

Optimization of Synthesis Gas to Methanol Conversion

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Abstract

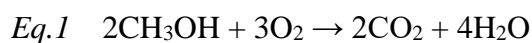
As global markets shift from petroleum usage to other fuel sources, methanol presents itself as a viable alternative. Methanol is a cleaner burning fuel than traditional hydrocarbons because it produces no particulates and significantly less carbon dioxide. A common way to make methanol is by the conversion of synthesis gas over a catalyst. Synthesis gas is a mixture of carbon monoxide and hydrogen commonly derived from anaerobic digestion of biogas from biomass or from dry-reforming of methane. This research utilizes the cleaner energy source of syngas to produce methanol in an optimized conversion process by varying parameters of reactor temperature conditions and catalyst particle size. Previous research has focused on surface area effects of the catalysts but fails to thoroughly study reactor conditions in conjunction with the catalyst. In this experimental design, a pressurized batch reactor was used to flow the syngas mixture over various copper catalysts supported on zinc oxide and gamma alumina at different operating temperatures. Two types of catalysts were synthesized by sonication: 1) a nanocatalyst and 2) a mixed oxide, and compared these against a commercial catalyst. These catalysts were characterized by X-ray diffraction and their particle size and surface morphology were imaged and measured by transmission electron microscopy and scanning electron microscopy respectively. The experimental runs in the batch reactor operated at three different temperatures of 220°C, 230°C, and 240°C for each catalyst totaling in nine experimental batch runs. Liquid samples were taken after each run and analyzed by gas chromatography. Based on these analyses, we calculated for each run the space time yield, the activation energy, and the percent conversion. Our results showed that the mixed oxide catalyst achieved the highest overall percent conversion of 36.3% at a reaction temperature of 240°C and required the lowest activation energy of 138.2 J/mol. The nanocatalyst and commercial catalyst achieved the next highest conversions of 22.6% and 18.9% respectively when reacting at 220°C but had higher respective activation energies of 197.1 J/mol and 158.0 J/mol. Overall, the mixed oxide catalyst exhibited a trend of higher percent conversion at higher reacting temperatures, while the nanocatalyst and commercial catalyst exhibited converse trends of higher percent conversions at lower reacting temperatures.

Keywords: Catalysis, Methanol Production, Metal Oxides

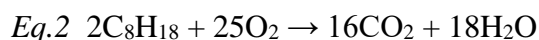
1. Introduction

With the rapidly declining reserves of remaining petroleum oil, there is a high demand for alternative fuel sources to satisfy increasing needs for the world's expanding population. China and India have recently decided to shift to "Methanol Economy" and this is helping renewed interest in methanol research to help switch the fuel source to methanol [1] [2].

One of the reasons these countries and many researchers are studying methanol as a replacement for traditional fuels is because methanol is a more environmentally friendly fuel.



In the combustion reaction 1, for every methanol molecule burned one CO_2 molecule is formed [3]. In comparison, octane is a popular fuel and when burned, as seen in Equation 2 below, 8 CO_2 molecules are produced when it is fully combusted.



Methanol creates less greenhouse gases when burned, and since there are no carbon to carbon bonds, there is no possibility for particulates to be formed [3]. Additionally, the equipment or vehicles that run on traditional fuels can be easily converted to run on methanol [4]. For these reasons, methanol is a great alternative to traditional fuels.

Unlike fuels such as octane, methanol is a light compound that can be easily produced from a mixture of CO and H_2 , also known as synthesis gas, instead of being produced by the petroleum refining process. Producing synthesis gas is a more environmentally friendly process than producing most of the common fuel types. Traditionally, synthesis gas is synthesized by dry reforming of methane. One group of researchers studied the formation of synthesis gas from the anaerobic digestion of biomass as an alternative process [5].

The process of forming methanol from synthesis gas has not been drastically altered since the 1960's. The commercial catalyst in use now is copper on a zinc oxide support (Cu/ZnO) that operates under reaction temperatures ranging from 240°C to 280°C [6]. There is a search for a better catalyst for a cheaper operation of the conversion of synthesis gas to methanol.

Smaller catalyst particle sizes tend to have the more surface area per unit weight, which is directly related to an increase in active sites. There is much research to be done for the synthesis gas to methanol conversion process using nanocatalysts at different operating temperatures. For this process many different catalysts have been studied for the effect of their size on activity or the effect of changing the temperature but these parameters have not been studied simultaneously for a single catalyst. We propose utilizing the most common catalyst, Cu/ZnO , for this reaction and altering both of these parameters for true optimization of the process.

As mentioned before, the process of methanol synthesis from syngas is not new. Developed in the 1920's the process has not changed much, but with a more active catalyst that has the ability to reduce the time and energy input to drive the reaction forward to increase the per pass conversion to more than 20%. The specific reaction mechanism and how the carbon monoxide and hydrogen interact on different catalytic surfaces are only being able to be understood in recent years due to advances in spectroscopic techniques. Many recent papers in which methanol was produced from carbon monoxide include the secondary dimethyl ether (DME) synthesis reaction [7]. The focus on methanol as a product has recently been done using CO_2 as a reactant [7]. The traditional catalysts have problems with using CO_2 instead of CO due to water

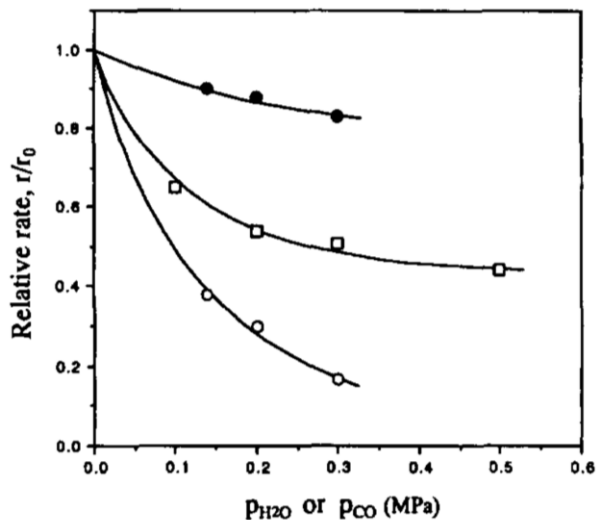


Fig 1. Inhibitory effects of H₂O (O, O) and CO (□) on methanol synthesis (O, □) and CO formation (●) from the CO₂ and H₂ over a Cu/ZnO/ZrO₂ catalyst. Reaction conditions: temperature = 523 K, SV = 1.8 x 10⁵ (1/h), pressure of CO₂ + 3H₂ = 5 MPa for H₂O addition and 3.2 MPa for CO₂ addition. r₀ and r are the rates of methanol synthesis or CO formation without and with the addition of H₂O or CO to the feed. O: methanol synthesis with the addition of H₂O to the feed. O: CO formation with the addition of H₂O to the feed. □: methanol synthesis with the addition of CO to the feed. [7]

formation via the CO₂ route, which has a detrimental effect on the catalyst. Saito et al quantified this detrimental effect [7]:

Liang et al [8] were able, through trial and error, to discover the optimal ratio of palladium onto zinc oxide of 1:10 onto the carbon nanotube support, which gives a good baseline for other metallic loading onto these materials. Grobmann et al. [9] conducted a similar experiment with Cu loaded onto ZnO on carbon nanotubes, and this catalyst, while showing excellent activity, was not very stable.

Karelovic and Ruiz [10] conducted an experiment that provides the largest basis for our further testing which measured reaction rates of methanol conversion based on Cu

particle size loaded onto ZnO. They

Table 1 Copper loadings, surface area and size of crystallites obtained from XRD data. Data for catalysts recovered after the catalytic test

Sample	Cu loading ^a (wt.%)	BET surface area (m ² g ⁻¹)	Pore volume BJH (cm ³ g ⁻¹)	XRD average crystal size (nm)	
				Cu(111)	ZnO(110)
ZnO	0	30.0	0.21	—	18
Cu(0.5)ZnO	0.5	24.4	0.15	n.d.	19
Cu(1)ZnO	1.05	22.2	0.16	n.d.	18
Cu(3)ZnO	2.76	17.6	0.12	25	22
Cu(5)ZnO	4.74	13.6	0.11	28	23
Cu(8)ZnO	7.54	9.8	0.06	35	26
Cu(15)ZnO	13.79	6.7	0.04	35	31

^a Obtained from inductive couple plasma (ICP). n.d.: not detected.

Fig. 2. Copper loadings, surface area and size of crystallites obtained from XRD data. Data for catalysts recovered after the catalytic test. [10]

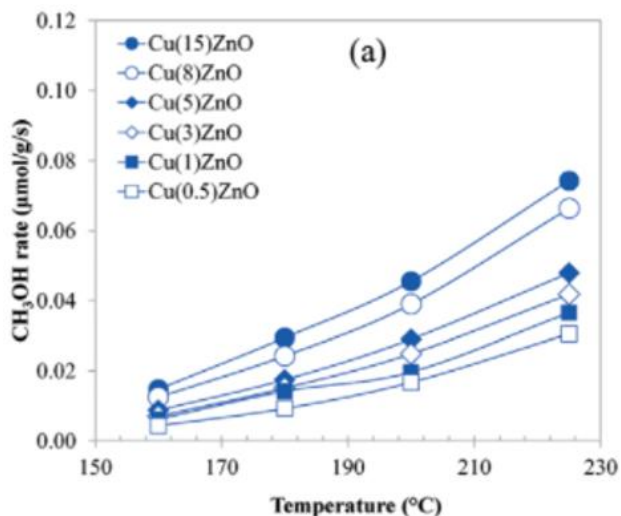


Fig. 3. Methanol conversion rates of Cu/ZnO nanocatalysts based on Cu % weight. [10]

synthesized several different catalysts with the following Cu weight percentages and characterizations by BET and XRD.

The same authors [10] found the following methanol conversion rates (Figure 3).

To summarize, the results show the highest methanol conversion rate for a Cu/ZnO nanocatalyst with a 15% weight Cu loading, the particle size was approximately 30 nm. However, their graph cuts off at

230°C for the reaction temperature during methanol conversion [10]. Our experiment is novel in that it investigates the methanol conversion and thus activity of slightly different catalysts at these higher temperatures where the conversion rates were highest. From the graphs in Karelavic and Ruiz's experiment, it is unclear what the following behavior of the conversion rate graph is going to be; it could continue exponentially, approach an asymptote, or peak then decline. We expect a peak then decline because temperatures that are too high would cause catalyst sintering and thus deactivation. Therefore, our experiment will verify this optimum operating temperature experimentally while also comparing the difference between a synthesized nanocatalyst, a mixed oxide catalyst, and a commercially available catalyst. It is also important to note that the aforementioned experiment synthesized their catalysts using the citrate method which is a form of wet chemistry synthesis [10]. Our synthetic methods will also differ from theirs since we used sonolysis technique that provides a much faster catalytic synthesis.

2. Experimental Section

2.1 Materials

Cu/ZnO supported on gamma-Al₂O₃ industrial catalyst was purchased from Haldor Topsoe. n-Hexadecane (95%) was purchased from Alfa Aesar. Copper (II) oxide nanopowder (<50 nm particle size) was purchased from Sigma Aldrich. Zinc oxide powder (<5 micrometer 99.9%) was purchased from Sigma Aldrich. Methanol (99.8%) was purchased from Sigma Aldrich. Polyethylene glycol 400 was purchased from Sigma Aldrich. Pressurized CO, H₂, He, and N₂ gas tanks were purchased from Airgas.

2.2 Experimental Methods

2.2.1 Catalyst Preparation

To prepare the industrial catalyst for

use in the batch reactor, pellets of the Haldor Topsoe Cu/ZnO/gamma-Al₂O₃ catalyst were placed into a mortar and pestle and ground down to a powder. The powder was then placed in an oven at 100°C to dry before being placed in the batch reactor.

The nanocatalyst was prepared by taking 3.0183 g of the aforementioned ground Cu/ZnO/gamma-Al₂O₃ catalyst with 80 mL of hexadecane and placing them into a Misonix Liquid Processor Sonicator 3000. The sonicator was purged with N₂ gas for 15 minutes to ensure that there was no oxygen present and then the sonicator was turned on. The solution was kept cool using a Thermo Scientific Neslab Merlin M33 chiller set to 20°C. Measurements of temperature and sonicator power were made every 15 min for over four hours. After the sonication was complete, the catalyst was separated from the hexadecane by centrifuge, washed with hexanes, and then centrifuged again to rinse away the hexanes. The sonicated catalyst was then placed in the oven at 100°C for at least 24 hours to dry before being placed in the batch reactor.

To prepare the mixed oxide catalyst, 3.97 g of ZnO and 0.047 g of Cu(II)O (1% by weight) were added with 90 mL of hexadecane to the sonicator. The sonicator was purged with N₂ gas for 15 minutes and then the sonicator was turned on. The solution was kept cool using the chiller set to 20°C. Measurements of temperature and power were taken every 15 min for four hours. After the sonication was complete, the hexadecane was removed and the catalyst dried in the same manner as before.

2.2.2 Parr Batch Reactor

A Parr model 4575 batch reactor with a 300 mL pressure vessel was used to conduct all reactions. The reactor was connected to and controlled by a Parr 4848 process controller. 0.6756 g of each catalyst and 60 mL of polyethylene glycol were added into

the batch reactor, which was then sealed and purged with nitrogen gas. 100 psi CO and 200 psi H₂ were added to the reaction vessel and the reactor was heated to the operating temperature. Internal temperature, internal pressure, and jacket temperature were all recorded every 15 minutes. Each reaction was run at the specified temperature for three hours, then the heating jacket was turned off, and the system was allowed to cool to room temperature. The final pressure was noted once the system had cooled, and liquid samples were taken for analysis.

2.3 Analytical Methods

2.3.1. Gas Chromatography (GC)

For Gas Chromatography, a Gow-Mac gas chromatograph series 580 was used. Experiments were run using helium as the carrier at a 24 ml/hr gas flow rate (measured with ProFLOW 6000 from Restek). The GC additionally used chromosorb 101 packing material. And the GC was set as follows: column temperatures: 150°C; detector temperature: 190°C; current: 200mA. To analyze the results, Clarity PC Chromatography software was used to collect the data for 10 min. Each set of data was compared to a standard of methanol that was injected under the same operating conditions

2.3.2. X-ray Diffraction (XRD)

X-ray Diffraction (PXRD) testing of the catalyst powder was carried out using a Rigaku Ultima IV diffractometer (Cu K α ; λ = 1.5405 Å). Additionally, a D/teX ultra high-speed 1D position sensitive detector was used.- Our catalysts were dried in an oven at 100°C before being packed and prepped for XRD.

2.3.3. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was carried out using a LEO-1550 Gemini microscope.

2.3.4. Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) was performed using the JEOL JEM 1400 microscope. It utilizes an acceleration voltage of 40-120 kV with a magnification of x5000-2,000,000/x120-4,000. Catalysts were suspended in a solution of hexadecane and mixed by sonic bath prior to TEM. Particle size was found using Image-J software and averaged across all images for each catalyst.

2.3.5. Energy Dispersive X-Ray Spectroscopy

Energy-Dispersive X-Ray Spectroscopy (EDS) was jointly carried out under scanning electron microscopy.

3. Results and Discussion

3.1 Catalyst Characterization

a. X-ray Diffraction (XRD):

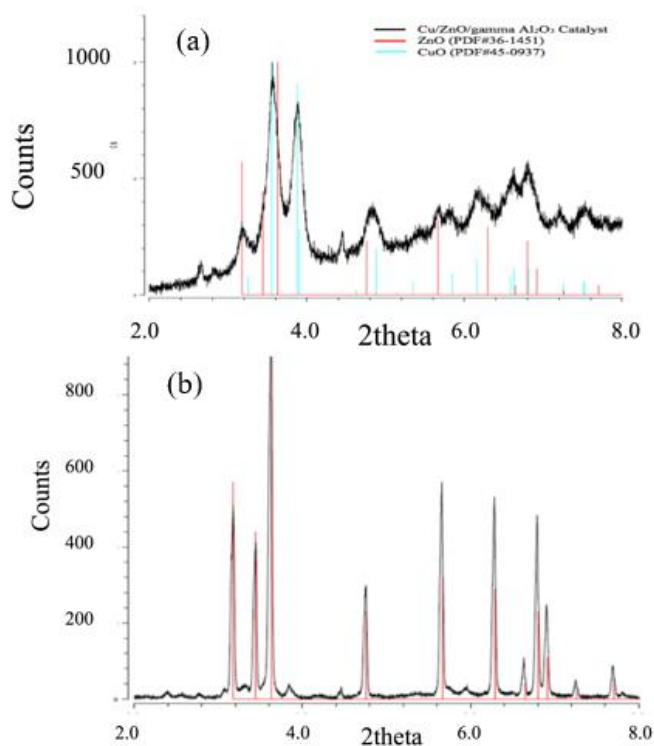


Fig. 4. XRD spectra of catalysts tested for methanol synthesis. (a) Nanocatalyst Cu/ZnO/gamma-Al₂O₃. (b) Mixed Oxide Catalyst: CuO/ZnO

The XRD data compares our two synthesized catalysts, which we expected to have a similar interference pattern and crystallinity in the nanoparticle range. The nanocatalyst showed similar peaks for both ZnO and CuO standards with broader peaks, indicating nano-sized crystallinity. However, the mixed oxide catalyst showed a high crystallinity with sharp peaks matching the ZnO standard and no presence of CuO.

b. Energy Dispersive X-ray Spectroscopy (EDS):

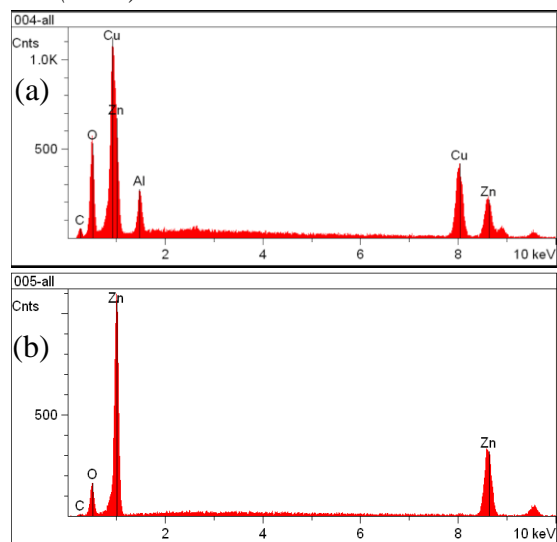


Fig. 5. EDS characterization of all three catalysts. (a) Nanocatalyst Cu/ZnO/gamma-Al₂O₃. (b) Mixed Oxide Catalyst: CuO/ZnO.

To further investigate the presence of CuO in the mixed oxide catalyst, we conducted EDS. The nanocatalyst in Fig. 5a has well-defined Cu, Zn, Al, and O peaks whereas the mixed oxide catalyst in Fig. 5b only defines Zn and O peaks. We attribute the Al in the nanocatalyst to the gamma-alumina support and did not expect this in the mixed oxide data. However, this confirms the lack of Cu or CuO in the mixed oxide catalyst. It is possible that this would not appear in either

XRD or EDS testing if the Cu did not attach to ZnO during the sonication process. It is also possible that CuO may have been present in such a low amount from the 1% weight addition that it did not manifest itself on either spectrum. This occurred for Karelavic and Ruiz's study when they used low weight percents of 0.5% and 1% of Cu on ZnO [10].

c. Scanning Electron Microscopy (SEM):

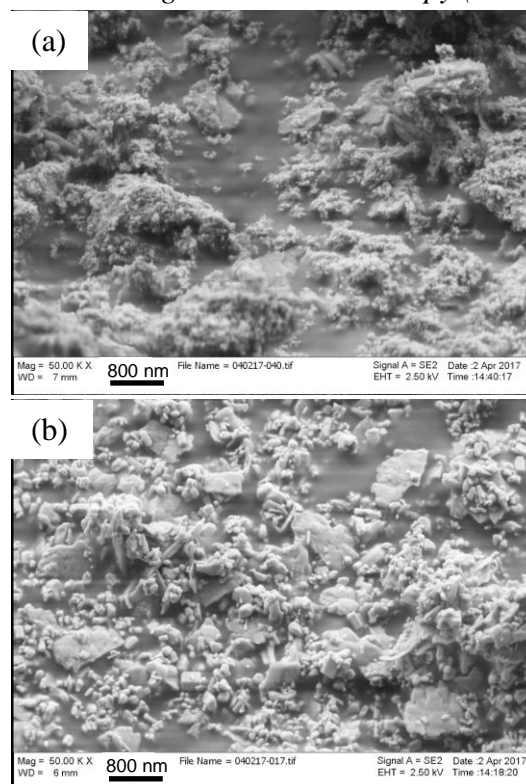


Fig. 6. SEM images of catalysts. (a) Nanocatalyst Cu/ZnO/gamma-Al₂O₃. (b) Mixed Oxide Catalyst: CuO/ZnO.

Since the EDS tests were coupled with SEM images, we were also able to view our catalysts' surface morphology. The images in Fig. 6 show that the mixed oxide catalyst had more defined particles than the nanocatalyst. There are clear, three-dimensional agglomerations present in the images in addition to singular particles dispersed throughout.

d. Transmission Electron Microscopy (TEM):

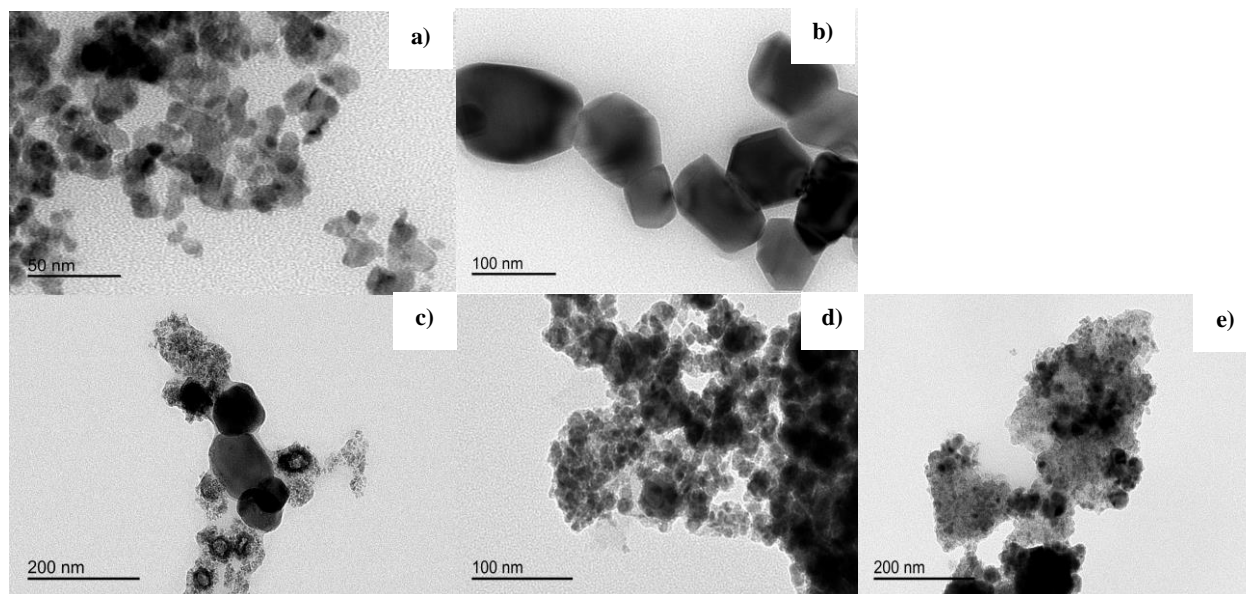


Fig. 7. TEM images of catalysts and corresponding average particle size. From left to right: (a) Nanocatalyst Cu/ZnO/ γ -Al₂O₃ (b) Mixed Oxide Catalyst: CuO/ZnO (c) Quenched Nanocatalyst Cu/ZnO/ γ -Al₂O₃ (d) Quenched Mixed Oxide Catalyst (e) Quenched Commercial Catalyst

Table 1. Average catalyst particle size

	Pre Batch, nm	Post 240°C, nm	Post 230°C, nm	Post 220°C, nm
Commercial	[data not available]	Agglomeration	Agglomeration	14.7
Nano-catalyst	12.0	Agglomeration	Agglomeration	Agglomeration
Mixed Oxide	52.7	48.8	63.9	75.2

The mixed oxide catalyst was the only catalyst to not agglomerate after being subjected to the reaction conditions within the batch reactor. The general trend for this catalyst was that a smaller particle size was correlated with a higher reaction temperature. While the SEM images showed agglomerations present prior to the catalysts undergoing reaction conditions, the TEM images still yielded some singular particles that were averaged to calculate the sizes in the chart. However, in the portions labeled “Agglomeration” there were no singular particles present, making measuring particle size impossible. This meant we could not determine whether sonication affected our nanocatalyst enough to significantly change particle size. In Fig. 7d, e, and f, the images are from the post 240°C batch runs for each quenched catalyst.

Table 2. Calculated kinetic results from batch data

Catalyst and Reaction Temperature	MeOH Formed, mol	Rate, mol/hr	Space Time Yield, kg MeOH / kg catalyst / hr	Conversion, %
Commercial catalyst 240°C	6.4	2.1	101.2	7.7
Commercial catalyst 230°C	5.3	1.8	83.8	6.3
Commercial catalyst 220°C	15.6	5.2	246.6	18.9
Nanocatalyst 240°C	3.3	1.1	52.8	4.0
Nanocatalyst 230°C	9.2	3.1	145.4	11.0
Nanocatalyst 220°C	18.9	6.3	298.8	22.6
Mixed oxide catalyst 240°C	30.3	10.1	479.0	36.3
Mixed oxide catalyst 230°C	8.3	2.8	131.2	9.9
Mixed oxide catalyst 220°C	8.9	3.0	140.7	10.7

3.2. Conversion Kinetics

The activation energies for the nanocatalyst, commercial catalyst, and mixed oxide catalyst were 197.1 J/mol, 158.0 J/mol, and 138.2 J/mol respectively for each reaction temperature. These were calculated using the Arrhenius equation and finding the slope of $\ln(k)$ vs. $1/T$ which gives E_A/R . This was then multiplied by R to give the activation energy for each catalyst throughout the three different reaction temperatures. As indicated in the table above the mixed oxide catalyst at a reaction temperature of 240°C showed the highest percent conversion to methanol of 36.3%. These represent the optimized reaction conditions for highest conversion and lowest initial energy input.

In terms of percent conversion, the next best catalyst and reaction temperature are the nanocatalyst at 220°C. However, the

SEM and TEM data showed large agglomerations for this, which most likely contributed to inhibited catalytic activity, and the main way this was overcome was by the large activation energy of 197.1 J/mol.

The catalyst with the overall lowest conversion was the nanocatalyst. According to the Table 1, its particle size was 12 nm which is significantly smaller than the mixed oxide's size of 52.7 nm. Typically smaller particle sizes for catalysts yield higher activity due to higher surface area exposed during the reaction. However, our results contradict this and show that depending on the reaction conditions coupled with each catalyst, sometimes a larger particle size is favored for overall higher reaction efficiency. It is possible that the large agglomeration of the nanocatalyst could be due to its uniquely small particle size, thus inhibiting its catalytic activity.

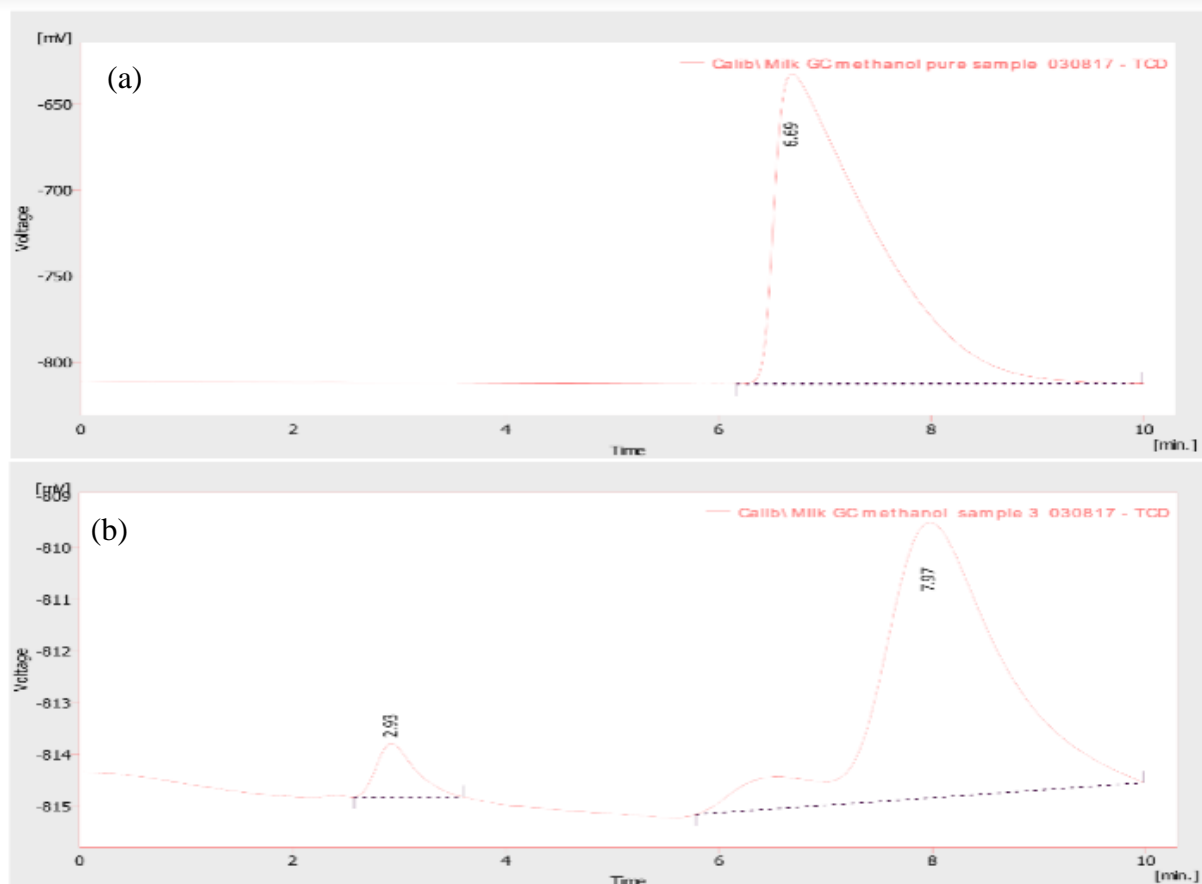


Fig. 8 Gas Chromatography Data; a) Baseline methanol peak. b) Peaks for Nanocatalyst Post-220°C.

3.3 Product Characterization

a. Gas Chromatography

Using the GC methods described above, pure methanol was found to have a retention time of 6-8 min as shown in Fig. 8.

For all of our liquid samples, we observed peaks at similar retention times that matched for a reference methanol sample. These data confirmed that we successfully produced methanol in all of our experimental batch runs. The small peak between 2 and 4 minutes was observed on most samples, which we attribute to unreacted syngas remaining in the PEG liquid.

4. Conclusions

After thorough experimentation using SEM, EDS, GC, XRD, and TEM for analysis

and characterization of multiple catalysts for methanol synthesis from syngas, we conclude that the mixed oxide catalyst is most efficient of all tested when coupled with a reaction temperature of 240°C. This combination of parameters yielded the fastest conversion and the highest percent conversion of methanol with the lowest activation energy. The lack of particle agglomeration as indicated by TEM is likely a contributing factor to the success of this material. This catalyst, like the others, was tested at 220 °C, 230 °C, and 240 °C. While the best-performing variation was mixed oxide catalyst at 240 °C, the next best was the nanocatalyst at 220°C indicating that the synthesis of methanol from syngas is a highly temperature-dependent reaction and varies

depending on catalyst. At 240 °C, the mixed oxide catalyst exhibited a 36.3% conversion and formed 30.3 mol of methanol at 10.1 mol/hr. Since the general temperature dependency trend showed that the commercial catalyst and nanocatalyst had poorer conversion at higher temperatures, we believe their optimal operating temperature was the lowest in our study of 220°C. This may be due to increased agglomeration at higher temperatures, particularly with the large gamma-alumina supports. The mixed oxide catalyst showed the opposite trend of increased conversion at higher temperatures, which is why further research is necessary to identify its optimal reaction temperature, which may in fact be even higher than 240°C. Further experiments should study other methods of catalyst synthesis exploring our sonication technique as well as continue to look into methods for preventing agglomeration. It would also be beneficial to continue to study these catalysts in broader reaction temperature ranges and other reactor types such as continuous or larger scale.

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catalyst for hydrogenation of CO₂ to