Catalytic Steam Reforming of Bio-Oil-Derived Acetic Acid over CeO$_2$-ZnO Supported Ni Nanoparticle Catalysts
Shan Luo, Peng Fu,* Fazhe Sun,* Bing Wang, Andong Zhang, Jianlin Wang, and Qi Sun

ABSTRACT: The steam reforming of bio-oil-derived acetic acid over the developed Ni/CeO$_2$-ZnO nanoparticle catalysts for hydrogen production was studied. The correlations of CeO$_2$ to ZnO mass ratio (CZMR) and nickel loading with the properties and performances of Ni/CeO$_2$-ZnO catalysts were explored. The H$_2$, CO, and potential H$_2$ yields followed a Gaussian normal distribution with increasing the CZMR. An exponential function equation was established to correlate the H$_2$, CO, and potential H$_2$ yields with Ni loading. As the CZMR increased from 0 to 1/3, the H$_2$ yield increased from 57.8 to 69.4%, with a growth rate of 20.1%. Further, on increasing the CZMR from 1/3 to 3, the H$_2$ yield decreased by 37.6%. The CO yield showed a similar trend for the H$_2$ yield on increasing the CZMR, which first increased to a peak value, then started to decrease rapidly and finally stabilized. The yield of H$_2$ increased significantly from 20.6 to 73.5%, with the increase of nickel loading from 0 to 15%. Further, on increasing the nickel loading from 15 to 25%, the H$_2$ yield increased by only 5.8%. With the CZMR of 1/3 and the nickel loading of 15%, the selectivities of H$_2$ and CO were as high as 91.6 and 42.3%, respectively.

1. INTRODUCTION
Hydrogen is an ideal, pollution-free, green new energy in the 21st century. It has great development potential due to its high heating value, wide sources, pure quality, and multiple energy forms. Biomass is a highly potential feedstock for hydrogen production because it is carbon neutral, diverse, and renewable. Biomass pyrolysis oil (bio-oil) steam reforming is an important hydrogen production method, which has attracted more and more scholars’ extensive attention. The byproducts have high added value, can improve the economy of the entire process, and have good development and utilization potential. Bio-oil is a brown-black viscous liquid produced by rapid pyrolysis of biomass at moderate temperature, rapid heating, and anaerobic conditions. Its composition and properties are extremely complex and vary depending on the type of raw materials and pyrolysis conditions. Acetic acid is one of the main components of bio-oil, with its content being up to 9.4%. Thus, it has been recognized as an important and representative derivative of bio-oil to establish the structure–activity relationship of the steam reforming catalysts for hydrogen production.

The main constraints of hydrogen production by catalytic reforming of bio-oils are poor catalyst performance and easy deactivation due to carbon deposition. Therefore, the development of a catalyst with high activity, long-life cycle stability, and excellent carbon deposition resistance is a key technical issue in the reforming reaction. The deactivation and poor activity caused by coke deposition and high-temperature sintering should be minimized as much as possible. Nickel-based catalysts have low cost, abundant reserves, high economic practicality, and excellent hydrogenation activity,
which are favorable for the cleavage of C–C, O–H, and C–H bonds with good hydrogen selectivity.\textsuperscript{14,15} However, the carbon deposit generated during reforming reactions and the catalyst sintering caused by high temperature can affect the catalyst lifetime.\textsuperscript{16} To enhance the catalytic performance, the structural stability and antcarbon properties of the catalysts can be tuned via alkali/alkaline metals\textsuperscript{17} and rare-earth elements.\textsuperscript{18} Constructing composite supports or introducing promoters can improve the dispersion of the active components and thereby enhance the activity and stability of the catalysts. Most researchers on composite supports of nickel-based catalysts focus on composite oxides such as ZnO-TiO\textsubscript{2}, CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}, La\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2}, La\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}, and CeO\textsubscript{2}-ZrO\textsubscript{2}. Fan et al.\textsuperscript{19} studied Ni/ZnO-TiO\textsubscript{2} catalysts for hydrogen production from acetic acid steam reforming and found that the average pore size of the composite support catalyst was small and the proportion of micropores was high, which improved the dispersion of active components. Bizarra et al.\textsuperscript{20} studied a nickel-based catalyst with Al\textsubscript{2}O\textsubscript{3} as a support and performed steam reforming of bio-oil for hydrogen production to explore the effect of CeO\textsubscript{2}-modified Al\textsubscript{2}O\textsubscript{3} support. They pointed out that CeO\textsubscript{2} as an auxiliary agent, provided oxygen migration performance for the catalyst, improved the stability of the catalysts, and prolonged the time to maintain a higher H\textsubscript{2} yield. Valle et al.\textsuperscript{21} explored the effects of space-time and the steam-to-carbon ratio (S/C) on Ni/La\textsubscript{2}O\textsubscript{3}-αAl\textsubscript{2}O\textsubscript{3}-
catalyzed bio-oil steam reforming and found that the H\textsubscript{2} yield increased significantly with increasing space-time and S/C. Angeli et al.\textsuperscript{22} analyzed the effects of La\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} and La\textsubscript{2}O\textsubscript{3}-CeO\textsubscript{2}-ZrO\textsubscript{2} composite supports on active components in methane steam reforming and confirmed that the oxygen storage capacity of CeO\textsubscript{2} helped to improve the reforming efficiency and the carbon deposition resistance of nickel-based catalysts.

Nano ZnO has excellent performance as a catalyst support with small particle sizes and large specific surface areas,\textsuperscript{23,24} which are conducive to the dispersion of the Ni active component. It has high surface energy, good chemical stability, and homogeneous dispersibility.\textsuperscript{25} CeO\textsubscript{2} has high oxygen storage capacity and unique catalytic oxidative and reduction characteristics, which can improve the dispersion of active components on the catalyst supports, enhance the thermal stability and antisintering performance of the support, and improve the catalytic activity of the catalysts.\textsuperscript{26,27} However, there are currently few studies on CeO\textsubscript{2}-ZnO composite oxide support. In this study, the Ni/CeO\textsubscript{2}-ZnO nanoparticle catalysts were developed for hydrogen production from acetic acid steam reforming. The physiochemical properties of the catalysts were evaluated by H\textsubscript{2}-TPR, BET, and XRD methods. The correlations of the CeO\textsubscript{2} to ZnO mass ratio (CZMR) and nickel loading with the properties and performances of Ni/CeO\textsubscript{2}-ZnO catalysts were explored. This study helped to promote the development of effective nickel-based catalysts with CeO\textsubscript{2}-ZnO composite oxide supports.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterizations. 2.1.1. H\textsubscript{2}-TPR Analysis. Figure 1 shows that two reduction peaks appear in the H\textsubscript{2}-TPR spectrum of Ni/CeO\textsubscript{2}-ZnO with a CZMR value of 1/3. The main reduction peak located at about 430 °C is the reduction peak of free NiO.\textsuperscript{28} The highest peak and largest reduction area indicate that the catalyst contains a large amount of NiO. There is also a reduction shoulder, and the peak temperature is about 630 °C, which may be due to the interaction between NiO and CeO\textsubscript{2}-ZnO support. During the preparation process, some Ni\textsuperscript{2+} ions enter the crystal lattices of the support. Thus, the reduction of Ni\textsuperscript{2+} to Ni requires a higher temperature to escape from the crystal lattices. In addition, the reduction of a formation of nonstoichiometric Ce-oxide species occurs at 520 °C, which leads to the reduction peak.\textsuperscript{29–32} Therefore, the prepared catalysts were reduced at 800 °C, which ensured that all Ni ions were completely reduced to Ni.

2.1.2. BET Analysis. BET specific surface areas of Ni/CeO\textsubscript{2}-ZnO catalysts with different CZMR values are exhibited in Figure 2. The specific surface area of the catalysts increases from 5.7 to 13.7 m\textsuperscript{2}/g with a growth rate of 140.3% when elevating CZMR from 0 to 1/3. The specific surface area of the catalysts decreased by 17.1% on increasing the CZMR from 0 to 1/3. When only ZnO is contained in the support, a large number of Ni\textsuperscript{2+} ions enter the crystal lattice of ZnO and fill the vacancies. The particles are closely clustered together, which reduces the catalyst specific surface area. During the coprecipitation process of CeO\textsubscript{2} and ZnO, more pore structures are generated, resulting in an increase in the specific surface area.\textsuperscript{28}
2.1.3. XRD Analysis. The comparison of XRD patterns of Ni/CeO$_2$-ZnO catalysts with a nickel loading of 15% before and after steam reforming is shown in Figure 3. As can be seen, compared with the fresh Ni/CeO$_2$-ZnO catalyst, the diffraction peak intensities of the reformed catalyst are obviously weakened, which may be due to the formation of considerable amorphous carbon or sintering of the catalyst due to high temperature. The characteristic peaks of NiO in the fresh Ni/CeO$_2$-ZnO catalyst appear at $2\theta$ = 37.3, 43.3, 62.9, and 75.4°, which are assigned to the NiO(111), NiO(200), NiO(220), and NiO(311) bands, respectively. However, only weak Ni characteristic peaks are observed at $2\theta$ = 44.4, 51.6, and 76.1° in the reformed catalyst, corresponding to the Ni(111), Ni(200), and Ni(220) peak. The possible and reasonable reason is that the surface of the catalyst support is covered with amorphous carbon deposits. The above results prove that a certain amount of NiO is reduced to Ni, which is consistent with the H$_2$-TPR results.

XRD patterns of the reformed Ni/CeO$_2$-ZnO catalysts with different CZMR values and different nickel loadings are displayed in Figure 4. As observed, as the CZMR increases, the characteristic diffraction peaks of ZnO at $2\theta$ = 31.8, 34.5, 36.2, and 62.7° become weaker. At the same time, the intensities of the CeO$_2$(111), CeO$_2$(220), and CeO$_2$(311) diffraction peaks at $2\theta$ = 28.6, 47.5, and 56.3° are significantly increased. Compared with the CeO$_2$ diffraction peaks, ZnO has wider peak shape and lower intensity, indicating that the particle size of ZnO is smaller than CeO$_2$. Furthermore, Ni/CeO$_2$-ZnO has the characteristic diffraction bands of Ni with $2\theta$ of 44.4, 51.6, and 76.1°. The intensities of Ni diffraction peaks increase with increasing nickel loading (Figure 4b). However, the characteristic peaks of Ni are not obvious, and the peak shapes are relatively diffuse, which are related to the high dispersion of Ni on the support.

2.2. Catalytic Performance in the Acetic Acid Steam Reforming. The reaction conditions were temperature = 800 °C, water-to-carbon molar ratio (S/C) = 3, weight hourly space velocity (WHSV) = 5 h$^{-1}$, and catalyst mass = 3 g. Prior to each experiment, the Ni/CeO$_2$-ZnO nanoparticle catalysts were reduced at 800 °C. The effects of the Ni/CeO$_2$-ZnO catalysts with different CZMR values and different nickel loadings on the yield, selectivity, and the content of steam reforming gas components were investigated.

2.2.1. Effect of Ni/CeO$_2$-ZnO Catalysts with Different CZMR Values on Acetic Acid Steam Reforming. The variation of H$_2$, CO, CO$_2$, and CH$_4$ yields with respect to time on stream over Ni/CeO$_2$-ZnO catalysts with different CZMR values is shown in Figure 5. From Figure 5a, the H$_2$ yield exhibits a downward trend at the beginning of the acetic acid steam reforming process, and finally stabilized over time. The H$_2$ yield increases from 57.8 to 69.4%, with a growth rate of 20.1% when raising the CZMR from 0 to 1/3. Further increasing the CZMR from 1/3 to 3, the H$_2$ yield shows a downward trend with a decrease of 37.6%. CeO$_2$ is a stable rare-earth oxide with good oxygen storage and oxygen release capacity, which is beneficial to improve the resistance of the catalyst to carbon deposition and can also promote the occurrence of the water vapor shift reaction, thereby improving the activity and stability of Ni/CeO$_2$-ZnO catalysts. When elevating CZMR from 1/3 to 3, the specific surface areas of the catalysts decrease, which are not conducive to the dispersion of active components, resulting in the reduction of active sites and the decrease of the catalyst hydrogen production activity. The CO yield on the catalyst with a CZMR value of 3 first continues to decline with time, and eventually slowly increases. However, the CO yields show a completely opposite trend for catalysts with CZMR values of 1 and 3. At the same time, the

Figure 3. Comparison of XRD patterns of Ni/CeO$_2$-ZnO catalysts with a nickel loading of 15% before and after steam reforming.

Figure 4. XRD patterns of the reformed Ni/CeO$_2$-ZnO catalysts with different CZMR values and different nickel loadings.

Figure 5. Variation of H$_2$, CO, CO$_2$, and CH$_4$ yields with respect to time on stream over Ni/CeO$_2$-ZnO catalysts with different CZMR values.
CO yields for catalysts with CZMR values of 0 and 1/3 slowly increase with time. The yields of both CO and CH4 increase rapidly to the highest values, but then the yield of CO2 tends to be stable, while the yield of CH4 decreases continuously with time. The yields of H2, CO, and CO2 show a similar trend as the CZMR increases, which all increase first and then decrease. The highest yields of H2, CO, and CO2 were stable at 69.4, 38.2, and 48.4%, respectively. At 360 min, the CH4 yield of the Ni/CeO2-ZnO catalyst with a CZMR value of 1 is stable at 11.2%.

H2 and CO selectivities with time over Ni/CeO2-ZnO catalysts with different CZMR values are exhibited in Figure 6. The selectivities of both H2 and CO first decrease to the minimum with time. After that, the selectivities of H2 and CO for the catalyst with CZMR of 1 tend to stabilize with time, while the others slowly increase. The selectivities of H2 and CO are similar to their yield trend, with the highest reaching 90.5 and 40.7%, respectively. Nickel-based catalysts have good C–C bond breaking properties, but are prone to carbon deposition leading to catalyst deactivation. Adding a certain amount of Ce can significantly enhance the performance of Ni/CeO2-ZnO, which is attributed to the reaction 2CeO2 → Ce2O3 + 1/2O2. CeO2 that has a strong redox capacity and can be reused while continuously removing carbon deposition. On the one hand, the generated oxygen can oxidize C to remove carbon deposition; on the other hand, low-cost
Ce³⁺ is easily oxidized by O₂ and H₂O into high-value Ce, which achieves the purpose of storing oxygen. Therefore, adding Ce is beneficial for improving the stability of the catalyst. The highest H₂ yield and selectivity suggest that the optimal catalyst support occurs at the CZMR of 1/3. As shown in Figure 7, the H₂, CO, CO₂, and CH₄ contents maintain good stability for 6 h over the Ni/CeO₂-ZnO catalyst with a CZMR value of 1/3, reaching 59.6, 16.4, 20.8, and 3.1%, respectively.

2.2.2. Effect of Ni/CeO₂-ZnO Catalysts with Different Nickel Loadings on Acetic Acid Steam Reforming. The variation of H₂, CO, CO₂, and CH₄ yields with respect to time on stream over Ni/CeO₂-ZnO catalysts with different nickel loadings are compared in Figure 8. The yield of H₂ first decreases continuously with time, and then stabilizes (see Figure 8a). The H₂ yield increases with increasing the nickel loading. The yield of H₂ increased significantly from 20.6 to 73.5%, with the increase of nickel loading from 0 to 15%. Further, on increasing the nickel loading from 15 to 25%, the H₂ yield increases by only 5.8%. The CO, CO₂, and CH₄ yields slowly increase with time and then tend to stabilize, while the CO yield slowly decreases and tends to become stable when the nickel loading is 0%. Figure 8b,c shows that the CO yield first increases and then decreases as the nickel loading increases from 15 to 25%, which is contrary to the trend of CO₂. Figure 8d shows that the CH₄ yield decreases with increasing nickel loading. The steam reforming reaction is accompanied by more acetic acid pyrolysis and methanation reactions when the nickel loading is low, resulting in a lower H₂ yield. With increasing nickel loading, the catalysts provide more active sites throughout the reforming reaction, accelerating the overall reaction of acetic acid steam reforming. At this time, the H₂ and CO yields also increase. Therefore, the nickel loading plays a crucial role in the steam reforming process.

Figure 9 shows H₂ and CO selectivities with time over Ni/CeO₂-ZnO catalysts with different nickel loadings. The selectivities of H₂ and CO decrease with time and then

![Figure 7](image_url)

Figure 7. Evolution of the produced gas compositions with time over the Ni/CeO₂-ZnO catalyst with a CZMR value of 1/3.

![Figure 8](image_url)

Figure 8. Variation of (a) H₂, (b) CO, (c) CO₂, and (d) CH₄ yields with respect to time on stream over Ni/CeO₂-ZnO catalysts with different nickel loadings.
tends to be stable or slightly increase. When increasing nickel loading from 0 to 25%, the selectivities of H2 and CO increase from 55.5 and 22.9% to 93.4 and 45.0%, respectively. When the nickel loading is from 15 to 20%, the CO selectivity decreases from 42.3 to 39.9%, which is consistent with the variation trend of CO yield. These data show that the nickel-based catalyst has a significant effect on hydrogen production from acetic acid steam reforming. Under the same preparation conditions, the pore structure and specific surface area of the supported catalyst determine the specific value of the catalyst’s saturated loading. The actual number of active sites and the catalytic effect will not change significantly even if the theoretical loading is increased. Considering the catalytic effects and industrial economic applications, 15% was used as a more reasonable nickel loading. The Ni/CoO-ZnO catalyst with nickel loading of 15% is relatively stable for the acetic acid steam reforming within 6 h, corresponding to the stable H2 and CO contents of 60.1 and 16.9%, which can be confirmed in Figure 10.

Figure 9. (a) H2 and (b) CO selectivities with time over Ni/CoO-ZnO catalysts with different nickel loadings.

explored the yield data of H2 and CO and established quantitative relationships, as shown in Figures 11, 12, and Table 1.

As shown in Table 1, the H2, CO, and potential H2 yields followed a Gaussian normal distribution (Yi) with the CZMR. R2 was 1.00, which indicated that the model was significant and the effects of CZMR for H2, CO, and potential H2 yields were determined. On increasing the CZMR, the yields of H2, CO, and potential H2 showed a similar trend, which first increased to the peak, then rapidly decreased, and finally stabilized. The yields of H2, CO, and potential H2 conform to an exponential function relationship (Yi) with nickel loading. Only the correlation coefficient (R2) values were different, corresponding to 0.99, 0.97, and 0.99, respectively. R2 was significantly higher, confirming the rationality of the simulation results, which means that the ‘Y’ relationship could predict the gas yield under different nickel loadings. The H2 yields continued to increase with the increase of nickel loading from 0 to 15%, while H2 yields tended to stabilize when the nickel loading was ≥15%. It indicates that there is a single-layer distribution threshold for nickel loading on the composite support. The number of actual active sites and catalytic activity does not increase significantly even if the theoretical loading is increased.

3. CONCLUSIONS

The steam reforming of bio-oil-derived acetic acid over the developed Ni/CoO-ZnO nanoparticle catalysts for hydrogen production was studied. The correlations of CZMR and nickel loading with the properties and performances of Ni/CoO-ZnO catalysts were revealed. The H2, CO, and potential H2 yields followed a Gaussian normal distribution with increasing the CZMR while conforming to an exponential function equation with nickel loading. As the CZMR increased from 0 to 1/3, the specific surface area of the catalysts increased from 5.7 to 13.7 m²/g with an increase of 140.3%, while the H2 yield increased from 57.8 to 69.4%, with a growth rate of 20.1%. Further, on increasing the CZMR from 1/3 to 3, the specific surface area and H2 yield decreased by 17.1 and 37.6%, respectively. With increasing the CZMR, the CO yield showed a similar trend to H2 yield, which first increased to a peak value, then started to decrease rapidly, and finally stabilized. The H2 increased significantly from 20.6 to 73.5%, with the increase of nickel loading from 0 to 15%. Further increasing the nickel loading from 15 to 25%, the H2 yield increased by only 5.8%. With the CZMR of 1/3 and the nickel loading of
15%, the selectivities of H\(_2\) and CO were as high as 91.6 and 41.3%, respectively.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. The preparation of CeO\(_2\)-ZnO was supported by the coprecipitation method. First, Zn-(CH\(_3\)COO)\(_2\)·H\(_2\)O and Ce(NO\(_3\))\(_3\)·6H\(_2\)O were dissolved in deionized water, heated to 70 °C in a constant temperature magnetic stirrer, and a certain amount of 4 mol/L NaOH solution was added dropwise at a rate of 0.5 drops/second and stirred for 1 h until the reaction was complete. The precipitate was dried at 100 °C for 12 h after centrifugation at 3000 rpm for 15 min. The resulting sample was ground to a powder to obtain a composite metal oxide support with the CeO\(_2\) to ZnO mass ratio of \(x\) (\(x = 0\), 1/3, 1, 3).

A Ni-based catalyst was prepared by the impregnation method. Ni(NO\(_3\))\(_3\)-6H\(_2\)O was weighed and dissolved in deionized water to obtain nickel nitrate solutions with different concentration gradients. The sample was then placed in a constant temperature magnetic stirrer at 70 °C followed by the addition of CeO\(_2\)-ZnO. It was then stirred and impregnated thoroughly for 2 h. After centrifugation at 3000 rpm for 15 min, the resulting precipitate was dried in a constant temperature drying oven at 100 °C for 12 h. The sample was then calcined in a muffle furnace at 600 °C for 3 h to obtain highly dispersive nickel-based catalysts with different nickel loadings. When the nickel loading was 10%, Ni/CeO\(_2\)-ZnO catalysts with different CZMR values were 0, 1/3, 1, and 3, respectively. When the CZMR was 1/3, Ni/CeO\(_2\)-ZnO catalysts with different nickel loadings were 0, 5, 10, 15, 20, and 25%, respectively.

4.2. Catalyst Characterization. The reduction performance of the catalyst was determined by H\(_2\)-programmed temperature reduction (H\(_2\)-TPR) on AutoChem II 2920. Prior
to testing, impurities were removed. The sample was first heated to 200 °C and held for 60 min and then cooled to 40 °C. The carrier gas was 50 cm³/min of helium. The gas was then switched to 10% H₂/Ar (v/v) and purged in an atmosphere of 50 cm³/min until the baseline stabilized. The temperature increased to 900 °C at a rate of 10 °C/min, and the temperature reduction was performed under program temperature. The H₂-TPR spectrum of the catalyst was recorded online in real time.

The specific surface area of the catalyst was determined by ASAP2460 WJGS-029 full-automatic specific surface area analyzer. The N₂ adsorption–desorption measurements were performed on the treated samples with high-purity nitrogen as the adsorption medium to determine the specific surface area of the catalyst.

The crystallization properties of the catalyst were determined using a D8 ADVANCE polycrystalline X-ray diffractometer (XRD) of Bruker AXS, Germany. The operating voltage was 40 kV, and the current was 50 mA.

4.3. Catalytic Tests. The catalyst activity evaluation device consisted of a feed part, a reforming reactor, a condensation separation part, and a gas analysis part. Before the reaction, the catalyst (3 g, 35 mm) was placed on a bracket in the middle of the fixed-bed tube reactor, and the catalyst was reduced by passing 10% H₂/N₂ at 800 °C for 30 min. After the reduction was completed, the mixed gas was switched to N₂ to exhaust hydrogen. At the beginning of the reaction, the acetic acid aqueous solution with a water–carbon mole ratio of 3 was pumped into the fixed-bed device by a peristaltic pump (BT100-2), Baoding Lange Constant Flow Pump Co., Ltd.) with a weighted hourly space velocity of 5. N₂ was used as a carrier gas during the reaction, and the flow rate remained constant. The reacted products were condensed to collect the unreacted acetic acid solution and liquid byproducts. The noncondensable gas was dried over activated carbon and passed into an infrared flue gas analyzer (Gasboard-3100, Wuhan Cube Optoelectronics Co., Ltd., China) to perform real-time online detection of H₂, CO, CO₂, and CH₄. The feeding was stopped after the reaction was completed, and the catalyst was removed for subsequent characterization after cooling to room temperature in an N₂ atmosphere. The reactor was fired at 800 °C after each reaction to remove impurities such as carbon deposits to ensure the accuracy of the experimental results and the consistency of the experimental conditions.

4.4. Calculation Method. The products produced by the steam reforming of acetic acid are mainly H₂, CO, CO₂, and CH₄. The yield and selectivity of each gas product are used as the measurement standards, and are mainly calculated by the following formulas.

### Table 1. Quantitative Structure–Activity Correlations of Catalysts with H₂, CO, and Potential H₂ Yields

| Catalysts | Formula | Gas Yield | Coefficients | R² |
|-----------|---------|-----------|--------------|----|
| Different CZMRs | Y₁ = a·exp\[-\left(\frac{x}{b}\right)^c + d\] | H₂ yield | a = 26.07, b = 0.33, c = 0.43, d = 43.31 | 1.00 |
| Different nickel loadings | Y₂ = a + b·exp(c·x) | CO yield | a = 18.42, b = 0.25, c = 0.63, d = 20.12 | 1.00 |

**H₂ yield (%):**

\[
\text{H₂ yield} = \frac{\text{moles of H₂ actually produced}}{\text{theoretical maximum quantity of the produced H₂}} \times 100
\]

**CO(CO₂, CH₄) yield (%):**

\[
\text{CO(CO₂, CH₄) yield} = \frac{\text{moles of CO(CO₂, CH₄) in gas phase products}}{\text{moles of carbon in the acetic acid that actually reacted}} \times 100
\]

**H₂ selectivity (%):**

\[
\text{H₂ selectivity} = \frac{\text{moles of H₂ in gas phase products}}{\text{moles of H₂ + 2 × CH₄}} \times 100
\]

**CO selectivity (%):**

\[
\text{CO selectivity} = \frac{\text{moles of CO in gas phase products}}{\text{moles of carbon in gas phase products}} \times 100
\]

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