

Article

The Influence of the ZrO₂ Crystal Phase on Cu/ZrO₂-Al₂O₃ Catalysts in Methanol Steam Reforming

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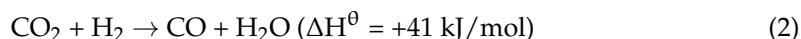
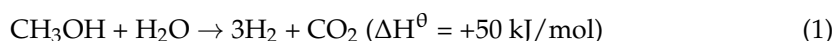
Abstract: Copper-based catalysts are widely used in methanol steam reforming to produce hydrogen. In this paper, the supportive effect of the crystal phase of ZrO₂ on Cu-based catalysts in methanol steam reforming is discussed. Monoclinic(*m*-), Tetragonal(*t*-) and mixed ZrO₂ phases were prepared, and structure–activity relationships were investigated with XRD, H₂-TPR, BET, HR-TEM and XPS. It was found that the catalyst with a 81.4% monoclinic ZrO₂ crystal phase exhibited the highest methanol conversion (88.5%) and the highest hydrogen production rate (104.6 μmol/g_{cat}·s) at 275 °C as it displayed the best reducing properties and more oxygen vacancies on the catalyst surface. Oxygen vacancies can produce more Cu¹⁺ + Cu⁰, which is the active species for methanol steam reforming on the catalyst surface, and therefore affect catalytic activity.

Keywords: copper-based catalysts; methanol steam reforming; oxygen vacancies; hydrogen production

1. Introduction

With the rapid growth of population and industrialization, environmental pollution is becoming more and more serious. The overuse of traditional fossil fuels is one of the reasons for this [1–3]. As one kind of clean and green secondary energy, hydrogen can be a good alternative to traditional fossil fuels. It comes from a wide range of sources, and is more efficient than gasoline in energy conversion [4]. However, the efficient utilization of hydrogen energy is still a difficult but urgent problem. As we all know, hydrogen is an inflammable and explosive gas, the explosion limit of which is 4–75.6% (volume concentration). Therefore, the safe storage and transportation of hydrogen is a huge problem. What is more, the establishment of hydrogen stations is also a problem, since it is very expensive and complicated with current technology [5].

Recent studies have shown that methanol steam reforming (MSR) is a promising method for hydrogen production; the stoichiometric equations of MSR are shown in Equations (1) and (2) [6]. Methanol has many advantages. Firstly, methanol has a high H/C ratio, high volume energy density, biodegradability and low sulfur content [7–10]. Secondly, methanol is liquid at room temperature and pressure, which is more conducive to storage and transportation. Thirdly, methanol has a low boiling point (65 °C), which means its vaporization amplitude is roughly the same as that of water, and it is soluble in water and easily handled [7]. In addition, methanol lacks a C–C bond, resulting in a temperature requirement of 150–300 °C for its conversion to hydrogen, significantly lower than that of other alcohols. For example, the steam reforming temperature of ethanol is about 400 °C [11].



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In recent years, the development of fuel cells has been much more rapid, the technological advancement of which also urgently requires the efficient utilization of hydrogen energy [12]. Methanol steam reforming is widely used in polymer electrolyte membrane fuel cells, which is a power generation component used in small transport vehicles such as new energy cars [13–16]. In general, hydrogen production from methanol reforming is very promising since it can not only produce hydrogen efficiently, but also solve the hydrogen transportation problem.

High concentrations of carbon monoxide cause irreversible damage to fuel cells [17]. Therefore, they require both low carbon monoxide selectivity and high hydrogen selectivity for methanol steam reforming with high methanol conversion at low temperatures. Catalysts for MSR are mainly divided into noble metal catalysts [18–20], and copper-based catalysts [21–23]. Although noble metal catalysts have the advantages of high stability and good selectivity and activity, its cost is too high, which makes its commercial application at a large scale unrealistic. For this reason, copper-based catalysts have received more focus from researchers. Initially, Zn and Cu were used to synthesize catalysts for methanol steam reforming. It was found that the addition of Zn significantly improved the activity of the catalyst [24]. In order to overcome the shortcomings of copper-based catalysts such as easy sintering and easy deactivation, and improve the activity of the catalyst, stabilizers and promoters are often added. Alejo et al. [25] investigated the effect of the Al_2O_3 component on Cu/ZnO/ Al_2O_3 catalysts for MSR. It was found that the catalyst without Al_2O_3 was completely deactivated after a reaction at 230 °C for 20 h, while for the catalyst with Al_2O_3 , at the same temperature for 110 h, the catalyst exhibited observable activity, and the selectivity of hydrogen and carbon dioxide were improved compared to that without Al_2O_3 . Meanwhile, Al_2O_3 is also used as catalyst support due to its excellent properties [26,27]. In addition to the Al component, ZrO_2 is also used as promoter for methanol steam reforming reactions. Wu et al. [22] found that adding Zr components to Cu/ZnO catalysts could improve the stability and performance of copper-based catalysts by preventing Cu particles from aggregating, therefore stabilizing Cu crystals. Jeong et al. [28] also reported that the addition of ZrO_2 to Cu/ZnO/ Al_2O_3 catalysts promoted the dispersion of Cu on the catalyst surface and the formation of smaller copper particles on the catalyst surface.

Numerous studies have explored the impact of the ZrO_2 crystal phase on catalytic activity for methanol synthesis from CO_2 . Scholars have demonstrated that copper-based catalysts, when supported by ZrO_2 in various crystalline forms, including monoclinic (*m*- ZrO_2), tetragonal (*t*- ZrO_2) and amorphous (*a*- ZrO_2), exhibits distinctly different catalytic performances in the hydrogenation of carbon dioxide [29–31]. Witton et al. [29] found that Cu/*a*- ZrO_2 catalysts had bigger copper surface area than Cu/*m*- ZrO_2 and Cu/*t*- ZrO_2 . The surface area of copper is the main factor controlling the yield of methanol and CO. Therefore, Cu/*a*- ZrO_2 catalyst shows higher catalytic activity. Samson et al. [31] discussed the catalytic activity of Cu-based catalysts for methanol synthesis from CO_2 with different ZrO_2 crystal phase contents. They discovered that the catalytic activity escalates as the proportion of *t*- ZrO_2 to *m*- ZrO_2 increases. Therefore, enhancing the activity and stability of catalysts by altering the ZrO_2 crystal phase is scientifically grounded. While these insights offer hints for MSR, the literature on the specific influences of ZrO_2 crystal phases in relation to MSR remains scarce.

MSR is the reverse reaction of carbon dioxide hydrogenation to methanol, and many catalysts for carbon dioxide hydrogenation to methanol might be also suitable for MSR. Therefore, it is interesting to see whether changes in the ZrO_2 crystal phase affect the activity of MSR. In our previous work [32], a Cu/ ZrO_2 - Al_2O_3 catalyst was prepared via mechanical mixing and the impregnation method for MSR. It was found that the catalyst with a 1:8 molar ratio of ZrO_2 and Al_2O_3 showed the best activity, and the catalyst obtained by mechanical mixing was not just a simple mixture of Cu/ ZrO_2 and Cu/ Al_2O_3 . Several publications have reported that ZrO_2 of varying crystal phases can be obtained through different preparation methods [29,30]. Therefore, based on our previous work, different ZrO_2 crystal phases have been prepared in this study by altering the preparation

techniques, obtaining various catalysts through mechanical mixing and impregnation methods, where all catalysts maintained the same Zr/Al molar ratio (1:8). Subsequently, the activity differences among these catalysts were investigated, and several characterizations were conducted to explore the relationship between catalyst structure and its activity.

2. Results

2.1. Catalyst Activity for MSR

The activity of different catalysts for MSR is shown in Figure 1. It can be seen that the methanol conversion and hydrogen production rate of all catalysts except Cu/Zr-Al-2 increased with the increase of temperature, and the Cu/Zr-Al-3 catalyst shows the best performance. For Cu/Zr-Al-2, it seems to be less active below 275 °C and the methanol conversion only increases slightly at 300 °C. As shown in Figure 1c, the CO selectivity of all catalysts increase with increasing temperature. It can be speculated that high temperature is conducive to the production of CO byproducts on all the catalysts used in the present work. Too high of a temperature will result in high CO selectivity, and too of a low temperature will result in low methanol conversion. The aim of the present work was to produce hydrogen from MSR at a low temperature; therefore, 275 °C was chosen as a suitable MSR reaction temperature for the Cu/Zr-Al catalyst. The activity data of different catalysts at 275 °C are shown in Figure 2. It is clear that the Cu/Zr-Al-3 catalyst shows the highest methanol conversion (88.5%) and hydrogen production rate (104.6 $\mu\text{mol/g}_{\text{cat}}\cdot\text{s}$). At the same time, the Cu/Zr-Al-3 catalyst shows low CO selectivity (1.9%). However, the Cu/Zr-Al-2 catalyst shows the lowest methanol conversion (10.2%), hydrogen production rate (9.5 $\mu\text{mol/g}_{\text{cat}}\cdot\text{s}$) and the highest CO selectivity (3.5%). Despite the small difference in CO selectivity, there is significant variation in the catalytic activity results. In addition, a stability experiment of the Cu/Zr-Al-3 catalyst was also performed, and the result is shown in Figure S1. It can be seen that this catalyst exhibits good stability. Therefore, Cu/Zr-Al-3 is relatively more suitable for MSR.

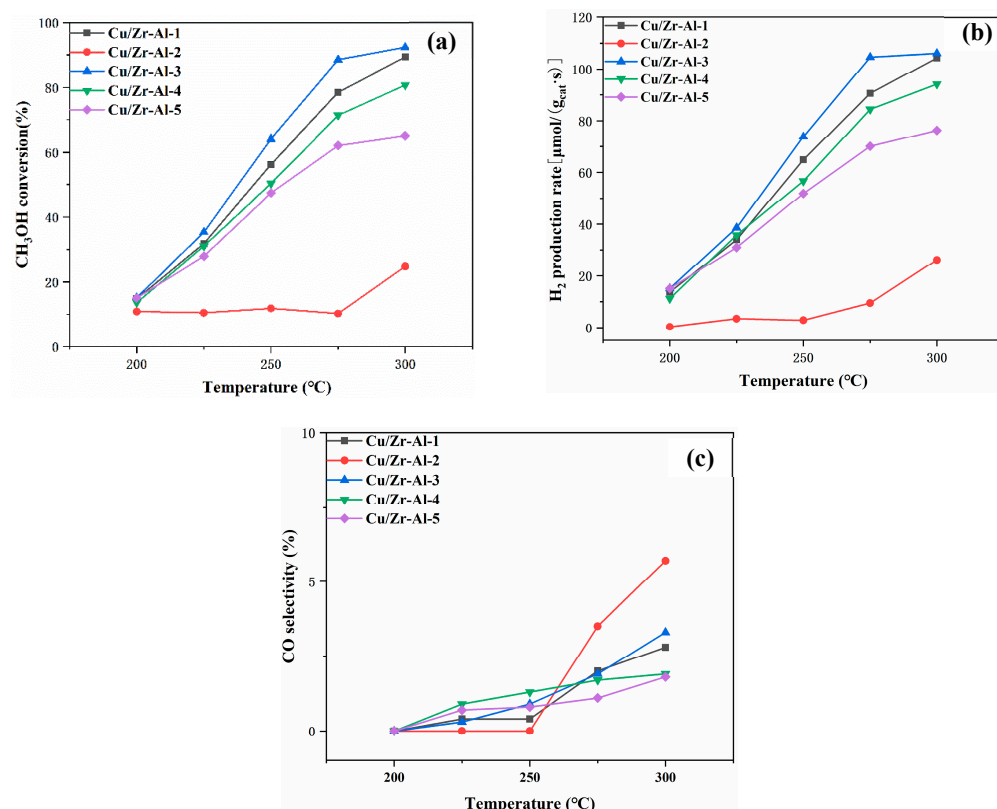


Figure 1. (a) Methanol conversion, (b) hydrogen production rate and (c) CO selectivity. Reaction conditions: $n\text{CH}_3\text{OH}:n\text{H}_2\text{O} = 1:1$, $m_{\text{cat}} = 0.5$ g, feed flow rate = 4 mL/h and 1 atm, WHSV = 9.9 h^{-1} .

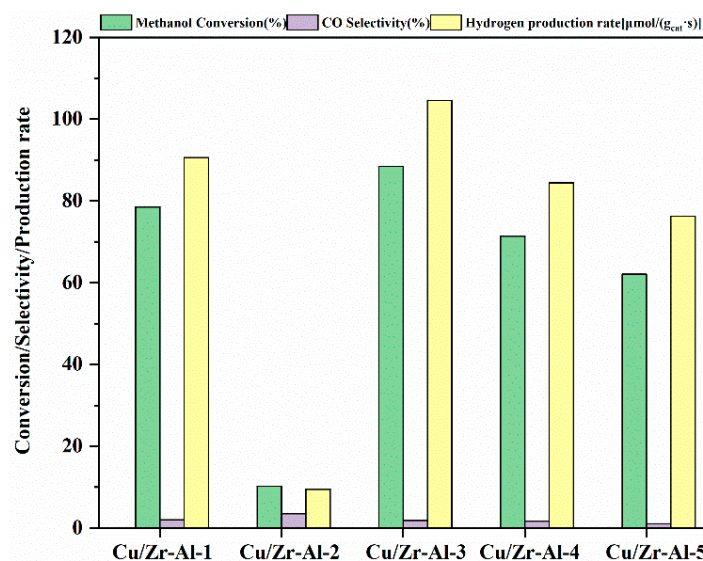


Figure 2. Comparison of the activities of different catalysts at 275 °C.

2.2. XRD Analysis

XRD patterns of the catalysts are shown in Figure 3. Figure 3a shows the XRD pattern of calcined catalysts. The characteristic peaks of CuO (PDF:89-2529), *m*-ZrO₂ (PDF: 83-0938) and *t*-ZrO₂ (PDF: 79-1764) can be observed [33–35]. The diffraction peaks of CuO on all catalysts are not obvious, which means that highly dispersed CuO species have been formed on the catalysts. Unusually, Cu/Zr-Al-2 contains only tetragonal crystal phase ZrO₂ and Cu/Zr-Al-4 contains only monoclinic crystal phase ZrO₂. However, other catalysts contain the mixed monoclinic and tetragonal crystal phase ZrO₂. Figure 3b shows the XRD pattern of reduced catalysts. It can be seen that there is no clear change in the characteristic peaks of ZrO₂, because it is hard to reduce bulk ZrO₂ below 500 °C [36]. It can be also seen from the figure that the reduced catalyst has few characteristic peaks of CuO and the characteristic peaks of Cu (PDF: 85-1326) appears, which indicates that most CuO has been reduced to Cu under this reduction condition, while the reduction process might cause some aggregation of metal Cu species.

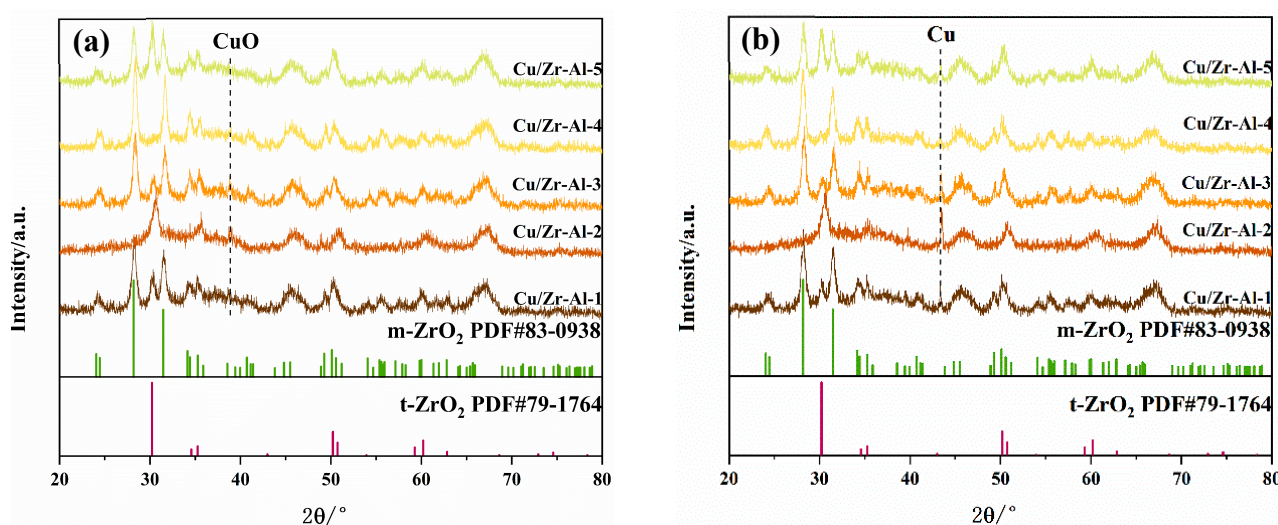


Figure 3. (a) XRD pattern of calcined catalysts. (b) XRD pattern of reduced catalysts.

In order to further investigate the influence of the ZrO₂ crystal phase on activity, the proportions of different ZrO₂ crystal phases in all catalysts were semi-quantitatively calculated with the normalized RIR method [37], and the results are shown in Figure 4

and Table S1. It can be seen that the proportion of monoclinic crystal phase ZrO_2 in mixed crystal phase catalysts is $\text{Cu/Zr-Al-3} > \text{Cu/Zr-Al-1} > \text{Cu/Zr-Al-5}$. Cu/Zr-Al-2 has pure tetragonal crystal phase ZrO_2 and Cu/Zr-Al-4 has pure monoclinic crystal phase ZrO_2 . It can be also found that the proportion of monoclinic crystal phase ZrO_2 of the reduced catalyst is slightly higher than the calcined catalyst. According to the results of catalytic activity, which is shown in Figure S2, the catalyst with a higher $m\text{-ZrO}_2$ proportion is more active, and the catalytic activity of the catalysts containing pure monoclinic ZrO_2 is much higher than that of the catalysts containing pure tetragonal ZrO_2 .

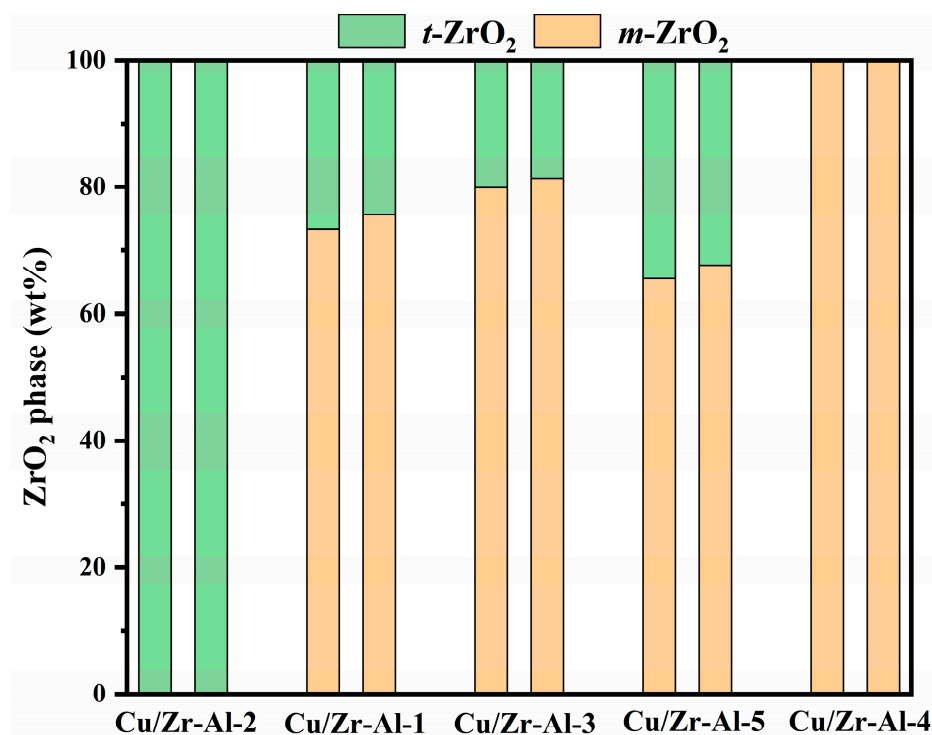


Figure 4. The proportion of different crystal phase ZrO_2 in calcined (left column) and reduced (right column) catalysts.

2.3. H_2 -TPR Analysis

Figure 5 shows the reducibility of the catalysts. There are four reduction peaks which are labeled a, b, c, d from low to high temperature. All the reduction peaks originate from the CuO species, because the reduction peaks of ZrO_2 and Al_2O_3 are higher than 500°C [36]. The reduction peaks of a and b originate from the stepwise reduction of highly dispersed Cu^{2+} to Cu^+ and Cu^0 [38]. It can be seen that the a and b reduction peaks of Cu/Zr-Al-3 move to a lower temperature region. The results show that the Cu/Zr-Al-3 has better reducing capacity, and the stepwise reduction of CuO species is promoted. The peak of c originates from the reduction of highly dispersed CuO with interactions between ZrO_2 species [38,39]. Cu/Zr-Al-2 and Cu/Zr-Al-4 have the obvious reduction peak of c, but the c reduction peak of Cu/Zr-Al-1 and Cu/Zr-Al-5 is relatively weak and Cu/Zr-Al-3 has almost no c reduction peak. The reduction peak of d originates from the bulk copper oxide crystalline [40–42]. It can be seen that this peak exists only in the Cu/Zr-Al-2 catalyst. Because the reduction temperature of d reaches 300.8°C , the reduction capacity of Cu/Zr-Al-2 is poor. This may be the reason why this catalyst has the worst performance in addition to the presence of pure tetragonal ZrO_2 .

2.4. BET Surface Area and ICP-AES Analysis

Figure 6 shows the nitrogen adsorption and desorption isotherms and pore diameter distributions of the catalysts. The hysteresis loops at $P/P_0 = 0.6\text{--}1.0$ mean that the catalyst

has a mesoporous character, and all isotherms are type IV [43]. The pore diameter distribution of the catalysts is mostly between 10–30 nm. Table 1 shows the actual Cu contents, the texture and chemical properties of the catalysts and supports. Cu/Zr-Al-2 with pure tetragonal crystal phase ZrO_2 has the smallest specific surface area, pore volume, pore diameter and particle size of ZrO_2 . This may be related to the step-wise impregnation of the catalyst in preparation. Unusually, Cu/Zr-Al-5 has the biggest specific surface area, the biggest particle size of ZrO_2 and the smallest particle size of Cu. For other catalysts, there is no obvious change in specific surface area, pore volume and pore diameter. In addition, Cu dispersion and surface area were calculated and the results are shown in Table 1. It can be seen that the Cu dispersion and surface area follow the order Cu/Zr-Al-3 > Cu/Zr-Al-1 > Cu/Zr-Al-4 > Cu/Zr-Al-5 > Cu/Zr-Al-2. Higher metal surface area illustrates better dispersion of the metal, which means more active metal sites, ultimately leading to higher catalytic activity. The results show that the catalyst with higher Cu dispersion and Cu surface area has higher activity in this work.

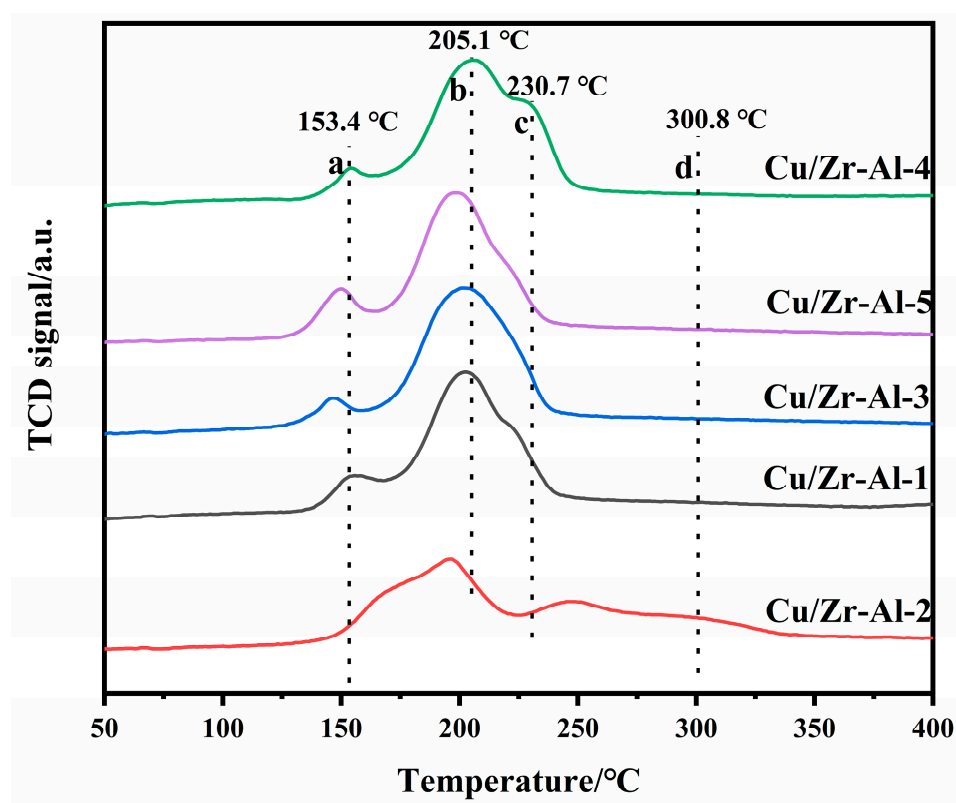


Figure 5. H_2 -TPR profiles of the calcined catalysts.

Table 1. Texture and properties of the catalysts and supports.

Catalyst	Cu Content ^a (wt%)	S_{BET} ^b ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{BJH} ^c ($\text{cm}^3 \cdot \text{g}^{-1}$)	D_p ^d (nm)	Cu Dispersion ^e (%)	Cu Surface Area ^e ($\text{m}^2/\text{g}_{\text{cat}}$)	Cu Particle Size ^f (nm)	ZrO_2 Particle Size ^f (nm)
Cu/Zr-Al-1	5.1	116.4	0.38	12.7	4.63	5.40	35.8	16.0
Cu/Zr-Al-2	4.5	86.4	0.24	9.7	1.98	2.24	35.5	13.8
Cu/Zr-Al-3	5.1	106.7	0.39	13.6	7.42	8.48	31.0	16.6
Cu/Zr-Al-4	5.1	113.9	0.39	13.3	2.19	2.55	32.3	16.3
Cu/Zr-Al-5	4.7	117.6	0.40	13.0	2.01	2.35	26.9	17.2

a: measured by ICP-AES; b: calculated by the BET equation; c: BJH adsorption pore volume; d: BJH adsorption average pore diameter; e: calculated by H_2 pulse chemisorption; f: calculated by the Debye–Scherrer equation from the diffraction peaks of Cu and ZrO_2 in Figure 3.

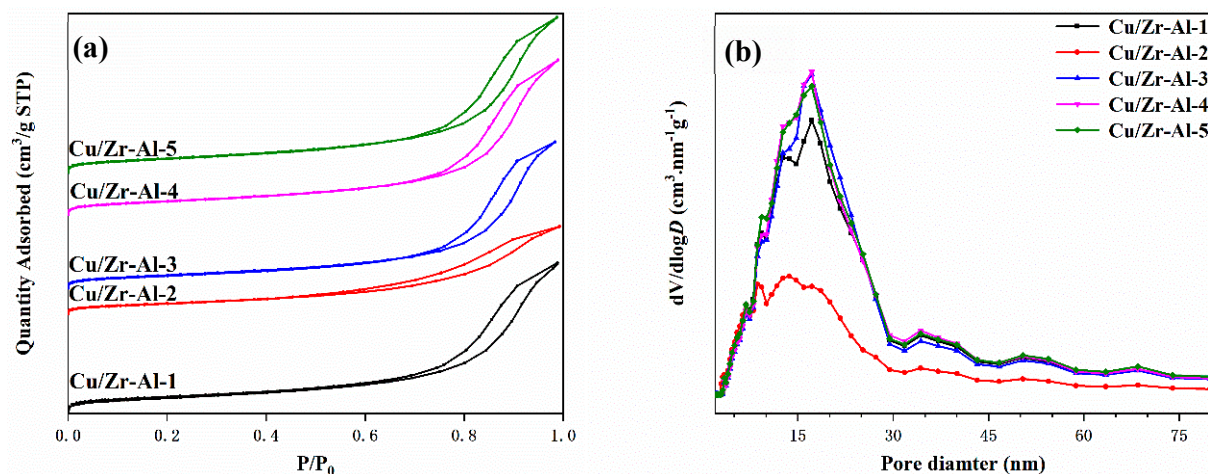


Figure 6. (a) Nitrogen adsorption and desorption isotherms and (b) pore diameter distribution of reduced catalysts.

2.5. XPS and AES Analysis

Figure 7 shows the surface elemental chemical valence states of reduced catalysts by X-ray photoelectron spectroscopy characterization. All the XPS data were analyzed by XPS PEAK41 software. The FWHM data of all fitting peaks are less than 2.7 eV, and the type of baseline used was the Shirley type. As shown in Figure 7a, there are two peaks at about 932.5 eV and 951.2 eV originating from Cu 2p_{3/2} and Cu 2p_{1/2}, respectively [44]. It is reported that the peaks at 953.8 eV and 934 eV are related to Cu²⁺, and the peaks at 952.1 eV and 932.3 eV are related to Cu⁰ + Cu¹⁺ [45–48]. The reason for the existence of Cu²⁺ in the reduced catalyst is that the reduced catalyst was passivated for 12 h under an atmosphere of 5% O₂/Ar, so there will be Cu²⁺ on the surface of the catalyst. Cu⁰ and Cu¹⁺ are too difficult to be distinguished since their binding energies are located too close to one another (Cu⁺ at 932.18 eV and Cu⁰ at 932.63 eV) [49]. Cu Auger spectra were used to distinguish Cu⁰ and Cu¹⁺ species and the result is shown in Figure S3. It can be seen that the characteristic peaks of Cu⁰ and Cu¹⁺ are also not obvious. There is also one peak at 942.7 eV, which originates from the satellite peak of Cu²⁺, that confirms the existence of Cu²⁺ [50]. In Figure 7b, there are two peaks about 530.0 eV and 531.2 eV originating from the lattice oxygen species and the surface oxygen species, respectively [51,52]. In Figure 7c, there are two peaks at about 180.7 eV and 183.1 eV originating from Zr 3d_{3/2} and Zr 3d_{5/2}, respectively [53,54]. It is reported that the peaks at 181.6 eV and 183.8 eV are related to Zr⁴⁺ and the peaks at 180.7 eV and 183 eV are related to Zr³⁺ [34].

Table 2 shows the relative content of elements on the reduced catalysts' surface. The Cu/Zr-Al-3 catalyst has the highest proportion of (Cu¹⁺ + Cu⁰) on its surface, which may be the active site of MSR [55]. A high proportion of (Cu¹⁺ + Cu⁰) is beneficial to MSR processing and this is why the Cu/Zr-Al-3 catalyst has the best performance. Zr⁴⁺ is derived from the lattice ions of ZrO₂ species, while Zr³⁺ is derived from the partially reduced oxygen-deficient ZrO₂ [52,54]. Therefore, the ratio of Zr³⁺ can be used to reflect the concentration of oxygen vacancy on the ZrO₂ support [52,54]. The Cu/Zr-Al-3 catalyst has the highest surface proportion of Zr³⁺ (89.1%) and the Cu/Zr-Al-2 catalyst has the lowest proportion of Zr³⁺ (79.8%). This means that the Cu/Zr-Al-3 catalyst has the highest concentration of oxygen vacancy and the Cu/Zr-Al-2 catalyst has the lowest concentration of oxygen vacancy. It is reported that oxygen vacancy concentration can be evaluated using the formula $O_{\text{surface}} / (O_{\text{lattice}} + O_{\text{surface}})$ [35,52,54]. The highest proportion of O_{surface} is observed in Cu/Zr-Al-3 and the lowest proportion of O_{surface} is observed in Cu/Zr-Al-2. This is consistent with the results for the Zr 3d spectra. For other catalysts, it can be seen that the concentration of oxygen vacancy is positively correlated with the activity of catalysts. In addition, the O₂-TPD characterization experiment was used to detect the concentration of oxygen vacancy and the results are shown in Figure 7d. The α region oxygen desorption

peak (70–200 °C) is attributed to the desorption of weakly chemically oxygen [56], and the β region oxygen desorption peak (200–450 °C) is attributed to the desorption of strongly chemically oxygen which originates from the oxygen vacancy [57]. The γ region oxygen desorption peak (450–650 °C) is attributed to the desorption of O^- [58]. It can be seen that the strongest β region oxygen desorption peak appears on the Cu/Zr-Al-3 catalyst, which proves that this catalyst exhibits the most oxygen vacancies. This result is consistent with the results from O 1s and Zr 3d spectra. In general, the Cu/Zr-Al-3 catalyst has the highest concentration of oxygen vacancy, which may affect the valence state of Cu and further promote the occurrence of MSR.

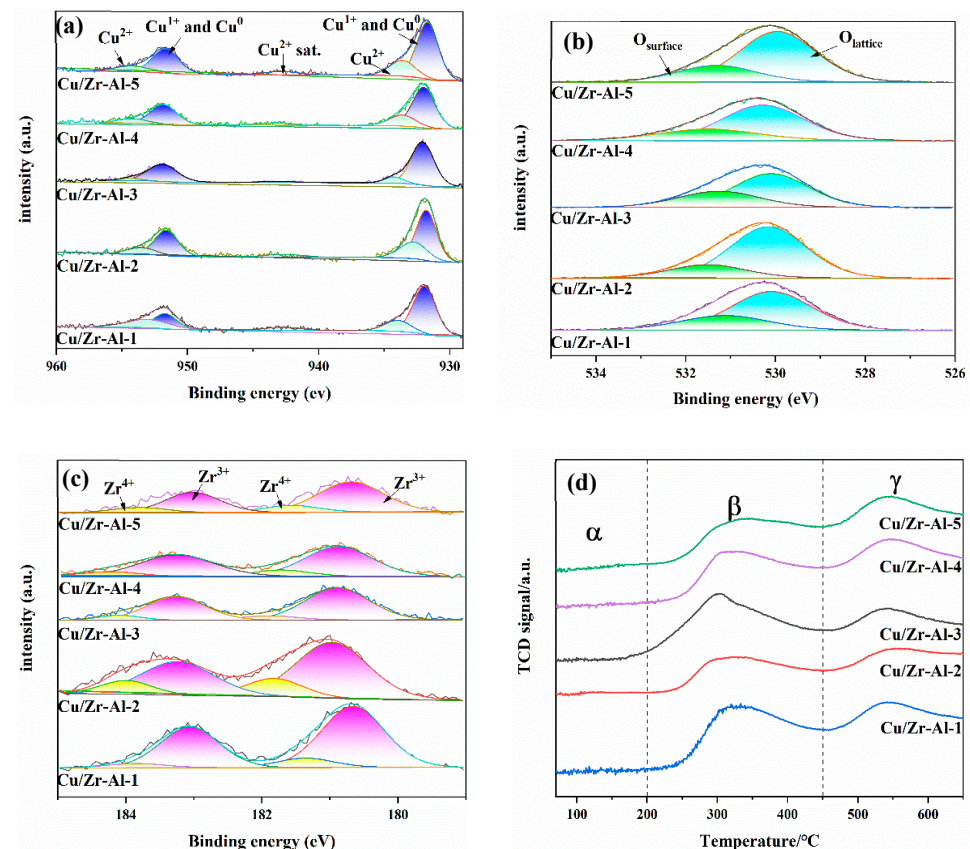


Figure 7. XPS curves of (a) Cu 2p, (b) O 1s and (c) Zr 3d for reduced catalysts; (d) O₂-TPD of different catalysts.

Table 2. The relative content of elements on the reduced catalyst surface.

Catalysts	Cu ²⁺ (%)	Cu ¹⁺ and Cu ⁰ (%)	Zr ³⁺ (%)	Zr ⁴⁺ (%)	O _L ^a (%)	O _S ^b (%)	O _V ^c	O _V ^d (mmol/g)
Cu/Zr-Al-1	21.0	79.0	87.7	12.3	70.4	29.6	0.296	0.102
Cu/Zr-Al-2	31.1	68.9	79.8	20.2	79.5	20.5	0.205	0.056
Cu/Zr-Al-3	10.7	89.3	89.1	10.9	65.8	34.2	0.342	0.136
Cu/Zr-Al-4	23.9	76.1	85.6	14.4	71.7	28.3	0.283	0.075
Cu/Zr-Al-5	25.5	74.5	83.2	16.8	74.6	25.4	0.254	0.063

a: O_L: lattice oxygen species. b: O_S: surface oxygen species. c: O_V: amount of surface oxygen vacancy. O_V = O_S/(O_L + O_S). d: O_V: measurement by O₂-TPD.

2.6. TEM and HRTEM Analysis

Figure 8 shows TEM and HRTEM images of the reduced catalysts. The interplanar spacings observed in the image of Cu/Zr-Al-1 and Cu/Zr-Al-5 are 0.29, 0.31 and 0.21 nm, respectively, indicating the exposure of *t*-ZrO₂ (101), *m*-ZrO₂ (−111) and Cu (111) lattice

planes. For Cu/Zr-Al-2, the lattice fringes in the spacings of 0.21, 0.26 and 0.29 nm are attributed to Cu (111), *t*-ZrO₂ (002) and *t*-ZrO₂ (101) lattice planes. For Cu/Zr-Al-4, the lattice fringes in the spacings of 0.21, 0.28 and 0.31 nm are attributed to Cu (111), *m*-ZrO₂ (111) and *m*-ZrO₂ (−111) lattice planes. For Cu/Zr-Al-3, the lattice fringes in the spacings of 0.26 and 0.28 nm are attributed to *t*-ZrO₂ (002) and *m*-ZrO₂ (111) lattice planes, which is not present on other catalysts with mixed crystal phase ZrO₂. Significantly, the lattice planes of *t*-ZrO₂ (101) and *m*-ZrO₂ (−111) in Cu/Zr-Al-1 and Cu/Zr-Al-5 are also not present on the Cu/Zr-Al-3 catalyst. Based on the results of XPS and activity, it can be deduced that the co-existence of *t*-ZrO₂ (101) and *m*-ZrO₂ (−111) lattice planes leads to the appearance of more defective ZrO₂ species on the Cu/Zr-Al-3 catalyst, resulting in a higher concentration of oxygen vacancy, which further affects the valence change of the active species Cu. Eventually, the Cu/Zr-Al-3 catalyst has the best catalytic activity.

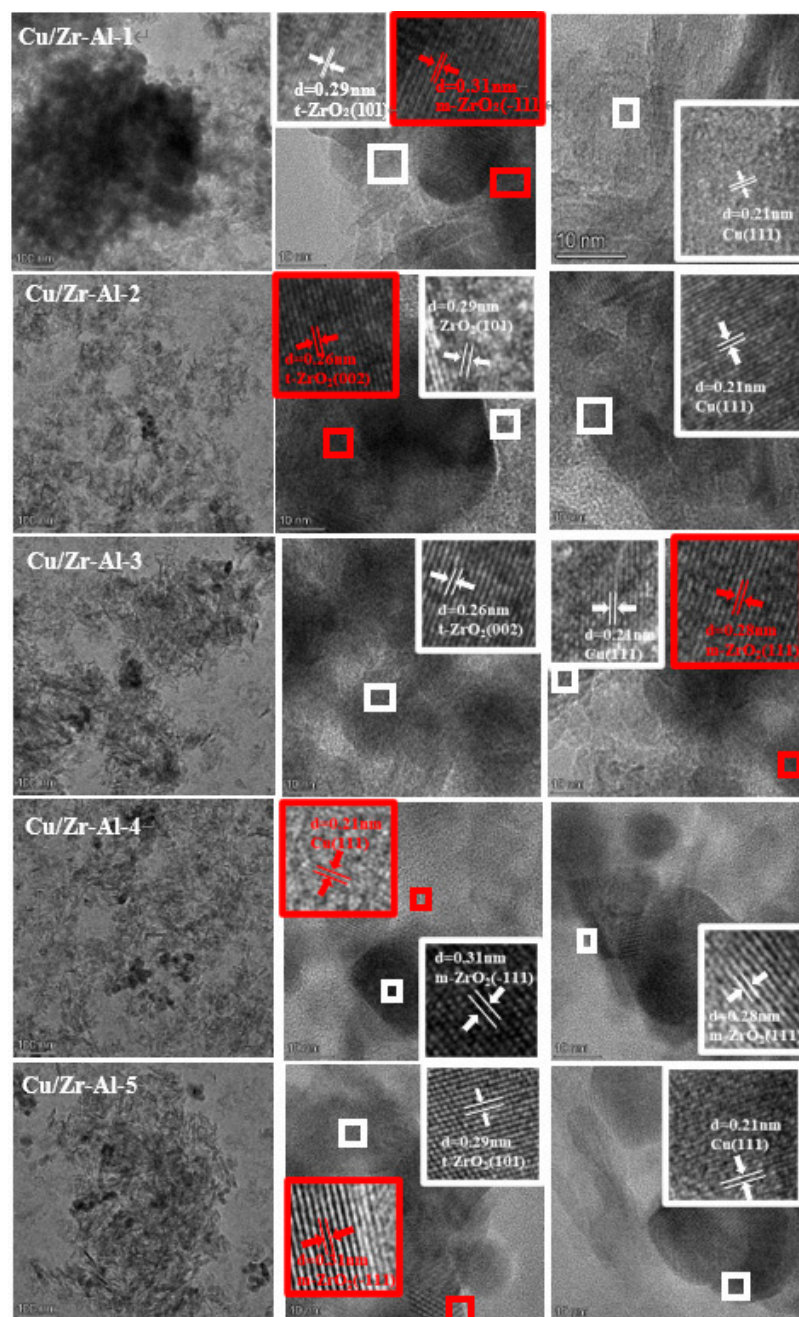


Figure 8. TEM and HRTEM images of the reduced catalysts.

3. Discussion

Cu/Zr-Al catalysts were synthesized by different methods to obtain different crystal phase ZrO_2 . It was found that the Cu/Zr-Al-3 catalyst had the best performance with the highest methanol conversion (88.5%), hydrogen production rate ($104.6 \mu\text{mol/g}_{\text{cat}}\cdot\text{s}$) and low CO selectivity (1.9%) at 275°C . From the characterization of the catalysts, it can be seen that the mixed crystal phase catalyst with a higher proportion of $m\text{-ZrO}_2$ exhibits higher catalytic activity, and the catalytic activity of the catalysts containing pure $m\text{-ZrO}_2$ is much higher than that of the catalysts containing pure $t\text{-ZrO}_2$. Meanwhile, the highly dispersed Cu^{2+} stepwise reduction peaks move to a low temperature region in the Cu/Zr-Al-3 catalyst. This means that this catalyst has better reducing capacity, and the stepwise reduction of Cu^{2+} species is promoted. The Cu/Zr-Al-3 catalyst has the characteristic lattice planes of $t\text{-ZrO}_2$ (002) and $m\text{-ZrO}_2$ (111), which is absent on other catalysts with mixed crystal phase ZrO_2 . It is possible that the co-existence of these two characteristic lattice planes influences the growth of copper species. Catalysts with higher $m\text{-ZrO}_2$ ratios have the highest concentrations of oxygen vacancy, which further affects the valence state of Cu over the catalyst. Therefore, the Cu/Zr-Al-3 catalyst contains the highest proportion of $\text{Cu}^{1+}+\text{Cu}^0$, which promotes the occurrence of MSR. In summary, a series of catalysts are obtained by changing the preparation method of ZrO_2 . These catalysts have different structural characteristics, such as the ratio of monocline and the tetragonal ZrO_2 crystal phase, the exposed lattice planes of ZrO_2 , the content of oxygen vacancy, and the content of active species $\text{Cu}^{1+}+\text{Cu}^0$. It is the structural changes of these catalysts that lead to the differences in catalytic activity. Meanwhile, in order to better compare the performance of the catalysts, the performance of some reported catalysts for MSR are listed in Table 3. Compared to other reported catalysts, the Cu/Zr-Al-3 catalyst exhibits good activity at lower temperatures with higher WHSVs. Compared to our previous work [32], the Cu/Zr-Al-3 catalyst also exhibits higher methanol conversion and higher hydrogen production rate at a lower temperature than the Cu/ZrO₂-8Al₂O₃ catalyst in our previous work, which indicates that Cu/Zr-Al-3 performs well.

Table 3. Performance of different copper-based catalysts for MSR.

Catalyst	Temperature (°C)	S/C ^a	Space-Time Ratio (h ^{−1})	Conversion (%)	H ₂ Production Rate (μmol/g _{cat} ·s)	CO Selectivity (%)	References
ZrO ₂ -CeO ₂ -Cu/KIT-6	300	2	2 (WHSV)	96	S _{H2} = 99.8%	0.7	[59]
Cu/ZnO-3Al	250	1	15.3 (WHSV)	57.3	-	1.3	[55]
Cu/ZnAl-R10	225	1.3	6 (WHSV)	67	-	-	[60]
1Cu/1Zr/AZ	400	1.2	10.8 (WHSV)	90.6	182.0	3.2	[36]
Cu/ASA1	300	0.5	1.8 (WHSV)	91.0	S _{H2} = 96.8%	9.6	[61]
CuO-Al ₂ O ₃	350	5	36,000 (GHSV)	72.2	S _{H2} = 87.5%	0.5	[62]
CuZnAl-5Mg	200	1	3.84 (WHSV)	70	47.2	1.0	[63]
Cu/ZnCeZrAl	250	1.2	2.6 (WHSV)	96.1	-	0.37	[64]
Cu-Ce/SBA-15	270	1.2	3 (WHSV)	90.1	-	2.1	[65]
Cu/ZrO ₂ -8Al ₂ O ₃	300	1	9.9 (WHSV)	84.5	98.7	1.5	[32]
Cu/Zr-Al-3	275	1	9.9 (WHSV)	88.5	104.6	1.9	This work

a: molar ratio of steam to methanol.

4. Experimental Section

4.1. Materials

$\text{NH}_3\cdot\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2\cdot x\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4\cdot 5\text{H}_2\text{O}$, acetone and polyethylene oxide-polypropylene oxide-polyethylene oxide (P123) were purchased from Chron Chemical in China, and Al_2O_3 was purchased from Adamas-beta in China. All chemical reagents are analytically pure.

4.2. Synthesis of $\text{ZrO}_2\text{-Al}_2\text{O}_3$

Zr-Al-1: ZrO_2 was obtained by the calcination of $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ at $600\text{ }^\circ\text{C}$ for 4 h. Then, Zr-Al-1 was obtained by mechanically mixing ZrO_2 and Al_2O_3 with a molar ratio of 1:8 via placing the ZrO_2 and the Al_2O_3 in a mortar to grind evenly.

Zr-Al-2: Zr-Al-2 was obtained by the impregnation method to obtain the designed phase [33,66]. Firstly, Al_2O_3 was impregnated in the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution which was prepared by adding 30 grams of solid $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ to 100 mL of deionized water (the Zr/Al molar ratio is 1:8). Then, the solid component was obtained by oscillating, oil bath drying and drying in oven at $80\text{ }^\circ\text{C}$ for 12 h. Finally, the solid component was calcined at $600\text{ }^\circ\text{C}$ for 4 h to obtain Zr-Al-2.

Zr-Al-3: Zr-Al-3 was obtained by our previous method [53]. $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (30 g) was dissolved in 100 mL ultra-pure water and stirred until completely dissolved. Then, $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added with stirring to $\text{pH}=9.5$ to produce zirconium hydroxide precipitation. After stirring for another hour, the mixture was transferred to a hydrothermal reactor (200 mL) where it was kept at $140\text{ }^\circ\text{C}$ for 24 h. The precipitate was then filtered and the resulting solid portion as rinsed with deionized water to $\text{pH}=7$. The solid was then dried at $80\text{ }^\circ\text{C}$ for 12 h and calcined at $600\text{ }^\circ\text{C}$ for 4 h to obtain ZrO_2 . Finally, Zr-Al-3 as obtained by the mechanical mixing of ZrO_2 and Al_2O_3 with a molar ratio of 1:8.

Zr-Al-4: Zr-Al-4 was obtained by the same method as Zr-Al-3. The only difference is that the precursor was $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ instead of $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$.

Zr-Al-5: 9.25 g $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and 6.96 g P123 were dissolved in ultrapure water. Subsequently, ammonia was added to adjust the pH of the solution to 11, and the mixture was stirred at $88\text{ }^\circ\text{C}$ for 24 h. Then, the mixture was washed three times with acetone and three times with water. Finally, ZrO_2 was dried at $80\text{ }^\circ\text{C}$ for 12 h and calcined at $600\text{ }^\circ\text{C}$ for 4 h. Zr-Al-5 was obtained by mechanically mixing ZrO_2 and Al_2O_3 with a molar ratio of 1:8.

4.3. Synthesis of $\text{Cu/ZrO}_2\text{-Al}_2\text{O}_3$

The $\text{Cu/ZrO}_2\text{-Al}_2\text{O}_3$ catalyst was prepared by the impregnation method. Copper (II) nitrate trihydrate (0.4 g) was dissolved in 10 mL ultrapure water by ultrasound for 20 min. Then, the designed amount of prepared $\text{ZrO}_2\text{-Al}_2\text{O}_3$ was added into the solution. Subsequently, the slurry was maintained at $25\text{ }^\circ\text{C}$ for 24 h under stirring, and then dried at $80\text{ }^\circ\text{C}$ to remove the remaining water and desiccated at $110\text{ }^\circ\text{C}$ in a drying oven overnight. Lastly, the prepared solid was calcined in air at $350\text{ }^\circ\text{C}$ ($2\text{ }^\circ\text{C}/\text{min}$) for 4 h. The prepared catalysts were named as 5 wt% Cu/Zr-Al-x , where $x = 1, 2, 3, 4, 5$.

4.4. Catalyst Activity Study

The catalyst activity test was performed in a stainless-steel fixed bed reactor of length 60 cm and 1.4 cm inside diameter at atmospheric pressure, with 0.5 g prepared catalyst (20–40 mesh) used. The temperature was increased to $300\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$ in an Ar atmosphere at 30 mL/min. Then, the catalyst was reduced at $300\text{ }^\circ\text{C}$ for 2 h under a hydrogen and argon atmosphere at a total flow rate of 60 mL/min ($V_{\text{H}_2}:V_{\text{Ar}} = 1:1$). After cooling to $200\text{ }^\circ\text{C}$, the feed flow mixture ($n_{\text{MeOH}}:n_{\text{H}_2\text{O}} = 1:1$) was introduced through the micro pump at 4 mL/h. Then, the mixture was vaporized by the carburetor and preheater at $135\text{ }^\circ\text{C}$. The performance of the Cu/Zr-Al-x catalysts over the temperature range of 200 to $300\text{ }^\circ\text{C}$ was investigated. Finally, product gas flow was detected by a mass flowmeter and all the gaseous outcomes were detected by on-line gas chromatography (GC Plot-C 2000 Capillary column). The gas chromatography model used is PANNA-A91 and the specific parameters were as follows: column temperature: $160\text{ }^\circ\text{C}$, detector temperature: $200\text{ }^\circ\text{C}$, injector temperature: $120\text{ }^\circ\text{C}$ and carrier (Ar) gas flow: 20 mL/min.

According to the literature, methanol conversion (X_{MeOH}), CO selectivity (S_{CO}) and H_2 production rate (P_{H_2}) are calculated using the following Equations [36,63]:

$$X_{\text{MeOH}}(\%) = \frac{n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{CH}_4}}{n_{\text{MeOH}}} \times 100 \quad (3)$$

$$S_{\text{CO}}(\%) = \frac{n_{\text{CO}}}{n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{CH}_4}} \times 100 \quad (4)$$

$$P_{\text{H}_2}[\mu\text{mol}/(\text{g}_{\text{cat}} \cdot \text{s})] = \frac{n_{\text{H}_2} \times 10^6}{m_{\text{catalyst}} \times 60} \quad (5)$$

where n_{CO} , n_{CH_4} , n_{CO_2} and n_{H_2} are the product gas molar flow rates of CO, CH₄, CO₂ and H₂ (mol/min) and n_{MeOH} is the feed of molar rates of methanol (mol/min).

4.5. Catalyst Characterizations

The calcined catalysts were reduced at 300 °C for 2 h under a hydrogen and argon atmosphere at a total flow rate of 60 mL/min ($V_{\text{H}_2}:V_{\text{Ar}} = 1:1$). Then, the reduced catalysts were passivated for 12 h under an atmosphere of 5% O₂/Ar to prevent catalyst oxidation according to the literature [67,68].

The actual loading of Cu on all calcined catalysts were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and was carried out on an Optima 8000 from Perkin Elmer device in Waltham, MA, USA. The prepared catalysts were absolutely dissolved in mixed acid (3 mL HCl, 1 mL HNO₃, three or four drops of HF) before testing.

The texture and chemical properties of the reduced catalysts were analyzed by nitrogen adsorption on a Tristar II 3020 from Micromeritics company in Norcross, GA, USA. Approximately 120 mg of catalysts were pretreated at 120 °C for 2 h and 300 °C for 2 h under vacuum.

X-ray diffraction (XRD) of the catalysts was tested on a Shimadzu XRD-6100 diffractometer from PANalytical B.V company in Shanghai, China with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 eV and 30 mA, over a 2θ range of 20–80°. The crystal size (d) was calculated by the Debye–Scherrer Equation (6).

$$d = K\lambda/(\beta \cos \theta) \quad (6)$$

where K is the Scherrer constant, λ is the wavelength of the incident X-ray, β is the FWHM of the diffraction peak and θ is the Bragg diffraction angle.

The reduction behavior of the calcined catalysts was measured by hydrogen temperature programmed reduction (H₂-TPR) on an Autochem II 2920 from Micromeritics company in USA. Approximately 100 mg of catalysts were treated in an argon atmosphere at 140 °C for 30 min and then cooled to 50 °C. After that, the gas flow was changed to 5% H₂ + N₂ (totally 50 mL/min) and the TPR test was operated with a temperature increasing rate of 5 °C/min from 50 °C to 800 °C.

The H₂ pulse chemisorption of the catalysts was performed at 40 °C by injecting loop gas (5% H₂-He totally 50 mL/min) repeatedly until the adsorption became saturated. Metal surface area (S) and dispersion (D) were calculated by the following (Equations (7) and (8)):

$$S = V_m \times A_x \times SF \times N_A \quad (7)$$

$$D = V_m \times SF \times M/(100L) \quad (8)$$

where V_m is the adsorbed hydrogen volume, A_x is the cross-sectional area of metal atoms, SF is the chemisorption measurement number, N_A is the Avogadro constant, M is the metal molar mass and L is the metal load.

O₂-TPD was carried out to test the types of adsorption oxygen on catalysts' surfaces. This was conducted from 40 °C to 900 °C at 10 °C/min under a helium atmosphere (50 mL/min) after the adsorption of O₂ was saturated.

The surface elemental chemical valence states of reduced catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) characterization, using an AXIS Ultra DLD spectrometer from Kratos company in Manchester, UK. All the binding energies were corrected by the peak of C1s at 284.6 eV.

The catalyst samples were subjected to transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) characterization using an FEI

Talos F200S apparatus (from Thermo Fisher Scientific company, Waltham, MA, USA), operated with 0.25 nm resolution and 10–10,000 magnification.

5. Conclusions

In this paper, the catalyst with 81.4% monoclinic ZrO_2 crystal phases (Cu/Zr-Al-3) exhibited the highest methanol conversion (88.5%) and the highest hydrogen production rate ($104.6 \mu\text{mol/g}_{\text{cat}} \cdot \text{s}$) at 275°C . This catalyst showed the best reducing properties and many more oxygen vacancies in its surface. The amount of oxygen vacancies can affect the chemical valence state of the active center, and accordingly affect the catalytic activity. In addition, the presence of characteristic $t\text{-ZrO}_2$ (002) and $m\text{-ZrO}_2$ (111) lattice planes on the Cu/Zr-Al-3 catalyst may influence the growth of copper species and promote catalytic activity. This study not only successfully prepared MSR catalysts with high activity and stability but also confirmed the feasibility of enhancing the catalytic activity of the MSR reaction by altering the ZrO_2 crystal phase. This provides guidance for designing and developing efficient MSR reaction catalysts in mixed-phase systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14080480/s1>, Figure S1: 9h stability of Cu/Zr-Al-3 catalyst; Figure S2: Effect of $m\text{-ZrO}_2$ ratio and oxygen vacancy amount on methanol conversion; Figure S3: Cu Auger spectra of the reduced catalysts; Table S1: The proportion of different crystalline ZrO_2 in catalysts after calcination and reduction.

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