The Effects of the Crystalline Phase of Zirconia on C–O Activation and C–C Coupling in Converting Syngas into Aromatics

Sheng Wang, Yue Fang, Zhen Huang *, Hualong Xu and Wei Shen *

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433, China; swang14@fudan.edu.cn (S.W.); yfang17@fudan.edu.cn (Y.F.); shuhl@fudan.edu.cn (H.X.)
* Correspondence: huangzhen@fudan.edu.cn (Z.H.), wshen@fudan.edu.cn (W.S.);
Tel.: +86-021-3124-2401 (W.S.)

Received: 16 January 2020; Accepted: 19 February 2020; Published: 21 February 2020

Abstract: Zirconia has recently been used as an efficient catalyst in the conversion of syngas. The crystalline phases of ZrO$_2$ in ZrO$_2$/HZSM-5 bi-functional catalysts have important effects on C–O activation and C–C coupling in converting syngas into aromatics and been investigated in this work. Monoclinic ZrO$_2$ (m-ZrO$_2$) and tetragonal ZrO$_2$ (t-ZrO$_2$) were synthesized by hydrothermal and chemical precipitation methods, respectively. The results of in situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) revealed that there were more active hydroxyl groups existing on the surface of m-ZrO$_2$, and CO temperature programmed desorption (CO-TPD) results indicated that the CO adsorption capacity of m-ZrO$_2$ was higher than that of t-ZrO$_2$, which can facilitate the C–O activation of m-ZrO$_2$ for syngas conversion compared to that of t-ZrO$_2$. And the CO conversion on the m-ZrO$_2$ catalyst was about 50% more than that on the t-ZrO$_2$ catalyst. $^{31}$P and $^{13}$C magic angle spinning nuclear magnetic resonance (MAS NMR) analysis revealed a higher acid and base density of m-ZrO$_2$ than that of t-ZrO$_2$, which enhanced the C–C coupling. The selectivity to CH$_4$ on the m-ZrO$_2$ catalyst was about 1/5 of that on the t-ZrO$_2$ catalyst in syngas conversion. The selectivity to C$_{2+}$ hydrocarbons over m-ZrO$_2$ or t-ZrO$_2$ as well as the proximity of the ZrO$_2$ sample and HZSM-5 greatly affected the further aromatization in converting syngas into aromatics.

Keywords: zirconia crystalline phase; syngas; aromatics; C–O activation; C–C coupling

1. Introduction

With declining petroleum resources, the efficient use of carbon-containing resources has received widespread interest in recent years [1]. The conversion of syngas is a promising route to obtain high value chemicals from non-petroleum resources due to the wide variety of sources of syngas [2]. Considerable efforts have been made in the conversion of syngas to a range of hydrocarbons such as lower olefins, gasoline, diesel, and aromatics [3–6]. Syngas to hydrocarbons reaction was firstly achieved in 1923, known as the Fischer-Tropsch synthesis (FTS). According to the mechanism of FTS, CH$_2$ intermediates are generally considered as polymerizable monomers, and products with different carbon chain lengths are formed on the catalyst surface via C–C coupling reactions, followed by hydrogenation or dehydrogenation [2]. However, the distribution of products follows the Anderson-Schulz-Flory (ASF) model, according to which the production of light olefins and paraffins for C$_2$–C$_4$ hydrocarbons is limited to about 58% [7]. Recently, bi-functional catalysts have been developed by combining metal oxides with zeolites (OX-ZEO), and high selectivity of light
olefins and aromatics has been achieved, which has broken through the limitations of ASF distribution in FTS [8–17]. OX-ZEO catalysts composed of oxides (ZnCrOₓ) and zeolite (ZSM-5) were developed by physical mixing, which achieved a selectivity of 74% in direct converting syngas into aromatics [10]. Meanwhile, ZrOₓ-based oxides have shown a decent catalytic activity in syngas conversion. An 80% selectivity of aromatics with 20% CO conversion was achieved by a bi-functional catalyst composed of Zn-ZrOₓ and HZSM-5 [11]. Mo-doped ZrOₓ has also been adopted, and exhibited a 76% selectivity to aromatics [14]. It is worth noting that the ZrOₓ possessed tetragonal crystalline phase with a small amount of monoclinic phase in these two catalysts. Others showed that 62% selectivity to aromatics with 12% CO conversion in the direct conversion of syngas can be achieved over nano-sized t-ZrOₓ and HZSM-5 bifunctional catalyst [15]. However, the different crystalline phases of ZrOₓ might affect its catalytic performance on this reaction, which still need to be investigated.

Due to the different coordination environments of zirconium and oxygen, the surface properties of m-ZrOₓ and t-ZrOₓ are different [18], which affect the C–O activation and C–C coupling in the reaction. The crystalline phase of ZrOₓ can be controlled by the synthesis method. Different crystalline phases of ZrOₓ have diverse catalytic activities in many reactions [19–27]. In the conversion of syngas to isobutane, m-ZrOₓ with strong basicity performed higher reaction rate and selectivity to isobutene [24]. In the hydrogenation of CO₂ to methanol, Cu/t-ZrOₓ catalyst showed a higher turnover frequency due to the stronger interaction between Cu and t-ZrOₓ as well as the higher ratio of H₂/CO₂ on the surface [25]. A similar effect is found in CO hydrogenation to methanol and higher alcohols, where the crystal phase of ZrOₓ could affect the activity of the catalysts as well as the product selectivity [26]. Therefore, the crystalline phase of ZrOₓ plays a very important role in the C–O activation and C–C coupling reactions in the conversion of syngas to aromatics.

As mentioned above, ZrOₓ-based oxides and HZSM-5 bifunctional catalysts have shown good selectivity and stability in converting syngas into aromatics. To the best of our knowledge, there is no research on the effects of the crystalline phases of ZrOₓ on converting syngas into aromatics and the crystalline phases of ZrOₓ could play a very important role in the C–O activation and C–C coupling. We believe that such research is of great value to further optimize the ZrOₓ-based bifunctional catalysts. In this work, we prepared ZrOₓ samples with monoclinic and tetragonal crystalline phases. Then, the surface properties of these ZrOₓ materials were investigated by CO-TPD, in situ DRIFTS, and 31P/13C MAS NMR. The effects of the crystalline phases of ZrOₓ on C–O activation and C–C coupling in converting syngas into aromatics have been evaluated.

2. Results and Discussion

2.1. Characterization of ZrOₓ Samples

2.1.1. Texture Properties of the Crystalline Phase of ZrOₓ Samples

ZrOₓ samples with different crystalline phase were synthesized by hydrothermal and chemical precipitation methods, respectively. X-ray diffraction (XRD) and high-resolution transmission electron microscope (HRTEM) were performed to investigate the morphology of ZrOₓ. XRD patterns of the ZrOₓ samples were shown in Figure 1a. m-ZrOₓ showed characteristic peaks at 28.2°, 31.5°, 34.2°, 49.3° and 50.1° (PDF#37-1484). t-ZrOₓ showed characteristic peaks at 30.3°, 35.3°, 50.4°, 50.7°, 59.6°, and 60.2° (PDF#50-1089). The unit cell parameters were calculated for both samples which are in accordance with the PDF cards (see Table S1). The XRD patterns demonstrated that both m-ZrOₓ and t-ZrOₓ were successfully synthesized. Crystallite sizes of m-ZrOₓ and t-ZrOₓ were 10.2 nm and 11.7 nm, respectively (see Table 1). The HRTEM images also showed that m-ZrOₓ and t-ZrOₓ were mainly composed of ~10 nm crystals, which were consistent with the results calculated by Scherrer’s equation. The measured interplane spacing of 0.316 nm shown in Figure 1b can be attributed to the [111] planes of m-ZrOₓ, while that of 0.294 nm in Figure 1c can be attributed to [011] lattice planes of t-ZrOₓ.
Figure 1. XRD patterns (a) and HRTEM images (b & c) of the ZrO$_2$ samples.

Table 1. Physical and morphological properties of ZrO$_2$ samples.

| Sample  | $S_{BET}$ (m$^2$/g) | $V_{pore}$ (cm$^3$/g) | $D_{pore}$ (nm) | Crystallite size (nm)$^b$ |
|---------|---------------------|------------------------|----------------|-------------------------|
| $m$-ZrO$_2$ | 60                   | 0.23                   | 15.8           | 10.2                    |
| $t$-ZrO$_2$ | 67                   | 0.33                   | 19.5           | 11.7                    |

$^a$ Total pore volume adsorbed at $P/P_0=0.99$. $^b$ Average crystallite size calculated by Scherrer’s equation from the peak at 2$\theta = 28.2^\circ$ ($m$-ZrO$_2$) and 2$\theta = 30.2^\circ$ ($t$-ZrO$_2$), respectively.

2.1.2. Interactions of CO with the ZrO$_2$ Samples

The C–O activation on ZrO$_2$ samples is a key step in syngas conversion, the adsorption behavior of CO on the surface of ZrO$_2$ was firstly investigated. The CO-TPD profiles of the ZrO$_2$ samples are depicted in Figure 2. The desorption peak at around 380 K indicated $m$-ZrO$_2$ as well as $t$-ZrO$_2$ had weak interactions with CO molecules. However, two desorption peaks at around 638 K and around 841 K on $m$-ZrO$_2$ indicated that there were moderate and strong interactions between CO molecules and the surface of $m$-ZrO$_2$. It can be speculated that more CO molecules can be absorbed on the surface of $m$-ZrO$_2$ at the reaction temperature (673 K), which are beneficial to C–O activation. Due to the different calcination temperature of samples (773 K for $m$-ZrO$_2$ and 873 K for $t$-ZrO$_2$), the peak areas for CO-TPD were calculated from 298 K to 773 K. The results showed that the CO adsorption capacity of $m$-ZrO$_2$ was 1.6 times higher than that of $t$-ZrO$_2$. As a result, the CO adsorption studies revealed that $m$-ZrO$_2$ could adsorb more CO molecules and promote C–O activation.
Figure 2. CO-TPD profiles of the ZrO₂ samples.

After CO molecules were absorbed on the surface of ZrO₂ samples, further changes on the catalytic surface were investigated by in situ DRIFTs. According to the mechanism of CO activation over ZrO₂ [12], CO molecules are first adsorbed on the surface of ZrO₂, then the adsorbed CO molecules react with adjacent hydroxyl groups on the surface and formate species are subsequently formed. Figure 3 shows the DRIFT spectra from 4000 to 2400 cm⁻¹, corresponding to the O–H region and C–H region. Negative peaks at O–H region were observed after introduction of CO and the peak area increased with the time prolonging. This could be attributed to the reaction between the hydroxyl groups and absorbed CO molecules [12]. Two bands of hydroxyl groups at around 3762 cm⁻¹ and around 3654 cm⁻¹ were observed on m-ZrO₂, and hydroxyl groups at around 3762 cm⁻¹ and around 3660 cm⁻¹ were observed in t-ZrO₂ [28]. Meanwhile, formate species were detected on m-ZrO₂ (2965 cm⁻¹, 2874 cm⁻¹ and 2745 cm⁻¹) and t-ZrO₂ (2981 cm⁻¹, 2867 cm⁻¹ and 2745 cm⁻¹) [29]. It can be clearly seen that more formate species were formed on the surface of m-ZrO₂ than that of t-ZrO₂. The integral area of two negative peaks changed over time were calculated and shown in Figure 4a. Apparently, the integral area of m-ZrO₂ increased more quickly than that of t-ZrO₂ and was nearly twice as large as t-ZrO₂ at each moment. Figure 4b showing the consumption rate of –OH indicated that –OH sites on m-ZrO₂ were more active than those on t-ZrO₂. These results indicate that more CO molecules can interact with the surface hydroxyl groups of m-ZrO₂ than that of t-ZrO₂, which make m-ZrO₂ a better catalyst for C–O activation.

Figure 3. in situ DRIFT spectra of the ZrO₂ samples under CO flow. (a) m-ZrO₂, (b) t-ZrO₂.
2.1.3. Acidity and Basicity Analysis of the ZrO₂ Samples

Usually, the acid and base properties of ZrO₂-based catalysts can significantly affect product distribution in isosynthesis [30]. Therefore, the acidity and basicity of ZrO₂ samples were analyzed by NMR spectroscopy. Trimethylphosphine (TMP) and ¹³CO₂ were used as the probe molecules to investigate the acid and base properties of the ZrO₂ samples, respectively [31]. Figure 5a shows the ³¹P MAS NMR spectra of TMP adsorbed on ZrO₂ samples. ³¹P signals of adsorbed TMP at around −42 ppm corresponded to Lewis acid sites on the surface of m-ZrO₂. There was a broad ³¹P signal at around 60 ppm, which was assigned to adsorbed trimethylphosphine oxide (TMPO) on the Lewis acid sites [32]. Differing from m-ZrO₂, two peaks at around −42 ppm and around −29 ppm were found and were assigned to Lewis acid sites on the t-ZrO₂ surface [33]. Besides, a ³¹P signal at −5 ppm assigned to Brønsted acid sites was observed. A quantitative study of Lewis and Brønsted acid sites was shown in Table 2. The total acid content of m-ZrO₂ was 217.4 µmol/g compared to 153.5 µmol/g on t-ZrO₂, which was similar to the acidity determined by NH₃-TPD (Table S3). The acidic sites on ZrO₂ can promote CO adsorption and activation [34], and therefore m-ZrO₂ should have better catalytic performance on C–O activation for syngas conversion due to its high acid density.

![Figure 4. Integral area of –OH peaks (a) and the –OH consumption rate (b) over the ZrO₂ samples.](image)

![Figure 5. ³¹P MAS NMR spectra of TMP absorbed on ZrO₂ samples (a) and ¹³C MAS NMR spectra of ¹³CO₂ absorbed on ZrO₂ samples (b).](image)
Table 2. Acid and base density of the catalysts characterized by the NMR technics [31].

| Sample   | Acid density (µmol/g) | Base density (µmol/g) |
|----------|-----------------------|-----------------------|
|          | Lewis acid | Bronsted acid | Total | Weak | Moderate | Strong | Total |
| m-ZrO2   | 217.4      | -             | 217.4 | 49.0 | 68.1     | 3.1    | 120.2 |
| t-ZrO2   | 145.2      | 8.3           | 153.5 | 9.1  | 5.5      | -      | 14.6  |

Figure 5b presents the $^{13}$C MAS NMR spectra of $^{13}$CO$_2$ adsorbed on ZrO$_2$ samples. Signal of physisorbed $^{13}$CO$_2$ is found at around 125 ppm and spinning sideband appeared at around 155 ppm. Three signals at 162, 166, and 172 ppm could be assigned to bidentate bicarbonate species, bidentate carbonate species, and unidentate carbonate species, corresponding to weak, moderate, and strong Lewis basic sites on the ZrO$_2$ surface, respectively [31]. The respective spinning sidebands were found at 130–145 ppm, 190–203 ppm and 220–232 ppm. Table 2 summarized base density of the ZrO$_2$ samples, including contributions from the spinning sidebands. The results showed that there were more basic sites on m-ZrO$_2$ than that of t-ZrO$_2$ and the density of total basic sites on m-ZrO$_2$ was 8.2 times higher than that of t-ZrO$_2$. The density of strong Lewis basic sites on m-ZrO$_2$ was 3.1 µmol/g while it was negligible on t-ZrO$_2$. It has been reported that the basic sites of ZrO$_2$ were favorable for the chain growth reactions [34]. Therefore, the abundant Lewis basic sites on m-ZrO$_2$ due to the coordinative unsaturated Zr$^{4+}$-O$_2^-$ pairs can enhance the C–C coupling in syngas conversion reactions.

2.2. Catalytic Performance

The catalytic performance of ZrO$_2$ and ZrO$_2$/HZSM-5 catalysts for conversion of syngas was systematically investigated and the results are summarized in Table 3. At 673 K, it is found that the CO conversion was 12.9% on the m-ZrO$_2$ catalyst, which was about 50% more than that of t-ZrO$_2$ catalyst (8.6%). Higher CO conversion could be attributed to higher CO adsorption capacity as well as more active hydroxyl groups on m-ZrO$_2$. As described above, CO molecules were first adsorbed on the surface of ZrO$_2$ samples, and then absorbed CO molecules were reacted with adjacent hydroxyl groups. Our CO-TPD results showed a stronger interaction between the CO molecules and the surface of m-ZrO$_2$ at high temperature. As a result, higher CO conversion could be achieved over m-ZrO$_2$. Similar results were observed at different temperatures, pressure, and gas hourly space velocity (GHSV) (Table S4). Meanwhile, it was found that the selectivity to CH$_4$ on the m-ZrO$_2$ catalyst was only 5.4%, much lower compared to 29.5% on the t-ZrO$_2$ catalyst, indicating a facilitated C–C coupling on m-ZrO$_2$, which can be attributed to the abundant basic sites on the surface of m-ZrO$_2$ samples.

Table 3. Catalytic results over the ZrO$_2$ and ZrO$_2$/HZSM-5 catalysts. a

| Catalyst                  | CO conv. (%) | CO$_2$ sel. (%) | Product selectivity (%) b |
|---------------------------|--------------|-----------------|---------------------------|
|                           |              |                 | CH$_4$ | C$_2$-$^*$ | C$_3$-$^*$ | C$_4$-$^*$ | C$_5$ | Ar |
| m-ZrO$_2$                 | 12.9         | 38.3            | 5.4   | 57.8       | 6.7        | 30.1      | -    |
| t-ZrO$_2$                 | 8.6          | 36.9            | 29.5  | 26.1       | 19.3       | 25.1      | -    |
| m-ZrO$_2$/HZSM-5-mix      | 24.0         | 36.4            | 4.3   | 2.7        | 21.4       | 4.2       | 67.4 |
| t-ZrO$_2$/HZSM-5-mix      | 14.2         | 33.5            | 4.9   | 2.6        | 20.6       | 6.9       | 65.0 |
| m-ZrO$_2$/HZSM-5-db       | 14.7         | 41.7            | 5.8   | 1.0        | 66.2       | 22.1      | 4.9  |
| t-ZrO$_2$/HZSM-5-db       | 8.7          | 38.5            | 21.0  | 1.5        | 49.5       | 14.2      | 13.8 |

a Reaction conditions: 1.50 g for ZrO$_2$ and 3.00 g for ZrO$_2$/HZSM-5 (mass ratio = 1:1); H$_2$/CO = 1:1(volume ratio), P = 3.8 MPa, T = 673K, time on stream (TOS) = 8 h. b Selectivity in hydrocarbons (C$_2$-$^*$, C$_3$-$^*$, C$_4$-$^*$, and Ar denote C$_2$–C$_4$ olefins, C$_3$–C$_5$ paraffins, C$_4$-$^*$ hydrocarbons exclusive of aromatics, and aromatics, respectively).

Bi-functional ZrO$_2$/HZSM-5 catalysts are known to selectively convert syngas to aromatics [11]. We combined both m-ZrO$_2$ and t-ZrO$_2$ with HZSM-5 (physical and chemical properties of HZSM-5 see Figure S1, Table S2 and Table S3) and tested the catalytic performance for the reaction syngas to aromatics (see Table 3). And two types of catalyst loading were adopted for the catalyst evaluation,
which are the single catalyst bed consisted of a blend of ZrO2 and HZSM-5 samples (denoted as -mix) and the dual bed layered by ZrO2 and HZMS-5 in sequence (denoted as -db). It is found that the CO conversion was enhanced significantly after \( m \)-ZrO2 or \( t \)-ZrO2 was combined with HZSM-5 at 673 K. Meanwhile, CH4 formation was significantly suppressed, especially on the \( t \)-ZrO2/HZSM-5-mix catalyst. This phenomenon could be explained by improving the thermodynamic driving force of the reaction due to the rapid removal of intermediates. These intermediates diffuse rapidly into HZSM-5, shifting the chemical equilibrium to the right. It is worth noting that the proximity of the ZrO2 sample and HZSM-5 were crucial for the diffusion, which was confirmed by dual bed experiments. It can be seen that the CO conversion increased just a little compared to that of ZrO2 catalysts. Since HZSM-5 was separated by quartz wool, the distance between ZrO2 and HZSM-5 was too far for intermediates to diffuse into HZSM-5. As a result, the chemical equilibrium remained unchanged. Selectivity to CH4 was still above 20% on the \( t \)-ZrO2/HZSM-5-db catalyst, which meant C1 intermediates were hydrogenated directly into CH4 by ZrO2. Compared to ZrO2, selectivity to C2–C4 olefins on dual bed catalysts decreased while C2–C4 paraffins increased, this was due to the hydrogenation ability of HZSM-5. Herein, the combination between ZrO2 and HZSM-5 is crucial for converting syngas into aromatics. To reduce the distance between the two components and increase the diffusion of the intermediates to HZSM-5, physical mixing was used. After combining ZrO2 with HZSM-5, the majority of the C2–C4 intermediates from the ZrO2 catalyst can be converted to aromatics over ZrO2/HZSM-5-mix. The selectivity to C2–C4 olefins on both catalysts decreased significantly, and the secondary most products are mainly C2–C4 paraffins. The selectivity to aromatics was 67.4% at 673 K over \( m \)-ZrO2/HZSM-5-mix catalyst, slightly higher than that of \( t \)-ZrO2/HZSM-5-mix catalyst (65.0%). As we are aware, HZSM-5 is widely used to catalyze methanol to aromatics reaction (MTA) for its excellent acidity and pore structure [35]. Intermediates diffused into the channel of HZSM-5 and C–C coupling took place mostly on Brønsted acid sites of HZSM-5 rather than active sites on the ZrO2. Therefore, the selectivity to aromatics increased significantly. As mentioned above, \( m \)-ZrO2 was better at C–C coupling than \( t \)-ZrO2, therefore there were more intermediates generated on \( m \)-ZrO2, which were essential precursors for aromatization in HZSM-5, which accounted for the superior activity of the \( m \)-ZrO2/HZSM-5-mix in the selective conversion of syngas to aromatics.

3. Materials and Methods

3.1. Catalyst Preparation

The \( m \)-ZrO2 samples were synthesized by a hydrothermal method [36]. Firstly, ZrO(NO3)2·xH2O (7.40 g, 99%, Sigma Aldrich, Shanghai, China) and CO(NH2)2 (19.22 g, AR, Sinopharm, Shanghai, China) were completely dissolved in deionized water (80 mL) at 298 K under stirring. Then, the solution was transferred to a Teflon-lined stainless-steel autoclave (100 mL) and heated in the oven at 433 K for 20 h. The resulting solids were filtered and washed with deionized water, followed by drying at 373 K overnight and calcination at 773 K for 4 h with a heating rate of 2 K/min.

The \( t \)-ZrO2 samples were synthesized via precipitation method [36]. Namely, ZrOCl2·8H2O (24.17 g, AR, Sinopharm, Shanghai, China) was dissolved in deionized water (150 mL) under stirring, and 50 mL of NH3·H2O (14.8 M, AR, Sinopharm, Shanghai, China) was added dropwise. Then, the solution was kept at 298 K for 3 h and then heated to 373 K for 48 h under stirring. The precipitates were filtered and washed with deionized water, which was followed by drying at 383 K overnight and calcination at 873 K for 5 h with a heating rate of 10 K/min.

The ZrO2/HZSM-5 bi-functional catalysts were prepared via a physical mixing method. The two components ZrO2 and HZSM-5 (Si/Al molar ratio = 120, Nankai University Catalyst Co., Ltd., Tianjin, China) were mixed and ground in an agate mortar for 30 min.

3.2. Catalyst Characterization

The XRD patterns were obtained using a Bruker D8 X-ray diffractometer (Bruker, Karlsruhe, Germany) with a position sensitive detector (PSD) detector and Cu Ka radiation (40 kV, 40 mA) with 20 range of 10-80°. HRTEM images were obtained by a JEOL JEM-2001 microscope (JEOL, Tokyo,
Japan) at 200 kV. The BET surface areas were measured by N₂ physisorption at 77 K on a Quantachrome, Ashland, VA, America. Prior to the measurements, all samples were treated at 523 K for 3 h under vacuum conditions. CO-TPD was measured on a Micromeritics Autochem II 2920 apparatus (Micromeritics, Norcross, GA, America) equipped with a thermal conductivity detector (TCD) detector. Typically, a 100 mg sample was reduced in 10% H₂/Ar at 773 K for 90 min, following by cooling to room temperature under He flow. Pure CO was then introduced at 298 K for 30 min. After purging by He flow for 30 min, the sample was heated to 1073 K at a heating rate of 10 K/min. in situ DRIFTS were performed on a Nicolet 6700 instrument (ThermoFisher, Waltham, MA, America). Before the measurement, catalyst was pretreated with 2% H₂/He flow at 773 K for 1 h. Subsequently, the catalyst was cooled down to 553 K in He atmosphere. The spectra were obtained by collecting 120 scans at 4 cm⁻¹ resolution after 5% CO/He being introduced with background collecting under the same condition in He flow. ³¹P MAS NMR experiments were performed on a Bruker AVANCE III 400 WB spectrometer (Bruker, Wormer, Switzerland) operating at a ³¹P frequency of 162.1 MHz. ¹³C MAS NMR measurement were performed on the same Bruker AVANCE III 400 WB spectrometer (Bruker, Wormer, Switzerland) operating at a ¹³C frequency of 100.7 MHz. NH₃-TPD was measured on a Micromeritics Autochem II 2920 apparatus (Micromeritics, Norcross, GA, America) equipped with a TCD detector.

3.3. Catalytic Reaction

Conversion of syngas was performed on an automated continuous fixed-bed reactor with a stainless-steel reactor lined with a quartz tube (inner diameter = 6 mm) as described before [13]. Typically, 1.5 g catalyst (40–60 mesh) for ZrO₂ or 3.0 g catalyst (40–60 mesh) for ZrO₂/HZSM-5 with the mass ratio = 1/1 was packed in the center of reactor. Normally, the ZrO₂ samples were mixed with HZSM-5 thoroughly and marked with -mix. In dual bed experiments, HZSM-5 was packed below ZrO₂ samples, separated by an inert layer of quartz wool and mark with -db. The catalyst was pretreated in H₂ at 773 K for 1 h before the reaction. The flow rate of syngas (H₂/CO/Ar = 48/48/4, volume ratio) was 25 mL/min (STP), and the reaction pressure was set to 3.8 MPa. The reaction temperature was 673 K and TOS was 8 h.

The permanent gases were analyzed by GC-9160 (Shanghai Sailuxin Analysis Technology Co., Ltd., Shanghai, China)equipped with a thermal conductivity detector (TCD) connected to a 13X molecular sieves packed column (2 m × 3 mm × 2 mm) with a pre-linked Porapak Q (2 m × 3 mm × 2 mm), while aromatics and other hydrocarbons were analyzed on-line by Trace GC Ultra (ThermoFisher, Shanghai, China) equipped with a flame ionization detectors (FID) connected to an AT-PEG-20M capillary column (30 m × 0.32 mm × 0.50µm) and GC-9160 equipped with a flame ionization detectors (FID) connected to a CP-PoraPLOT Q capillary column (50 m × 0.32 mm × 10µm), respectively.

The hydrocarbon products of the reaction are classified into CH₄, C₂–C₄ olefins, C₂–C₄ paraffins, C₅+ hydrocarbons exclusive of aromatics (consisted of paraffinic and mostly C₅ hydrocarbon), and aromatics (included BTX and C₆+ aromatics such as trimethylbenzene), which was denoted as CH₄, C₂–C₄, C₅–C₆, C₅–C₆ and Ar, respectively.

CO conversion was calculated as:

\[
\text{Conversion(CO)} = \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \times 100\%
\]

CO₂ selectivity was calculated as:

\[
\text{Selectivity(CO₂)} = \frac{\text{CO₂}_{\text{out}}}{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}} \times 100\%
\]

The selectivity of individual hydrocarbon based on hydrocarbon was calculated as:

\[
\text{Selectivity(C}_i\text{H}_j) = \frac{i \cdot \text{C}_i\text{H}_j_{\text{out}}}{\sum_i \cdot \text{C}_i\text{H}_j_{\text{out}}} \times 100\%
\]

The carbon balance is about 95%.

4. Conclusions
In this work, the crystalline phases of \( \text{ZrO}_2 \) significantly influence the activity for syngas conversion to form hydrocarbon intermediates. \( m\text{-ZrO}_2 \) exhibits higher conversion of CO with a higher selectivity to C\(_2\) hydrocarbons. The surface of \( m\text{-ZrO}_2 \) contains more hydroxyl groups which react with CO into formate species, and these are crucial for the activation of C–O. NMR results reveal that there are more acid and basic sites existing on \( m\text{-ZrO}_2 \), which exhibits higher activity for C–C coupling. Both CO conversion, as well as the selectivity of aromatic hydrocarbons, can be enhanced after the combination of \( \text{ZrO}_2 \) with HZSM-5, and \( m\text{-ZrO}_2/\text{HZSM-5-mix} \) exhibits superior activity for the selective conversion of syngas to aromatics with less CH\(_4\).

**Supplementary Materials:** The following are available online at www.mdpi.com/xxx/s1, Figure S1: XRD patterns of the HZSM-5 zeolite, Table S1: Unit cell parameters for \( \text{ZrO}_2 \) samples, Table S2: Physical and morphological properties of HZSM-5, Table S3: NH\(_3\)-TPD data of \( \text{ZrO}_2 \) samples and HZSM-5 zeolite, Table S4: Catalytic results over the \( \text{ZrO}_2 \) and \( \text{ZrO}_2/\text{HZSM-5} \) catalysts.

**Author Contributions:** S.W., Z.H. conceived and designed the experiments; S.W. and Y.F. performed the experiments; S.W. analyzed the data and wrote the paper; H.X. and W.S. revised the paper. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Key R&D Program of Ministry of Science and Technology (Grant No. 2017YFB0602204), National Natural Science Foundation of China (Grant No. 91645201) and the Shanghai Science and Technology Committee (Grant No. 14DZ2273900).

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Niziolek, A.M.; Onel, O.; Guzman, Y.A.; Floudas, C.A. Biomass-Based production of benzene, toluene, and xylenes via methanol: Process synthesis and deterministic global optimization. *Energy Fuels* **2016**, *30*, 4970–4998.

2. Torres Galvis, H.M.; de Jong, K.P. Catalysts for production of lower olefins from synthesis gas: A review. *ACS Catal.* **2013**, *3*, 2130–2149.

3. Olsbye, U.; Svelle, S.; Bjorgen, M.; Beato, P.; Janssens, T.V.; Joensen, F.; Bordiga, S.; Lillerud, K.P. Conversion of methanol to hydrocarbons: How zeolite cavity and pore size controls product selectivity. *Angew. Chem. Int. Ed.* **2012**, *51*, 5810–5831.

4. Kasipandi, S.; Bae, J.W. Recent advances in direct synthesis of value-added aromatic chemicals from syngas by cascade reactions over bifunctional catalysts. *Adv. Mater.* **2019**, doi:10.1002/adma.201803390.

5. Lu, Y.; Hu, J.; Han, J.; Yu, F. Synthesis of gasoline-Range hydrocarbons from nitrogen-Rich syngas over a Mo/\( \text{HZSM-5} \) bi-functional catalyst. *J. Energy Inst.* **2016**, *89*, 782–792.

6. Kang, J.; Wang, X.; Peng, X.; Yang, Y.; Cheng, K.; Zhang, Q.; Wang, Y. Mesoporous zeolite Y-Supported Co nanoparticles as efficient Fischer–Tropsch catalysts for selective synthesis of diesel fuel. *Ind. Eng. Chem. Res.* **2016**, *55*, 13008–13019.

7. Wang, C.; Xu, L.; Wang, Q. Review of directly producing light olefins via CO hydrogenation. *J. Nat. Gas Chem.* **2003**, *12*, 10–16.

8. Jiao, F.; Li, J.; Pan, X.; Xiao, J.; Li, H.; Ma, H.; Wei, M.; Pan, Y.; Zhou, Z.; Li, M.; et al. Selective conversion of syngas to light olefins. *Science* **2016**, *351*, 1065–1068.

9. Cheng, K.; Gu, B.; Liu, X.; Kang, J.; Zhang, Q.; Wang, Y. Direct and highly selective conversion of synthesis gas into lower olefins: Design of a bifunctional catalyst combining methanol synthesis and carbon–carbon coupling. *Angew. Chem. Int. Ed.* **2016**, *55*, 4725–4728.

10. Yang, J.; Pan, X.; Jiao, F.; Li, J.; Bao, X. Direct conversion of syngas to aromatics. *Chem. Commun.* **2017**, *53*, 11146–11149.

11. Cheng, K.; Zhou, W.; Kang, J.; He, S.; Shi, S.; Zhang, Q.; Pan, Y.; Wen, W.; Wang, Y. Bifunctional catalysts for one-step conversion of syngas into aromatics with excellent selectivity and stability. *Chin. J. Chem.* **2017**, *33*, 334–347.

12. Liu, X.; Zhou, W.; Yang, Y.; Cheng, K.; Kang, J.; Zhang, L.; Zhang, G.; Min, X.; Zhang, Q.; Wang, Y. Design of efficient bifunctional catalysts for direct conversion of syngas into lower olefins via methanol/dimethyl ether intermediates. *Chem. Sci.* **2018**, *9*, 4708–4718.
13. Huang, Z.; Wang, S.; Qin, F.; Huang, L.; Yue, Y.; Hua, W.; Qiao, M.; He, H.; Shen, W.; Xu, H. Ceria-Zirconia/zeolite bifunctional catalyst for highly selective conversion of syngas into aromatics. ChemCatChem 2018, 10, 4519–4524.
14. Zhou, W.; Shi, S.; Wang, Y.; Zhang, L.; Wang, Y.; Zhang, G.; Min, X.; Cheng, K.; Zhang, Q.; Kang, J.; et al. Selective conversion of syngas to aromatics over a Mo-ZrO2/H-ZSM-5 bifunctional catalyst. ChemCatChem 2019, 11, 1681–1688.
15. Liu, J.; He, Y.; Yan, L.; Li, K.; Zhang, C.; Xiang, H.; Wen, X.; Li, Y. Nano-Sized ZrO2 derived from metal–Organic frameworks and their catalytic performance for aromatic synthesis from syngas. Catal. Sci. Technol. 2019, 9, 2982–2992.
16. Xu, H.; Li, M.; Nawaz, M.A.; Liu, D. Doping of K and Zn elements in FeZr-Ni/ZSM-5: Highly selective catalyst for syngas to aromatics. Catal. Commun. 2019, 121, 95–99.
17. Xu, Y.; Liu, J.; Wang, J.; Ma, G.; Lin, J.; Yang, Y.; Li, Y.; Zhang, C.; Ding, M. Selective conversion of syngas to aromatics over FeO3@MnO2 and hollow HZSM-5 bifunctional catalysts. ACS Catal. 2019, 9, 5147–5156.
18. Pokrovski, K.; Jung, K.T.; Bell, A.T. Investigation of CO and CO2 adsorption on tetragonal and monoclinic zirconia. Langmuir 2001, 17, 4297–4303.
19. Fan, Y.; Cheng, S.; Wang, H.; Tian, J.; Xie, S.; Pei, Y.; Qiao, M.; Zong, B. Pt–WOx on monoclinic or tetrahedral ZrO2: Crystal phase effect of zirconia on glycerol hydrogenolysis to 1,3-Propanediol. Appl. Catal. B Environ. 2017, 217, 331–341.
20. Liu, S.; Wang, H.; Wei, Y.; Zhang, R.; Royer, S. Morphology-Oriented ZrO2-supported vanadium oxide for the NH3-SCR process: Importance of structural and textural properties. ACS Appl. Mater. Interfaces 2019, 11, 22240–22254.
21. Foraita, S.; Fulton, J.L.; Chase, Z.A.; Vjunov, A.; Xu, P.; Barath, E.; Camaioni, D.M.; Zhao, C.; Lercher, J.A. Impact of the oxygen defects and the hydrogen concentration on the surface of tetragonal and monoclinic ZrO2: on the reduction rates of stearic acid on Ni/ZrO2. Chem. Eur. J. 2015, 21, 2423–2434.
22. de Souza, P.M.; Rabelo-Neto, R.C.; Borges, L.E.P.; Jacobs, G.; Davis, B.H.; Graham, U.M.; Resasco, D.E.; Noronha, F.B. Effect of zirconia morphology on hydrodeoxygenation of phenol over Pd/ZrO2. ACS Catal. 2015, 5, 7385–7398.
23. Gu, H.; Ding, J.; Zhong, Q.; Zeng, Y.; Song, F. Promotion of surface oxygen vacancies on the light olefins synthesis from catalytic CO hydrogenation over Fe-K/ZrO2 catalysts. Int. J. Hydrog. Energ. 2019, 44, 11808–11816.
24. Maruya, K.-I.; Komiya, T.; Hayakawa, T.; Lu, L.; Yashima, M. Active sites on ZrO2 for the formation of isobutene from CO and H2. J. Mol. Catal. A Chem. 2000, 159, 97–102.
25. Witoon, T.; Chalormgatham, J.; Dumrongbunditkul, P.; Charoenpanich, M.; Limtrakul, J. CO: hydrogenation to methanol over Cu/ZrO2 catalysts: Effects of zirconia phases. Chem. Eng. J. 2016, 293, 327–336.
26. Ma, Z.-Y.; Yang, C.; Wei, W.; Li, W.-H.; Sun, Y.-H. Catalytic performance of copper supported on zirconia polymorphs for CO hydrogenation. J. Mol. Catal. A Chem. 2005, 231, 75–81.
27. He, D.; Ding, Y.; Luo, H.; Li, C. Effects of zirconia phase on the synthesis of higher alcohols over zirconia and modified zirconia. J. Mol. Catal. A Chem. 2004, 208, 267–271.
28. Bachiller-Baeza, B.; Rodriguez-Ramos, I.; Guerrero-Ruiz, A. Interaction of carbon dioxide with the surface of zirconia polymorphs. Langmuir 1998, 14, 3556–3564.
29. Wu, X.; Tan, M.; Tian, S.; Song, F.; Ma, Q.; He, Y.; Yang, G.; Tsubaki, N.; Tan, Y. Designing ZrO2-Based catalysts for the direct synthesis of isobutene from syngas: The studies on Zn promoter role. Fuel 2019, 243, 34–40.
30. Li, Y.; He, D.; Zhu, Q.; Zhang, X.; Xu, B. Effects of redox properties and acid–Base properties on isosynthesis over ZrO2-Based catalysts. J. Catal. 2004, 221, 584–593.
31. Fu, Y.; Zhang, L.; Yue, B.; Chen, X.; He, H. Simultaneous characterization of solid acidity and basicity of metal oxide catalysts via the solid-state NMR technique. J. Phys. Chem. C 2018, 122, 24094–24101.
32. Zheng, A.; Huang, S.-J.; Liu, S.-B.; Deng, F. Phys. Chem. Chem. Phys. 2011, 13, 14889–14901.
33. Shimizu, K.; Venkatraman, T.; Song, W. NMR study of tungstated zirconia catalyst: Acidic properties of tungstated zirconia and influence of tungsten loading. Appl. Catal. A Gen. 2002, 224, 77–87.
34. Li, Y.; He, D.; Yuan, Y.; Cheng, Z.; Zhu, Q. Selective formation of isobutene from CO hydrogenation over zirconium dioxide based catalysts. Energy Fuels 2001, 15, 1434–1440.
35. Stöcker, M. Methanol-To-Hydrocarbons: Catalytic materials and their behavior. *Micropor. Mesopor. Mater.* 1999, 29, 3–48.

36. Li, W.; Huang, H.; Li, H.; Zhang, W.; Liu, H. Facile synthesis of pure monoclinic and tetragonal zirconia nanoparticles and their phase effects on the behavior of supported molybdena catalysts for methanol-Selective oxidation. *Langmuir* 2008, 24, 8358–8366.

© 2020 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 (http://creativecommons.org/licenses/by/4.0/).