8	Zr-SBA-15-L	0.089	1	0.5	0	0	This work
9	Zr-SBA-15	0.167	1	0.5	0	0	This work
10	Zr-SBA-15-H	0.242	1	0.5	0.001	0.004	This work
11	Zr-SBA-15-S	0.321	1	0.5	0.003	0.009	This work
12	Zr-SBA-15	0.167	10	0.5	0	0	This work
13	Zr-SBA-15	0.334	10	1.0	0	0	This work
14	CeO ₂	0.058	1	0.01	0.024	0.413	[11]
15	Ce/SBA-15-6	-	2	0.5	0.075	-	[44]
16	ZrO_2	4.057	1	0.5	0.015	0.003	[45]

Reaction condition: reaction temperature, 130 °C; CH₃OH:CO₂ = 200 mmol:200 mmol; catalyst weight, 0.5 g; reactor volume, 50 mL; reaction pressure, 10 MPa. ^a Obtained from ICP-AES; ^b Turnover number (TON), expressed as mmol of DMC formed per mmol of Zr atoms.

Upon grafting of ZrO₂, the Zr/SBA-15 catalyst (molar ratio of Zr/Si = 0.021) exhibited a DMC yield of 0.029% (Table 1, Entry 4), and the DMC yield over the ZrO₂-grafted SBA-15 catalysts (Table 1, Entry 3~6) increased with the increase of the molar ratio of Zr/Si. Extending the reaction time, for the Zr/SBA-15 catalyst, the calculated turnover number (TON) on the basis of total number of Zr (0.167 mmol) was calculated to be 1.317 at 4 h, which was greater than 1, indicating that it is a catalytic process (Table 1, Entry 7). According to Honda's results [20], the TON was 0.413 on the CeO₂ (0.058 mmol) catalyst at 1 h (Table 1, Entry 15), which was comparable to that on the Zr/SBA-15-S catalyst (0.271) at 1 h (Table 1, Entry 6) in this work. In addition, the DMC yield on Zr/SBA-15-S at 1 h was higher than that on the Ce/SBA-15-6 (0.075%) catalyst (Table 1, Entry 16) and the ZrO_2 (0.015%) catalyst (Table 1, Entry 14) in our previous research work [44–46], and this may be because Zr atoms were highly dispersed on the ZrO_2 -grafted SBA-15 surface, and then increased the availability of active sites for DMC formation.

It was worth emphasizing that the Zr-SBA-15 catalyst with the same molar ratio of Zr/Si (0.021) as Zr/SBA-15 (Table 1, Entry 9, 4) showed no formation of DMC. Meanwhile, increasing the reaction time and catalyst dosage (Table 1, Entry 12, 13), there were still no DMC over the Zr-SBA-15 catalyst, suggesting that the existence form of Zr played a key role in the catalytic performance. That is to say, the Zr-SBA-15 catalyst did not activate methanol and CO_2 , but the Zr/SBA-15 catalyst could activate the methanol and CO_2 and then effectively form dimethyl carbonate.

Furthermore, increasing the Zr/Si molar ratio to 0.031, a small amount of DMC (0.001%) began to form over the Zr-SBA-15-H catalyst, and the DMC yield increased to 0.003% with a Zr/Si molar ratio of 0.042 over the Zr-SBA-15-S catalyst (Table 1, Entry 10, 11). These results may be because excess Zr ions could not be completely inserted into the SBA-15 skeleton, but could form some active ZrO₂ clusters and then deposit on the catalyst surface [38].

In order to study the influence of the existing form of Zr on catalytic activity, the most representative catalysts of Zr-SBA-15 (Zr-incorporated SBA-15), Zr/SBA-15 (ZrO₂-grafted SBA-15), and pure SBA-15 were selected for further study in the following section.

2.2. Structural and Textural Properties of Samples

 N_2 adsorption–desorption isotherms in Figure 1A showed that all catalysts exhibited type IV isotherms with H1-type hysteresis loops, which were the typical behaviors of ordered mesoporous structure [43]. Compared with the SBA-15 in Table 2 and Figure 1B, the specific surface area (S_{BET}), pore size (D_p), and pore volume (V_p) of the Zr-SBA-15 catalyst decreased slightly. Furthermore, these structural parameters continued to decrease in the Zr/SBA-15 catalyst, indicating that ZrO₂-grafted on SBA-15 may block the part of aperture.

Sample	$V_{ m p}$ (cm $^3{ m g}^{-1}$) a	$S_{ m BET}$ (m ² g ⁻¹) ^b	D _p (nm) ^c
SBA-15	1.32	858	6.8
Zr-SBA-15	1.12	836	5.7
Zr/SBA-15	1.02	796	5.4

Table 2. Physical properties of SBA-15, Zr-SBA-15, and Zr/SBA-15 catalysts.

^a Total pore volumes were obtained at $P/P_0 = 0.99$. ^b BET specific areas. ^c Average pore diameter calculated using the BJH method.

The TEM images of pure SBA-15, Zr-SBA-15, and Zr/SBA-15 catalysts are shown in Supplementary Figure S1. Few differences could be observed. It was indicated that the Zr-incorporated or ZrO₂-grafted had no obvious effects on the morphology of catalysts and the hexagonal SBA-15 phase was retained. The low-angle XRD (Figure 1C) also confirmed that the mesoporous SBA-15 structure was retained, with materials exhibiting the main peak at $2\theta = 0.85^{\circ}$ (1 0 0) and two weaker features at $2\theta = 1.50^{\circ}$ (1 1 0) and 1.71° (2 0 0) reflections [47], of the *pmm6* hexagonally symmetry. Wide-angle XRD (Figure 1D) exhibited a broad diffraction peak at $2\theta = 23^{\circ}$ for all catalysts, which was the typical peak of amorphous silica [48]. The absence of monoclinic or tetragonal phase diffraction features for zirconia suggested that the zirconium species were highly dispersed either in the silica framework or on the surface of the SBA-15 [38,49]. These results are consistent with TEM results of the corresponding materials.



Figure 1. Nitrogen adsorption–desorption isotherms (**A**), pore-size distribution (**B**), low-angle XRD patterns (**C**), and wide-angle XRD patterns (**D**) of the SBA-15, Zr/SBA-15, and Zr-SBA-15 catalysts. DR UV-vis (**E**) and XPS spectra of Zr 3d (**F**), for Zr/SBA-15 and Zr-SBA-15 catalysts, and XPS spectra of O 1s of Zr-SBA-15 (**G**) and Zr/SBA-15 (**H**) catalysts.

The chemical environment of zirconium incorporated into SBA-15 was investigated by DR UV-vis spectra and the results are depicted in Figure 1E. It can be seen that there was no absorbance in the range of 190–400 nm for SBA-15 because tetrahedral Si⁴⁺ ions in the framework were transparent in that UV region [50,51]. The bulk ZrO_2 displayed an extreme intense and broad band covering 190-245 nm, which was assigned to the overlap of the $O \rightarrow Zr(IV)$ ligand-to-metal charge transfer (LMCT) transition and the electron transition from the valence band to the conduction band of ZrO₂ crystallites [50,52]. Unlike bulk ZrO_2 , an absorption band of around 194 nm ascribed to the LMCT from O^{2-} to an isolated Zr⁴⁺ ion was observed in Zr-SBA-15 catalysts [53]. A narrow band at ca. 205 nm and a weak signal at 248 nm were observed on the Zr/SBA-15 catalyst, which were attributed to the band gap transition in small ZrO_2 clusters and the multi-coordinated Zr^{4+} species [52], respectively. According to Chen et al. [38], Zr-SBA-15 samples with Zr/Si molar ratios of 0.01–0.05 exhibited a sharp band around 194 nm, which proved that Zr atoms were mainly isolated Zr species in the SBA-15 framework. With the increase of Zr content, the 194 nm LMCT band was almost gone, and the 205 nm peak was predominant, indicating that Zr may migrate out of the silica framework and form extra-framework ZrO₂ clusters on the superficial areas of pore walls. Thus, we can conclude that the Zr-SBA-15 catalyst with the Si-O-Zr bonding was mainly the isolated Zr^{4+} ion. However, there may be some zirconium dioxide oligomers in the form of Zr-O-Zr bonding on the Zr/SBA-15 surface.

The above conclusions were also supported by the XPS measurements in Figure 1F. It displayed the XPS spectra of Zr 3d recorded for Zr-SBA-15 and Zr/SBA-15 materials. In the previous study, the binding energies of $Zr 3d_{5/2}$ and $Zr 3d_{3/2}$ for bulk ZrO_2 were around 182.4 and 185.3 eV [50,54]. Nevertheless, the Zr-SBA-15 showed doublets of Zr 3d appearing at around 183.3 and 185.7 eV. The shift to higher binding energy for Zr 3d in the Zr-SBA-15 sample could be attributed to the formation of Si-O-Zr bonds due to the higher electronegativity of the Si atom than that of the Zr atom [49]. Therefore, it could be deduced that the Zr atoms were mainly incorporated into the silica framework, while the spectra of Zr 3d showed no obvious change in the Zr/SBA-15 catalyst, indicating that the Zr atoms were successfully grafted onto SBA-15 surface. The deconvolution of the O 1 s peak also confirmed the above-mentioned conclusions in Figure 1G,H. Three peaks at 533.1, 532.5, and 531.9 eV assigned to the Si-O-Si, Si-O-Zr [55] and Zr-OH [46] respectively, were observed in the Zr-SBA-15 and Zr/SBA-15 catalysts, while an additional peak at a binding energy of 530.9 eV corresponding to Zr-O-Zr bonds [46,52] existed in the Zr/SBA-15 catalyst (Figure 1H) rather than that in the Zr-SBA-15 catalyst. Furthermore, this result was consistent with the observations of Thunyaratchatanon et al. [40], who concluded that no Zr-O-Zr bonds were detected with molar ratios of Zr/Si = 0.01-0.07, which possibly arose from the well-dispersed ZrO₂ on the surface of samples. Here, the Zr-SBA-15 catalyst with Zr/Si molar ratios of 0.021 proved again that the Zr-O-Zr bonds did not exist in the Zr-SBA-15 catalyst. These results were also in line with those achieved by DR UVvis (Figure 1E), supporting the conclusions that the Zr-O-Zr bonds only occurred in the Zr/SBA-15 catalyst.

Based on the above results, the difference of catalytic activity between Zr-SBA-15 and Zr/SBA-15 catalysts lies in the fact that Zr atoms are located in different chemical environments, such as Zr-O-Zr-OH, Si-O-Zr-OH, or Zr-O-Si-OH. Furthermore, these different chemical environments of Zr atoms are mainly due to the distance between Lewis acid, Zr^{4+} , and Lewis base, Zr^{4+}/O^{2-} , sites in the catalysts.

2.3. Reaction Mechanism

In order to clarify the effect of the distance between Zr^{4+} and Zr^{4+}/O^{2-} sites on the adsorption and activation of CO_2 and methanol, in situ FTIR was performed to observe the adsorption and reaction process of CO_2 and methanol over the Zr/SBA-15 and Zr-SBA-15 catalysts. Before adsorption, all samples were activated at 130 °C under vacuum until there was no change of the FTIR spectra, and the CO_2 was purified prior to use.

The adsorption of methanol on Zr/SBA-15 at 130 °C is illustrated in Figure 2. Before introducing methanol, only two absorbances of bands at 3739 cm⁻¹ (Figure 2A) and 1620 cm⁻¹ (Figure 2C) associated with Zr(Si)-OH and bidentate bicarbonate species (b-HCO₃-Zr) [56–59] respectively, were presented on the Zr/SBA-15 (0 s). Compared with the results of Jung et al. [35], the terminal (3768 cm⁻¹), bi-bridged (3745 cm⁻¹), and tri-bridged (3672 cm⁻¹) OH groups could not be distinguished over the Zr/SBA-15 catalyst due to the peak overlap from the strong intensity of the Si-OH on SBA-15. Besides that, the band for b-HCO₃-Zr was achieved because the CO₂ inevitably absorbed from the air could react with Zr-OH quickly, which was similar with results of Jung et al. [35], who found that the adsorption of CO₂ was very rapid.



Figure 2. In situ FTIR spectra of CH₃OH adsorption on Zr/SBA-15 catalyst in the regions of 3600 cm⁻¹–3800 cm⁻¹ (**A**), in situ FTIR spectra of CH₃OH adsorption on Zr/SBA-15 catalyst in the regions of 2700 cm⁻¹–3100 cm⁻¹ (**B**), in situ FTIR spectra of CH₃OH adsorption on Zr/SBA-15 catalyst in the regions of 1500 cm⁻¹–1700 cm⁻¹ (**C**), in situ FTIR spectra of CH₃OH adsorption on Zr/SBA-15 catalyst in the regions of 1300 cm⁻¹–1700 cm⁻¹ (**C**).

On adsorption, the peaks at 2956 and 2852 cm⁻¹ ascribed to the C-H stretching vibrations of methoxide groups and the peaks at 2931 and 2831 cm⁻¹ associated with the molecularly adsorbed CH₃OH [60–62] appeared and gradually increased in Figure 2B. Meanwhile, the growth in intensity of the bands at 1461 and 1450 cm⁻¹, associated with the Si-OCH₃ and Zr-OCH₃ [58,63] respectively, were seen in Figure 2D. The intensity of the band at 3739 cm⁻¹ associated with Zr(Si)-OH gradually decreased in Figure 2A. These results indicated that methanol reacted with the Zr-OH or Si-OH to form methoxide groups and simultaneously generated water. In addition, a band could also be seen at 2986 cm⁻¹ for bidentate formate species in Figure 2B. Furthermore, the most interesting discovery was that the band for b-HCO₃-Zr (1620 cm⁻¹) disappeared within the first 10 s of CH₃OH exposure (Figure 2C), and new bands at 1583 and 1389 cm⁻¹ associated with the m-CH₃OC(O)O-Zr(Si) appeared and gradually increased [35,64]. It was indicated that the above-formed Zr(Si)-OCH₃ could react with the pre-adsorbed CO₂ molecule on the Zr/SBA-15 to form methoxide groups, and this result was similar to that reported previously [35].

Figure 3 shows infrared adsorption spectra of CO₂ taken after the Zr/SBA-15 catalyst was previously exposed to CH₃OH for 60 min. With extending the exposure time of CO₂, the bands ascribed to Si-OCH₃ (1461 cm⁻¹), Zr-OCH₃ (1450 cm⁻¹), and C-H stretching vibrations of methoxide groups (2956 and 2852 cm⁻¹) gradually decreased, and the band associated with Zr(Si)-OH (3739 cm⁻¹) gradually recovered. At the same time, the growth in intensity of the bands for m-CH₃OC(O)O-Zr(Si) (1583 and 1389 cm⁻¹) indicated that the introduced CO₂ will continue to react with the Zr-OCH₃ or Si-OCH₃ to form m-CH₃OC(O)O-Zr(Si).



Figure 3. In situ FTIR spectra of CO₂ adsorption on Zr/SBA-15 pre-adsorbed CH₃OH in the regions of 3600 cm⁻¹–3800 cm⁻¹ (**A**), in situ FTIR spectra of CO₂ adsorption on Zr/SBA-15 pre-adsorbed CH₃OH in the regions of 2700 cm⁻¹–3100 cm⁻¹ (**B**), in situ FTIR spectra of CO₂ adsorption on Zr/SBA-15 pre-adsorbed CH₃OH in the regions of 1500 cm⁻¹–1700 cm⁻¹ (**C**), in situ FTIR spectra of CO₂ adsorption on Zr/SBA-15 pre-adsorbed CH₃OH in the regions of 1500 cm⁻¹–1700 cm⁻¹ (**C**), in situ FTIR spectra of CO₂ adsorption on Zr/SBA-15 pre-adsorbed CH₃OH in the regions of 1500 cm⁻¹–1700 cm⁻¹ (**C**).

Based on the above process, there may be four synthetic routes for the m-CH₃OC(O)O-Zr(Si) on the Zr/SBA-15 catalyst, as suggested in Schemes 1–4.



Scheme 2. Synthetic routes for the m-CH₃OC(O)O-Zr(Si) on the Zr/SBA-15 catalyst.



Scheme 3. Synthetic routes for the m-CH₃OC(O)O-Zr(Si) on the Zr/SBA-15 catalyst.



Scheme 4. Synthetic routes for the m-CH₃OC(O)O-Zr(Si) on the Zr/SBA-15 catalyst.

In order to clarify the active sites and confirm the DMC synthesis route, SBA-15, containing only Si-O-Si bonds, was used to study the adsorption process of methanol and CO₂ with in situ FTIR, and the results are shown in Figure 4. As can be seen from Figure 4A,B, in the CH₃OH adsorption process, the bands for C-H stretching vibrations of methoxide groups (2956 and 2852 cm⁻¹) and the band for Si-OCH₃ (1461 cm⁻¹) gradually increased, indicating that the Si-O-Si-OH can react with the CH₃OH to form Si-OCH₃ with the concurrent release of water (Scheme 2a). The exposure of SBA-15 containing methoxide groups to CO₂ showed that the bands for C-H stretching vibrations of methoxide group had almost no change in Figure 4C. Furthermore, there was no change on the band for b-HCO₃ (1620 cm⁻¹) with the extension of the CO₂ adsorption time (Figure 4D), showing that CO₂ could not be adsorbed on SBA-15 at a high temperature of 130 °C under vacuum. Combined with the catalytic performance (Table 1), it was demonstrated that Si-OCH₃ could be formed from Si-O-Si-OH and CH₃OH, but it could not further react with CO₂ to form m-CH₃OC(O)O-Si (Scheme 2b).



Figure 4. In situ FTIR spectra of CO₂ and CH₃OH adsorption on SBA-15 in the regions of 2700 cm⁻¹ –3100 cm⁻¹ (**A**), in situ FTIR spectra of CO₂ and CH₃OH adsorption on SBA-15 in the regions of 1300 cm⁻¹–1500 cm⁻¹ (**B**), in situ FTIR spectra of CO₂ and CH₃OH adsorption on SBA-15 in the regions of 2700 cm⁻¹–3100 cm⁻¹ (**C**), in situ FTIR spectra of CO₂ and CH₃OH adsorption on SBA-15 in the regions of 1500 cm⁻¹–1700 cm⁻¹ (**D**).

After proving that Si-O-Si-OH was not in the active sites (Scheme 2), the Zr-SBA-15 with other Si-O-Zr-OH and Zr-O-Si-OH groups was selected as the catalyst to further

explore active sites and reaction pathways. The in situ FTIR spectra of Zr-SBA-15 interacting with CH₃OH are shown in Supplementary Figure S2. With the increase of CH₃OH adsorption time, the bands for C-H stretching vibrations of methoxide groups (2956 and 2852 cm⁻¹) and Si-OCH₃ (1461 cm⁻¹) and Zr-OCH₃ (1450 cm⁻¹) gradually increased; meanwhile, the intensity of the band at 3739 cm⁻¹ associated with Zr(Si)-OH gradually decreased in Figure 5, suggesting that both Zr-O-Si-OH and Si-O-Zr-OH groups can react with the CH₃OH to form Zr(Si)-OCH₃ (Schemes 3a and 4a). Prior to CH₃OH adsorption, the band at 1620 cm⁻¹ associated with bidentate bicarbonate species (b-HCO₃-Zr) was observed on Zr-SBA-15, suggesting that the coordinately unsaturated Zr⁴⁺/O²⁻ sites formed by the incorporation of zirconium ions into the framework of SBA-15 can effectively adsorb CO₂. It was worth noting that the band for b-HCO₃-Zr (1620 cm⁻¹) decreased, and no bands for m-CH₃OC(O)O-Zr (1583 and 1389 cm⁻¹) appeared with the increase of CH₃OH adsorption time, indicating that the CH₃OH could not react with the bidentate bicarbonate species (b-HCO₃-Zr) initially formed to produce m-CH₃OC(O)O-Zr species.



Figure 5. Infrared peak intensities of the different functional groups for Zr-SBA-15 taken during the experiments shown in Supplementary Figures S2 and S3. Peaks intensities are normalized from 3739 to 1450 cm^{-1} .

After adsorbing methanol for 60 min, in situ FTIR spectra of CO₂ adsorption on Zr-SBA-15 pre-adsorbed CH₃OH are shown in Figure 5 and Supplementary Figure S3. By extending the adsorption time of CO₂, the bands ascribed to Si-OCH₃ (1461 cm⁻¹), Zr-OCH₃ (1450 cm⁻¹), and C-H stretching vibrations of methoxide groups (2956 and 2852 cm⁻¹) gradually decreased, and the bands associated with Zr-OH (3739 cm⁻¹) gradually recovered (Figure 5). Meanwhile, no new bands for m-CH₃OC(O)O-Zr(Si) (1583 and 1389 cm⁻¹) appeared, but only the growth in intensity of the band for b-HCO₃-Zr (1620 cm⁻¹), again proving that CO₂ could not be inserted into the Zr(Si)-O band of the Zr(Si)-OCH₃ species to form m-CH₃OC(O)O-Zr(Si) (Supplementary Figure S3C). This was because the competitive adsorption between CH₃OH and b-HCO₃-Zr initially formed on the Zr-SBA-15 catalyst.

Based on the above analysis, even though the $Zr-O-CH_3$ can be formed (Scheme 3a), the CO_2 could not be effectively adsorbed on the adjacent Si-O bond and then be inserted into the Zr-O band of the $Zr-OCH_3$ species. This scenario suggested that the reaction route in Scheme 3 was not feasible. In addition, although the Zr-O bond adjacent to Si-OCH₃ (Scheme 4a) species could adsorb and activate CO_2 , the CO_2 still could not be inserted into the Si-O band of the Si-OCH₃ species to form m-CH₃OC(O)O-Zr (Scheme 4b). This is because the silicon atom was more electronegative than zirconium (Si = 1.8 and Zr = 1.4),

hence the oxygen atom of Si-O-CH₃ only donated charge to the Si but not to the carbon atom of CO_2 , then the alkoxide group could not be transferred to the carbon atom of CO_2 . Combined with the catalytic performance (Table 1), it was clear that the reaction route in Scheme 4 was also not available.

2.3.2. Adsorption of Methanol after Adsorption of CO₂

The exposure of the Zr/SBA-15 catalyst to CO_2 is shown in Supplementary Figures S4 and S5. With increasing adsorption time of CO_2 , the intensity of the band at 3739 cm⁻¹ associated with Zr(Si)-OH gradually decreased (Figure 6 and Supplementary Figure S4A), while the pre-existence of b-HCO₃-Zr (1620 cm⁻¹) species led to an increase (Figure 6 and Supplementary Figure S4C), indicating that the CO_2 could be adsorbed and activated on the coordinately unsaturated Zr^{4+}/O^{2-} sites of the Zr/SBA-15 catalyst.



Figure 6. Infrared peak intensities of the different functional groups for Zr/SBA-15 taken during the experiments shown in Supplementary Figures S4 and S5. Peaks intensities are normalized from 3739 to 1389 cm⁻¹.

After CO₂ adsorption for 60 min, the Zr/SBA-15 catalyst was exposed to CH₃OH. As can be seen from Supplementary Figure S5C, the band for b-HCO₃-Zr (1620 cm⁻¹) disappeared rapidly, and new bands at 1583 and 1389 cm⁻¹ associated with the m-CH₃OC(O)O-Zr appeared and gradually increased with the increase of CO₂ adsorption time. The bands attributed to Si-OCH₃ (1461 cm⁻¹), Zr-OCH₃ (1450 cm⁻¹), and C-H stretching vibrations of methoxide groups (2956 and 2852 cm⁻¹) gradually increased (Figure 6). The bands associated with Zr(Si)-OH (3739 cm⁻¹) were not able to partially recover like that in Figure 3A, but further decreased, as in Figure 6. In addition, the rates of methyl carbonate species' formation were slower than that in Figure 3C, showing that methyl carbonate species were formed predominantly via CO₂ addition to methoxide species. The methyl carbonate intermediate formed via the reaction of Zr-OCH₃ with CO₂ was much faster than that formed from the reaction of b-HCO₃-Zr with CH₃OH. This phenomenon was similar to that reported by Jung et al. [35] and Xuan et al. [46].

Supplementary Figure S6 shows the infrared spectra of CO₂ adsorption on the Zr-SBA-15 catalyst. With increasing CO₂ adsorption time, the band for Zr(Si)-OH (3739 cm⁻¹) showed almost no change, as in Figure 7 and Supplementary Figure S6A, and even the band (Figure 7) intensities of b-HCO₃-Zr (1620 cm⁻¹) showed less increase than those of the Zr/SBA-15 catalyst in Figure 6, indicating that CO₂ adsorption capacity on the Zr-O-Zr of Zr/SBA-15 was higher than that on the Si-O-Zr of the Zr-SBA-15 catalyst.



Figure 7. Infrared peak intensities of the different functional groups for Zr-SBA-15 taken during the experiments shown in Supplementary Figures S6 and S7. Peak intensities are normalized from 3739 to 1389 cm⁻¹.

After CO₂ adsorption for 60 min, the Zr-SBA-15 catalyst was exposed to CH₃OH, and the in situ FTIR spectra are depicted in Supplementary Figure S7. The changes of bands for Zr(Si)-OH (3739 cm⁻¹), Si-OCH₃ (1461 cm⁻¹), Zr-OCH₃ (1450 cm⁻¹), b-HCO₃-Zr (1620 cm⁻¹), and C-H stretching vibrations (2956, 2852 cm⁻¹) of methoxide groups were similar to those of the Zr-SBA-15 catalyst shown in Supplementary Figure S2. It proved again that CH₃OH could not react with the bidentate bicarbonate species (b-HCO₃-Zr) to form m-CH₃OC(O)O-Zr species, and only the competitive adsorption between CH₃OH and b-HCO₃-Zr presented on Si-O-Zr of the Zr-SBA-15 catalyst (Schemes 3 and 4).

2.3.3. Co-Adsorption of Methanol and CO₂

The spectrum of co-adsorption of CH₃OH and CO₂ over Zr/SBA-15 surface is shown in Figure 8C. It showed that the band for b-HCO₃-Zr (1620 cm⁻¹) was replaced by the characteristic peaks of m-CH₃C(O)O-Zr (1583 and 1389 cm⁻¹). With increasing time, the surface concentration of m-CH₃C(O)O-Zr and Zr(Si)-OCH₃ grew, whereas the surface concentration of Zr(Si)-OH (3739 cm⁻¹) declined (Figure 8A). However, the Zr-SBA-15 catalyst showed no bands for m-CH₃C(O)O-Zr (1583 and 1389 cm⁻¹) in Figure 9C,D, and only a decrease in the surface concentration of b-HCO₃-Zr occurred due to the competitive adsorption between CH₃OH and CO₂ in Figure 9C. Combined with the catalytic performance (Table 1), it was demonstrated that the m-CH₃C(O)O-Zr could only be achieved on the Zr/SBA-15 catalyst. That is to say, CO₂ could only react with CH₃OH on the Zr-O-Zr in the Zr/SBA-15 catalyst; therefore, the reaction in Scheme 1 was feasible and the other reaction routes in Schemes 2–4 were invalid.

Based on the above conclusions, a possible reaction mechanism for the DMC synthesis over Zr-based catalysts with different chemical environments for the Zr atom was confirmed, which was similar to the results in Scheme 1. In addition, it was worth emphasizing that only the neighboring Zr^{4+} and Zr^{4+}/O^{2-} could activate methanol and CO_2 to yield DMC, while the Zr-SBA-15 catalyst with non-adjacent sites between Zr^{4+} and Zr^{4+}/O^{2-} (Si-O-Zr-OH and Zr-O-Si-OH structure) showed no catalytic performance for DMC production.



Figure 8. Infrared spectra of the co-adsorption of CH₃OH and CO₂ over Zr/SBA-15 in the regions of 3800 cm^{-1} – 3600 cm^{-1} (**A**), infrared spectra of the co-adsorption of CH₃OH and CO₂ over Zr/SBA-15 in the regions of 2700 cm^{-1} – 3100 cm^{-1} (**B**), infrared spectra of the co-adsorption of CH₃OH and CO₂ over Zr/SBA-15 in the regions of 1500 cm^{-1} – 1700 cm^{-1} (**C**), infrared spectra of the co-adsorption of CH₃OH and CO₂ over Zr/SBA-15 in the regions of 1300 cm^{-1} – 1700 cm^{-1} (**C**).



Figure 9. Infrared spectra of the co-adsorption of CH₃OH and CO₂ over Zr-SBA-15 in the regions of 3800 cm⁻¹–3600 cm⁻¹ (**A**), infrared spectra of the co-adsorption of CH₃OH and CO₂ over Zr-SBA-15 in the regions of 2700 cm⁻¹–3100 cm⁻¹ (**B**), infrared spectra of the co-adsorption of CH₃OH and CO₂ over Zr-SBA-15 in the regions of 1500 cm⁻¹–1700 cm⁻¹ (**C**), infrared spectra of the co-adsorption of CH₃OH and CO₂ over Zr-SBA-15 in the regions of 1300 cm⁻¹–1500 cm⁻¹ (**D**).

3. Experimental Section

3.1. Catalyst Preparation

3.1.1. Synthesis of SBA-15

The synthesis procedure is consistent with our previous reports [44]. First, 24 g of Pluronic P123 copolymer was dissolved in a mixture of HCl (37%) (120 mL, 12.1 M) and distilled water (636 mL). Once the P123 was dissolved, 54.2 mL of tetraethylorthosilicate (TEOS) (Aladdin Biochemical Technology Co., Ltd., Shanghai, CN, China) was added dropwise into the previously prepared solution, and then the resulting mixture was stirred at 40 °C for 20 h. Next, this milky mixture was transferred into the Teflon-lined stainless-steel autoclave and aged at 100 °C for 24 h without stirring. The mixture was quenched with 400 mL of distilled water and then immediately filtered and washed with deionized water, dried at 75 °C overnight, finally calcined in air at 200 °C for 1 h, and then increased temperature to 550 °C at a rate of 1.2 °C/min, and kept for 12 h.

3.1.2. Synthesis of Zr-Incorporated SBA-15

Zr-incorporated SBA-15 catalysts with different Zr/Si mole ratios were prepared by one-pot synthetic procedures according to the previous report, with minor adjustments [46]. First, 12 g of P123 block copolymer was dissolved in 480 mL of distilled water with 7.08 g of NaCl. Upon complete dissolution, appropriate amounts of zirconium oxychloride octahydrate and 6.44 g of TEOS were added sequentially and stirred for 20 h at 40 °C. The resultant suspension was hydrothermally aged at 100 °C under static conditions for 24 h. The solid was filtered and washed with distilled water several times and air-dried overnight at 75 °C. The solid was calcined under the same conditions as those used for the reference SBA-15. The obtained Zr-incorporated SBA-15 catalysts were named in terms of the amounts of zirconium oxychloride octahydrate was 0.209 g, while Zr-SBA-15-L, Zr-SBA-15-H, and Zr-SBA-15-S catalysts were 0.109, 0.308, and 0.418 g, respectively. Then, the ICP-AES was used to determine the Zr/Si mole ratios in the fresh catalysts, and the Zr-SBA-15-L, Zr-SBA-15, Zr-SBA-15-H, and 2r-SBA-15-H, and Zr-SBA-15-S catalysts had Zr/Si mole ratios of 0.011, 0.021, 0.031, and 0.042, respectively.

3.1.3. Synthesis of ZrO₂-Grafted SBA-15

To exclude the influence of Zr content on the catalytic activity, ZrO₂-grafted SBA-15 was synthesized by adjusting the amount of added zirconium precursors to achieve the same Zr/Si molar ratios as the Zr-SBA-15-L, Zr-SBA-15, Zr-SBA-15-H, and Zr-SBA-15-S catalysts above. In general, as reported in the literature [42], 3.0 g of SBA-15 was added to a solution of appropriate amounts of 70% zirconium propoxide in propanol (Sigma-Aldrich, Shanghai, CN., China) in 90 mL of anhydrous hexane. The reaction mixture was refluxed at 69 °C overnight, filtered, and washed three times with hexane to remove any unreacted precursor. The material was added into 100 mL of deionized water under stirring for 4 h to completely hydrolyze any residual propoxide groups. Finally, the solid was filtered and washed with distilled water several times and air-dried overnight at 75 °C. The solid was calcined at 550 °C for 12 h in air at the same conditions as those used above. The calcined sample was designated as the ZrO₂-grafted SBA-15 catalyst. Zr/SBA-15-L, Zr/SBA-15-F, and Zr/SBA-15-S catalysts indicated the Zr/Si mole ratios in the fresh catalysts of 0.011, 0.021, 0.031, and 0.042, respectively.

3.2. Physical Characterization

 N_2 adsorption–desorption isotherms were measured at -196 °C on a Micromeritics Tristar II (3020) apparatus. Prior to measurements, all the samples were degassed at 150 °C under vacuum overnight. The specific surface areas of all samples were determined by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution for the desorption branch of the isotherm was obtained by Barett–Joyner–Halenda (BJH) calculations. Total The silica and zirconium contents of catalysts were measured by the Thermo iCAP 6300 inductively coupled plasma spectrometer (ICP). Approximately 0.01 g of powder samples was entirely digested by concentrated hydrofluoric acid prior to analysis.

The general morphology of catalysts was examined by transmission election microscopy (TEM) using a JEOL JEM-2100F electron microscope operated at an acceleration voltage of 200 kV.

Powder small-angle X-ray diffraction (XRD) patterns have been analyzed on a Bruker D8 Advance (Germany) diffractometer using the CuK line. The XRD data were recorded in the 2θ range from 1° to 10°, with a step size of 0.04° for low-angle analysis, and in the 2θ range from 10° to 80° using a step size of 5° for high-angle analysis.

Diffuse reflectance UV-vis spectra (DR UV-vis) were recorded under ambient conditions in the wavelength range from 190 to 800 nm. These spectra were collected on a Hitachi U-3900 spectrophotometer.

X-ray photoelectron spectroscopy (XPS) measurement was performed in a Thermo Scientific ESCALAB 250 spectrometer equipped with Al Ka radiation (hv = 1486.6 eV) under ultra-high-vacuum. Prior to their analysis, samples were outgassed at <10⁻⁶ Torr for 24 h. Binding energies were referenced to the C1s line (284.8 eV) and deconvolution curves were achieved using the Casa XPS program.

The adsorption and activation of CO_2 and methanol over the synthesized catalysts were analyzed by in situ Fourier transform infrared spectra (FTIR). First, 10 mg of solid sample was pressed to a self-supporting thin wafer and placed in the in situ FTIR apparatus equipped with CaF₂ windows. Secondly, the sample was pretreated by heating at 130 °C in vacuum for 1 h to purify the surface of the catalyst, and the infrared spectrum was recorded as 0 s. Next, the methanol was introduced into the apparatus as vapor-phase by vacuum evaporation at 130 °C for a certain time of 10 s, 20 s, 1, 2, 5, 10, 30, and 60 min respectively, and then the non-activated methanol was removed with evacuation for 10 min. Finally, the infrared spectrum of the catalyst was recorded on a Nicolet Nexus 470 FTIR Spectrometer over the region of 4000–1000 cm⁻¹. CO₂ adsorption and the co-adsorption of methanol and CO₂ were similar to the methanol adsorption process.

3.3. DMC Synthesis from Methanol and CO₂

Synthesis of DMC from methanol and CO_2 was carried out in a 50 mL stainless-steel autoclave equipped with a magnetic stirrer. Typically, 0.5 g of catalyst (activated at 130 °C under vacuum for 4 h) was added into an autoclave, then 200 mmol of CO_2 was introduced into the reactor at 25 °C. After that, 6.4 g of anhydrous methanol (200 mmol) was pumped into the reactor by a high-pressure liquid pump. The reactor was heated to 130 °C for 4 h and the reaction pressure was maintained at 10 MPa for all experiments. After reaction, the autoclave was immediately cooled to room temperature and depressurized. Reaction products were analyzed by a gas chromatograph (FID-GC950) equipped with a capillary column (DB-210, 25 m, 0.22 mm) and benzene was added as an internal standard substance.

4. Conclusions

In the present study, both Zr/SBA-15 and Zr-SBA-15 with the same Zr content but in different chemical environments for the Zr atom were successfully prepared and used as catalysts for the DMC synthesis from CO_2 and methanol. The XRD, DR UV-vis and XPS results showed that Zr-SBA-15 had isolated Zr species in Zr-O-Si-OH or Si-O-Zr-OH groups, while the Zr/SBA-15 catalyst had Zr-O-Zr-OH as well as Zr-O-Si-OH and Si-O-Zr-OH groups. The Zr/SBA-15 catalyst exhibited good catalytic activity, while no DMC was detected over the Zr-SBA-15 catalyst under the same reaction conditions.

Combined with the DMC yield, it was found that the Zr^{4+}/O^{2-} sites of Zr-O-Si-OH and the Si⁴⁺/O²⁻ sites of Si-O-Zr-OH can effectively activate methanol molecules, and simultaneously remove one molecule of water with adjacent Si-OH or Zr-OH to form

H₃C-O-Zr-O-Si and CH₃-O-Si-O-Zr structures, respectively. However, methyl carbonate species Zr-O-Si-O(O)COCH₃-m were not formed on H₃C-O-Zr-O-Si because adjacent Si⁴⁺/O²⁻ could not activate CO₂. Although the adjacent Zr⁴⁺/O²⁻ in CH₃-O-Si-O-Zr could activate CO₂, the O-Si bond in the CH₃-O-Si could not be broken due to the stronger electron-withdrawing ability of the Si atom, thus the Si-O-Zr-O(O)COCH₃-m could also not be formed. Only when the neighboring Zr⁴⁺, Zr⁴⁺/O²⁻, and Zr-OH sites existed simultaneously in the Zr-O-Zr-OH group of the Zr/SBA-15 catalyst could they effectively activate methanol and CO₂ to form m-CH₃OC(O)O-Zr-O-Zr, and then synthesize dimethyl carbonate. This study offered strategies to design a high-performance catalyst for the direct synthesis of dimethyl carbonate from CO₂ and methanol.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/catal11060710/s1, Figure S1: TEM images of SBA-15 (A), Zr/SBA-15 (B), and Zr-SBA-15 (C); Figure S2: In situ FTIR spectra of CH₃OH adsorption on the Zr-SBA-15 catalyst; Figure S3: In situ FTIR spectra of CO₂ adsorption on Zr-SBA-15 pre-adsorbed CH₃OH; Figure S4: In situ FTIR spectra of CO₂ adsorption on the Zr/SBA-15 catalyst; Figure S5: In situ FTIR spectra of CH₃OH adsorption on Zr/SBA-15 pre-adsorbed CO₂; Figure S6: In situ FTIR spectra of CO₂ adsorption on the Zr-SBA-15 catalyst; Figure S7: In situ FTIR spectra of CH₃OH adsorption on Zr-SBA-15 pre-adsorbed CO₂.

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