catalysts

Article

Promoting the Synthesis of Ethanol and Butanol by Salicylic Acid

Jinxin Zou, Lei Wang and Peijun Ji *

Department of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China; Jinxin_zhou@outlook.com (J.Z.); wanglei410@outlook.com (L.W.)
* Correspondence: jipj@mail.buct.edu.cn; Tel.: +86-010-6442-3254

Received: 3 September 2017; Accepted: 22 September 2017; Published: 1 October 2017

Abstract: Multiwalled carbon nanotubes (MWCNTs) were functionalized with salicylic acid (SA). The copper-cobalt catalyst was impregnated on the SA functionalized MWCNTs (SA-MWCNTs). The catalyst copper-cobalt/SA-MWCNTs was used to catalyze the synthesis of alcohols from synthesis gas. Salicylic acid can promote the synthesis of ethanol and butanol from synthesis gas, thus reducing the synthesis of methanol. This work demonstrated that salicylic acid not only can be used to functionalize carbon nanotubes, but also can enhance the production of ethanol and butanol from synthesis gas. On the other hand, the copper-cobalt catalyst supported on MWCNTs of 30 nm in diameter can synthesize more ethanol and butanol than supported on MWCNTs of 15 and 50 nm in diameter, indicating that the diameter of MWCNTs also has an effect on the synthesis of alcohols.

Keywords: alcohols; salicylic acid; multiwalled carbon nanotubes; synthesis gas

1. Introduction

The conversion of synthesis gas producing higher alcohols as fuel benefits sustainable development [1]. Investigation on catalysts with a higher selectivity and yield has been continuously carried out [2,3]. Researchers are focusing on heterogeneous catalysts rather than on homogeneous ones, as homogeneous catalysts are difficult to recycle. Metals including Re, Ru, Rh, Co, Cu, and Mo have been extensively used for preparing heterogeneous catalysts for the conversion of synthesis gas [4–8]. Re, Ru, and Rh are noble metals and are effective for catalyzing the synthesis of alcohols [4–7]. However, these metals are expensive. In contrast, Co, Cu, and Mo are much cheaper than the noble metals [8,9]. The non-noble metal based catalysts are being paid much attention [10–13]. For preparing a heterogeneous catalyst, one or several metals are deposited or impregnated on a support [13]. Particle sizes and the distribution of the particles are affected by catalyst supports.

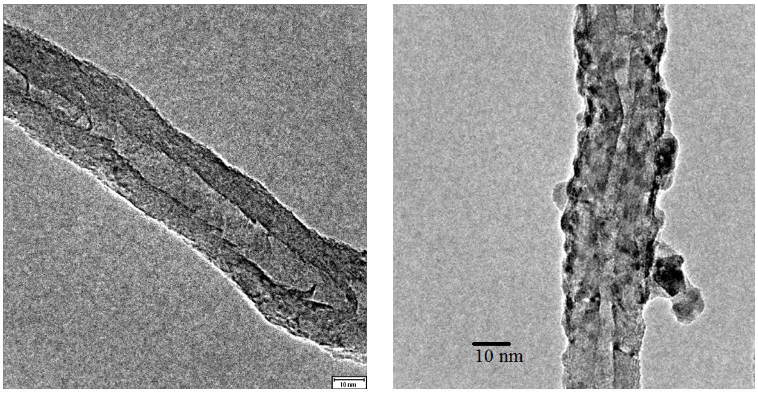
With a large surface area, good thermal conductivity, strong mechanical strength, and excellent electrical properties, carbon nanotubes (CNTs) have been investigated as supports for preparing Rh, Co, Cu, and Mo-based catalysts [5,14,15]. CO hydrogenation is facilitated by carbon nanotubes and the formation of ethanol is promoted on Rh/CNTs [16]. A relatively higher activity and space yield of higher alcohols can be achieved by the metals supported on carbon nanotubes. The high catalysis efficiency is ascribed to that the metals interacted with carbon nanotubes, on the other hand the metal particles were well distributed on the supports [14]. In addition, carbon nanotubes are capable of adsorbing hydrogen gas. This facilitates the interaction of the hydrogen with the metals.

In this work, multiwalled carbon nanotubes (MWCNTs) have been functionalized with salicylic acid (SA), then copper and cobalt have been deposited on the SA functionalized MWCNTs (SA-MWCNTs). The aim of this research is to investigate the effect of salicylic acid on the synthesis of higher alcohols from synthesis gas. The catalyst copper-cobalt/SA-MWCNTs have been used to catalyze the synthesis of higher alcohols, especially ethanol and butanol, from synthesis gas, as ethanol and butanol not only can be used as fuels but also can be used as feedstocks for producing chemicals [17,18]. The effect of the diameter of MWCNTs and salicylic acid on the conversion of syngas and the selectivity of higher alcohols, especially ethanol and butanol, have been investigated.

2. Results and Discussion

2.1. Characterization of the Copper-Cobalt/SA-MWCNTs Catalyst

For the characterization of the copper-cobalt/SA-MWCNTs catalyst, the MWCNTs with a diameter of about 30 nm were used. Figure 1a shows the transmission electron microscope (TEM) image of purified MWCNTs, which exhibited a smooth surface. In contrast, the catalyst copper-cobalt/SA-MWCNT exhibited nanosize particles on its surface (Figure 1b) due to the deposition of copper-cobalt particles. Figure 1b shows that the nanoparticles (copper-cobalt oxides) were well distributed on the surface of SA-MWCNT. The aromatic ring of salicylic acid can have a strong interaction with the wall of MWCNTs. Thus, salicylic acid can be used to functionalize MWCNTs though adsorption. The SA functionalized MWCNTs (SA-MWCNTs) possess functional hydroxyl and carboxyl groups. These groups can interact strongly with copper and cobalt. This facilitates the deposition of copper and cobalt on SA-MWCNTs.



(**a**) (**b**)

Figure 1. Transmission electron microscope (TEM) images for purified multiwalled carbon nanotubes (MWCNT) (**a**) and the catalyst copper-cobalt/SA-MWCNT (**b**).

The X-ray diffraction (XRD) pattern of the catalyst is shown in Figure 2. Supplementary Materials Figure S1 shows the XRD patterns for SA-MWCNTs and purified MWCNTs. In Figure 2, peak 1 is for MWCNTs, and the peaks indicated by 2, 3, and 4 correspond to crystalline structures of the oxidized metals. Using the JCPDS chemical spectra data bank [19], the peaks were recognized representing CuO, $Cu_xCo_{3-x}O4$, and Cu_2O, respectively. The XRD pattern indicates the interaction between cobalt and copper species in the catalyst. This is possibly ascribed to that copper and cobalt ions can interact with salicylic acid of SA-MWCNTs, and further interacted with each other.

The spectra of X-ray photoelectron spectroscopy (XPS) for the catalyst are presented in Figure 3a,b. Supplementary Materials Figure S2 shows the XPS spectra for SA-MWCNTs and purified MWCNTs. The parent peak in Figure 3 was deconvoluted into three peaks. Figure 3a shows the XPS spectra for the copper states. The two peaks at 933.3 and 934.6 eV are ascribed to Cu(I) and Cu(II) oxides [20], respectively. The peak at 943.2 eV is ascribed to the satellite peak for the Cu(II) oxide. Figure 3a demonstrates two oxidation states of Cu(I) and Cu(II) for copper in the catalyst. Figure 3b shows the spectra for different cobalt states. The two peaks at 780 and 781.5 eV are ascribed to Co(III) oxide and Co(II) oxide [21], respectively, and the peak at 787.4 eV is due to the satellite peak for the Co(II) oxide. The results demonstrate the two oxidation states of Co(II) and Co(III) for cobalt in the catalyst. Figure 3 further confirms the interaction of copper and cobalt after bring supported on SA-MWCNTs.

Figure 4 shows the temperature programmed reduction (TPR) profile for copper-cobalt/SA-MWCNTs. Supplementary Materials Figure S3 shows the TPR profile for SA-MWCNTs. In Figure 4, there are two prominent peaks at 278 and 363 °C. They are acribed to the reduction of Cu^{2+} to Cu. The right shoulder (450–636 °C) is ascribed to the reduction of Co^{2+} to Co.

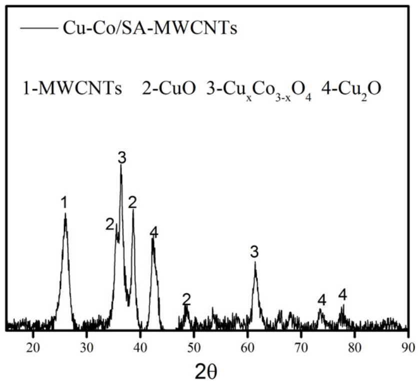


Figure 2. X-ray diffraction (XRD) pattern for the catalyst copper-cobalt/SA-MWCNTs.

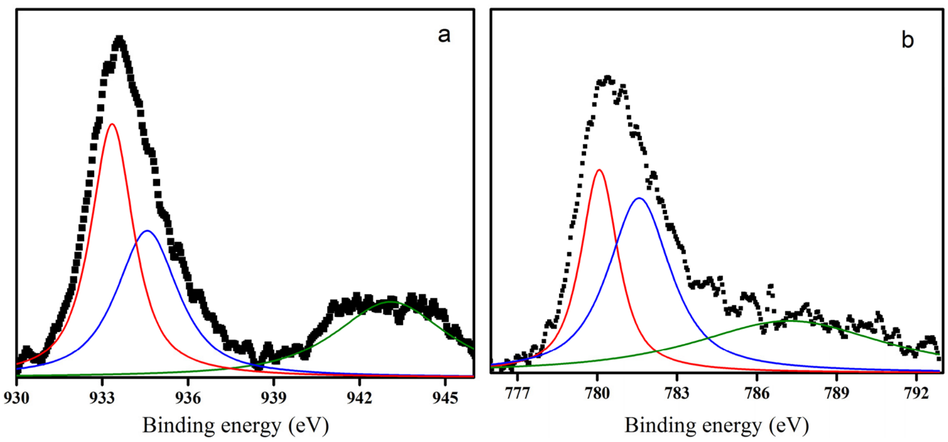


Figure 3. (**a**) XPS spectra of Cu 2p region of the catalyst; (**b**) XPS spectra of Co 2p region of the catalyst.

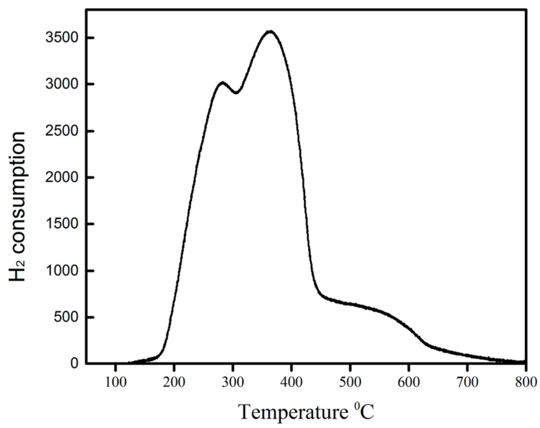


Figure 4. Temperature programmed reduction (TRP) profile for copper-cobalt/SA-MWCNTs.

2.2. Alcohol Synthesis from Syngas

Experimental results showed that both the purified MWCNTs and SA-MWCNTs cannot catalyze the reaction of synthesis of alcohols from syngas. That is no alcohols were produced when using the carbon nanotubes as catalysts. Prior to evaluating the catalyst copper-cobalt/SA-MWCNTs and studying the efffect of salicylic acid on the production of alcohols, the effect of purification of MWCNTs and diameter of MWCNTs were first investigated. MWCNTs were purified by refluxing in HNO_3. Copper-cobalt supported on the purified MWCNTs has exhibited a better conversion of syngas and selectivity of ethanol and butanol than the copper-cobalt supported on the non-purified MWCNTs (Figure 5). The result showed that for preparing copper-cobalt based catalyst, MWCNTs should be purified. The residues on non-purified carbon nanotubes are amorphous carbon [22]. Amorphous carbon on the surface of MWCNTs not only affects the interaction of SA with the wall of MWCNTs, but also affects the deposition of copper and cobalt. This is the reason that using non-purified MWCNTs has exhibited a lower alcohol production than using purified MWCNTs. The effect of the diameter of MWVNTs on the synthesis of alcohols was also investigated (Figure 6). Using the MWCNTs with a diameter of 30 nm, the conversion of syngas (Figure 6a) and selectivity for the alcohols of ethanol + butanol (Figure 6b) are larger than the MWCNTs with diameters of 15 nm and 50 nm, indicating that the MWCNTs of 30 nm in diameter are better as supports for preparing the copper-cobalt based catalyst. The diameter of carbon nanotubes can roughly reflect the surface area of carbon nanotubes. Possibly, the carbon nanotubes with a diameter of about 30 nm can provide an appropriate surface area. When investigating the effect of salicylic acid on the synthesis of alcohols, salicylic acid was added to the reaction solutions according to predetermined weight ratios. Figure 7 shows the effect of salicylic acid on the production of alcohols. With increasing the ratio of salicylic acid to MWCNTs, the conversion of syngas and the selectivity toward to ethanol and butanol are increased. The optimal ratio is 0.3, at which the syngas conversion and the selectivity toward ethanol and butanol have reached highest values.

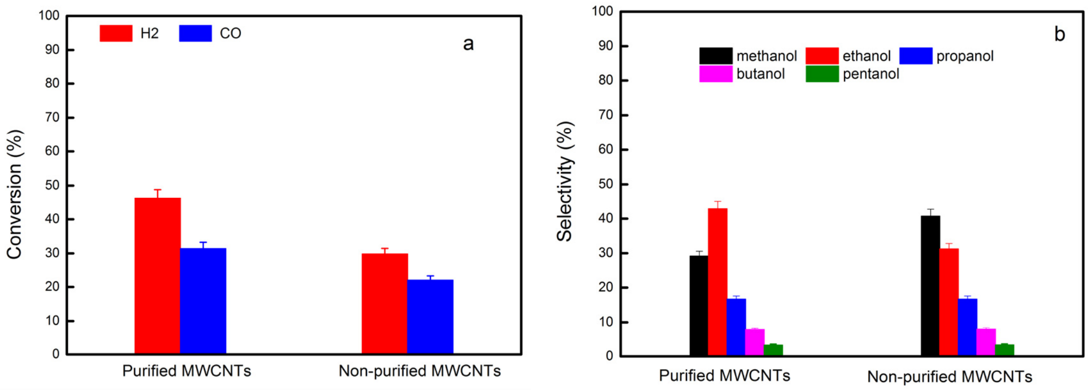


Figure 5. Effect of purification of MWCNTs on the synthesis of alcohols. Conversion of syngas (**a**) and Selectivity of alcohols (**b**).

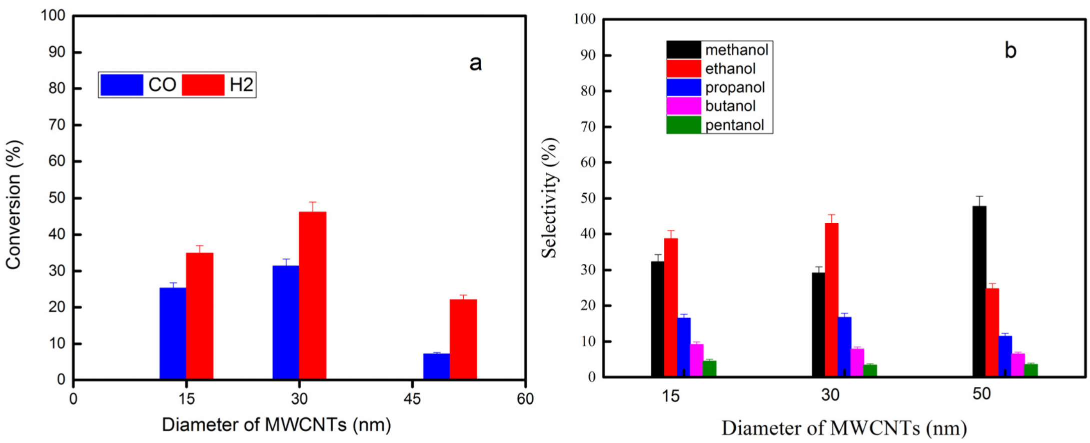


Figure 6. Effect of the diameter of MWCNTs on the syngas conversion (**a**) and alcohol selectivity (**b**).

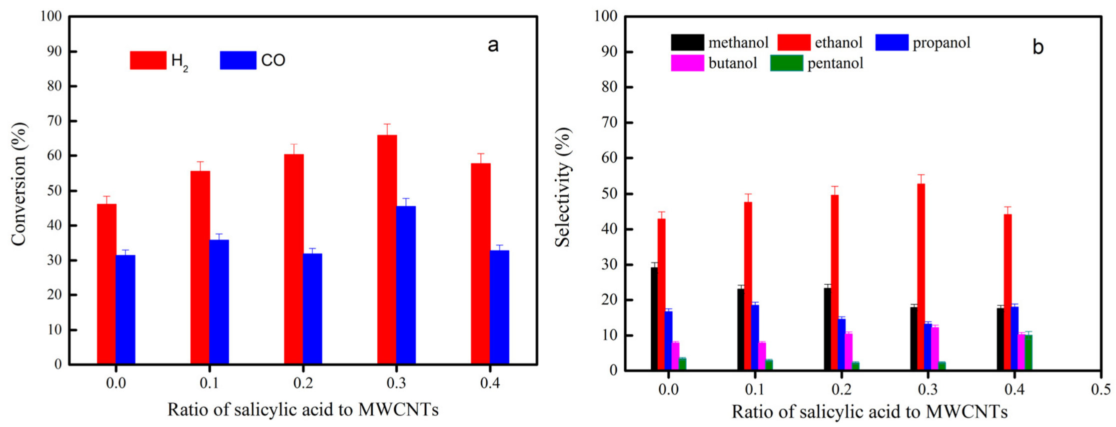


Figure 7. Effect of salicylic acid on the syngas conversion (**a**) and alcohol selectivity (**b**).

3. Experimental Section

3.1. Materials

Multiwalled carbon nanotubes (MWCNTs, diameters 15 ± 5 nm, 30 ± 10 nm, 50 ± 10 nm) were obtained from Nacen Nanotechnologies Inc. (Shenzhen, China). Salicylic acid (SA), ethanol, propanol, butanol, pentanol, $Cu(NO_3)_2$ $3H_2O$, and Co-$(NO_3)_2$ $6H_2O$ were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). All chemicals were of analytical reagent grade.

3.2. Catalyst Preparation

MWCNTs were refluxed in HNO_3 (2.5 M) at 70 °C for 10 h. Then, the MWCNTs suspensions were filtered by a 450 nm polycarbonate membrane. The purified MWCNTs were then mixed with the salicylic acid solutions with different concentrations. The mixtures were sonicated for 20 min. Then, salicylic acid functionalized MWCNTs (SA-MWCNTs) were filtered through a 450 nm polycarbonate membrane and rinsed with deionized water. The collected SA-MWCNTs were dried at 70 °C under vacuum.

The catalyst copper-cobalt/SA-MWCNTs was prepared as follows. 800 mg of SA-MWCNTs were dispersed in 200 mL of deionized water by sonication for 5 min. Then, the solution (115 mL) containing $Cu(NO_3)_2$ $3H_2O$ (10.2 mg/mL) and $Co(NO_3)_2$ $6H_2O$ (12.3 mg/mL), was added and sonicated for 3 min. After 50 min incubation, the mixture was dried at 50 °C under vacuum. The dried catalyst was calcined at 450 °C for 3 h by introducing nitrogen at a flow rate of 160 mL/min. The amounts of copper and cobalt deposited on MWCNTs-SA were determined using atomic absorption spectrometer (Model GGX-6). The concentrations of the metal ions in the stock solutions and in the residue solutions were measured. The difference between the concentrations was used to calculate the amount of copper and cobalt deposited on the support. The copper loading was finally determined to be 0.263 mg Cu/mg MWCNTs and that of cobalt was 0.271 mg Co/mg MWCNTs.

3.3. Catalyst Characterization

SA-MWCNTs and copper-cobalt/SA-MWCNTs were imaged by transmission electron microscopy (TEM) using a Hitachi H-800 system (Shanghai, China). Samples were first dispersed in ethanol by ultrasonication. Then the suspensions were dropped onto a carbon-coated copper grid. The X-ray diffraction (XRD) patterns of the catalysts were obtained with a diffractometer (Rigaku D/Max 2500 VBZ+/PC, Gu target at 35 kV, 30 mA) (Shanghai, China). The diffractograms were obtained by scanning at a rate of 2θ = 1°/min, the range was from 2θ = 5° to 2θ = 90°. TPD/R/O 1100 (Shanghai, China) was used to record temperature programmed reduction (TPR) spectra for the catalysts, using a gas mixture of 10% hydrogen in argon. The flow rate was controlled at 30 mL/min. The samples were heated up to 800 °C at a heating rate of 5 °C/min. A thermal conductivity detector was used to monitor the sample pretreatment, adsorption, and desorption. A Thermo VG ESCALAB250 X-ray photoelectron spectrometer (Beijing, China) was used to obtain X-ray photoelectron spectroscopy (XPS) spectra for the catalysts. The measurements were carried out at a pressure of 2×10^{-9} Pa using Mg Kα X-ray as the excitation source.

3.4. Alcohol Synthesis from Syngas

The reactions were carried out in a fixed bed microreactor with a length of 500 mm and 9 mm in diameter. A temperature controller was used to control the temperature of the microreactor. Introducing the gases H_2, CO, and N_2 at certain rates to the reactor was controlled by mass flow controllers. In all of the reactions, nitrogen was used as an internal standard gas. The copper-cobalt/SA-MWCNTs catalyst (1.5 g) was placed in the reactor bed. The reactor was heated up to 300 °C at a rate of 3 °C/min. The catalyst copper-cobalt/SA-MWCNTs was reduced in situ at 300 °C for 15 h, and the flow rate of H_2 was controlled at 50 mL/min. Then, synthesis gas (H_2/CO ratio of 1.0) with a flow rate of 92 mL/min was introduced. The reactor pressure was controlled at 5 MPa. The composition of effluent gas stream was determined by an online GC-2014C Shimadzu Gas Chromatograph (Beijing, China), which was equipped with a TCD detector and a Porapak Q column. The produced alcohols were analyzed off-line using a FID detector and a PEG-20 M capillary column.

4. Conclusions

Salicylic acid has been used to functionalize multiwalled carbon nanotubes. SA-MWCNTs were used as supports for preparing copper-cobalt based catalyst. The catalyst copper-cobalt/SA-MWCNTs was used to catalyze the synthesis of alcohols from synthesis gas. Salicylic acid can promote the synthesis of ethanol and butanol from synthesis gas, reducing the synthesis of methanol. For preparing the copper-cobalt based catalyst, purified MWCNTs are better than non-purified MWCNTs, and the diameter of MWCNTs also has an effect on the alcohol production. The copper-cobalt catalyst supported on MWCNTs of 30 nm in diameter can synthesize more ethanol and butanol than supported on MWCNTs of 15 and 50 nm in diameter, indicating that the diameter of MWCNTs also has an effect on the synthesis of alcohols. This work demonstrated that salicylic acid not only can be used to functionalize carbon nanotubes, but also can enhance the production of ethanol and butanol from synthesis gas.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/10/295/s1. Figure S1: XRD pattern for purified MWCNTs and SA-MWCNTs, Figure S2: XPS spectra for purified MWCNTs and SA-MWCNTs; Figure S3: TRP profile for SA-MWCNTs.

Acknowledgments: This work was supported by the National Science Foundation of China (21476023).

Author Contributions: Peijun Ji provided the idea and design for the study; Jinxin Zou and Lei Wang performed the experiments; Jinxin Zou drafted the manuscript; Peijun Ji revised it.

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

References

1. Xiong, H.; Jewell, L.L.; Coville, N.J. Shaped Carbons As Supports for the Catalytic Conversion of Syngas to Clean Fuels. *ACS Catal.* **2015**, *5*, 2640–2658. [CrossRef]
2. Yue, Y.; Ma, X.; Gong, J. An Alternative Synthetic Approach for Efficient Catalytic Conversion of Syngas to Ethanol. *Acc. Chem. Res.* **2014**, *47*, 1483–1492. [CrossRef] [PubMed]
3. Kim, T.W.; Kleitz, F.; Jun, J.W.; Chae, H.J.; Kim, C.U. Catalytic conversion of syngas to higher alcohols over mesoporous perovskite catalysts. *J. Ind. Eng. Chem.* **2017**, *51*, 196–205. [CrossRef]
4. Wang, J.; Liu, Z.; Zhang, R.; Wang, B. Ethanol Synthesis from Syngas on the Stepped Rh(211) Surface: Effect of Surface Structure and Composition. *J. Phys. Chem. C* **2014**, *118*, 22691–22701. [CrossRef]

5. Surisetty, V.R.; Dalai, A.K.; Kozinski, J. Effect of Rh Promoter on MWCNT Supported Alkali Modified MoS_2 Catalysts for Higher Alcohols Synthesis from CO Hydrogenation. *Appl. Catal. A* **2010**, *381*, 282–288. [CrossRef]
6. Lopez, L.; Velasco, J.; Montes, V.; Marinas, A.; Cabrera, S.; Boutonnet, M.; Järås, S. Synthesis of Ethanol from Syngas over Rh/MCM-41 Catalyst: Effect of Water on Product Selectivity. *Catalysts* **2015**, *5*, 1737–1755. [CrossRef]
7. Subramani, V.; Gangwal, S.K. A Review of Recent Literature to Search for an Efficient Catalytic Process for the Conversion of Syngas to Ethanol. *Energy Fuels* **2008**, *22*, 814–839. [CrossRef]
8. Zhao, L.; Li, W.; Zhou, J.; Mu, X.; Fang, K. One-step synthesis of Cu Co alloy/$Mn_2O_3Al_2O_3$ composites and their application in higher alcoholsynthesis from syngas. *Int. J. Hydrogen Energy* **2017**, *42*, 17414–17424. [CrossRef]
9. Gupta, M.; Smith, M.L.; Spivey, J.J. Heterogeneous Catalytic Conversion of Dry Syngas to Ethanol and Higher Alcohols on Cu-Based Catalysts. *ACS Catal.* **2011**, *1*, 641–656. [CrossRef]
10. Zuo, Z.J.; Wang, L.; Yu, L.M.; Han, P.D.; Huang, W. Experimental and Theoretical Studies of Ethanol Synthesis from Syngas over CuZnAl Catalysts without Other Promoters. *J. Phys. Chem. C* **2014**, *118*, 12890–12898. [CrossRef]
11. Yang, Q.; Cao, A.; Kang, N.; Ning, H.; Wang, J.; Liu, Z.T.; Liu, Y. Bimetallic Nano Cu–Co Based Catalyst for Direct Ethanol Synthesis from Syngas and Its Structure Variation with Reaction Time in Slurry Reactor. *Ind. Eng. Chem. Res.* **2017**, *56*, 2889–2898. [CrossRef]
12. Morrill, M.R.; Thao, N.T.; Shou, H.; Davis, R.J.; Barton, D.G.; Ferrari, D.; Agrawal, P.K.; Jones, K.W. Origins of Unusual Alcohol Selectivities over Mixed MgAl Oxide-Supported K/MoS_2 Catalysts for Higher Alcohol Synthesis from Syngas. *ACS Catal.* **2013**, *3*, 1665–1675. [CrossRef]
13. Hensley, J.E.; Lovestead, T.M.; Christensen, E.; Dutta, A.; Bruno, T.J.; McCormick, R. Compositional Analysis and Advanced Distillation Curve for Mixed Alcohols Produced via Syngas on a K-CoMoSx Catalyst. *Energy Fuels* **2013**, *27*, 3246–3260. [CrossRef]
14. Surisetty, V.R.; Dalai, A.K.; Kozinski, J. Synthesis of higher alcohols from synthesis gas over Co-promoted alkali-modified MoS_2 catalysts supported on MWCNTs. *Appl. Catal. A Gen.* **2010**, *385*, 153–162. [CrossRef]
15. Dong, X.; Liang, X.L.; Li, H.Y.; Lin, G.D.; Zhang, P.; Zhang, H.B. Preparation and characterization of carbon nanotube-promoted Co–Cu catalyst for higher alcohol synthesis from syngas. *Catal. Today* **2009**, *147*, 158–165. [CrossRef]
16. Sims, A.; Jeffers, M.; Talapatra, S.; Mondal, K.; Pokhrel, S.; Liang, L.; Zhang, X.; Elias, A.L.; Sumpter, B.G.; Meunier, V.; et al. Hydro-deoxygenation of CO on functionalized carbon nanotubes for liquid fuels production. *Carbon* **2017**, *121*, 274–284. [CrossRef]
17. Pomalaza, G.; Capron, M.; Ordomsky, V.; Dumeignil, F. Recent Breakthroughs in the Conversion of Ethanol to Butadiene. *Catalysts* **2016**, *6*, 203. [CrossRef]
18. Kim, M.; Park, J.; Kannapu, H.P.R.; Suh, Y.W. Cross-Aldol Condensation of Acetone and n-Butanol into Aliphatic Ketones over Supported Cu Catalysts on Ceria-Zirconia. *Catalysts* **2017**, *7*, 249. [CrossRef]
19. Eswaramoorthi, I.; Sundaramurthy, V.; Das, N.; Dalai, A.K.; Adjaye, J. Application of Multi-Walled Carbon Nanotubes as Efficient Support to Nimo Hydrotreating Catalyst. *Appl. Catal. A* **2008**, *339*, 187–195. [CrossRef]
20. Contarin, S.; Kevan, L. X-ray Photoelectron Spectroscopic Study of Copper-Exchanged X- and Y-Type Sodium Zeolites: Resolution of Two Cupric Ion Components and Dependence on Dehydration and X-Irradiation. *J. Phys. Chem.* **1986**, *90*, 1630–1632. [CrossRef]
21. Ernst, B.; Bensaddik, A.; Hilaire, L.; Chaumette, P.; Kiennemann, A. Study on a Cobalt Silica Catalyst during Reduction and Fischer-Tropsch Reaction: In Situ EXAFS Compared to XPS and XRD. *Catal. Today* **1998**, *39*, 329–341. [CrossRef]
22. Rinaldi, A.; Frank, B.; Su, D.S.; Hamid, S.B.A.; Schlögl, R. Facile Removal of Amorphous Carbon from Carbon Nanotubes by Sonication. *Chem. Mater.* **2011**, *23*, 926–928. [CrossRef]