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Electrocatalysts for direct methanol fuel cells to demonstrate China’s renewable energy renewable portfolio standards within the framework of the 13th five-year plan

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ABSTRACT

A unified treatment of the renewable portfolio standards is given concerning direct methanol fuel. The current mechanism of electrocatalysis of methanol oxidation on platinum and non-platinum-containing alloys is summarized for the systematic improvement of the rate of electro-oxidation of methanol are discussed. Policy realignment under the five-year plan is discussed in length to demonstrate how policy, markets, and engineering designs contribute towards the development of model direct methanol fuel cells operational enhancement, and factors that affect critical performance parameters for commercial exploitation are summarized for catalytic formulations and cell design within the context of why this investment in technology, education, and finances is required within the global context of sustainable energy and energy independence as exposed by thirteenth the five-year plan. The prolog focuses on the way, whereas the section on methanol fuel cells on the how and the postlog on what is expected post-COVID-19 era in science and technology as China pivots to a post-fossil fuel economy.

China’s industrial growth has been through internal market reforms and supplies side economics from the Chinese markets for fossil fuels except for petroleum. The latest renewable portfolio standards adopted have common elements as adopted from North American and the United Kingdom in terms of adaptation of obligation in terms of renewable portfolio standards as well as a realization that the necessity for renewables standards for the thirteen five year plan (from 2016 to 2020) need to less rigorously implemented due to performance targets that were met during the eleventh (06–10) and twelfth five-year plans (11–15) in terms of utilization of small coal-ire power plants, development of newer standards, led to an improvement of energy efficiency of 15 %, reduction of SOx/NOx by an average of 90 % and PM2.5 by 96 % over the last two five-year plans.

The current phase of the plan has a focus on energy generation from coal and a slowing down of renewables or Renewable energy curtailment of approximately 400 T Wh renewables including 300 T Wh of non-hydro power, principally from Guangdong, and Jiangsu for transfer of hydropower and Zhejiang, Tianjin, Henan for non-hydro power transfer with Beijing and Shanghai playing important roles in renewables energy curtailment and realignment using an integrated approach to optimize each provinces energy portfolio. The realignment of the renewable energy portfolio indicates that the newly installed capacity in Sichuan, Yunnan, Inner Mongolia, and Zhejiang will account for less than 20 % of the current renewable energy portfolio but with the NOx SOx and PM2.5 savings already accrued.

The catalytic reduction of carbon dioxide to methanol (70 / 110 million metric tons from all sources in 2019 for China/world) is one technological approach to reduce global carbon dioxide emissions and suggests that catalytic methanol synthesis by CO2 hydrogenation may be a plausible approach, even if it is more expensive economically than methanol synthesis by the syngas approach. This is because the CO2 emissions of the synthesis are lower than other synthesis methodologies. The Chinese government has placed a premium on cleaner air and

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† In loving memory to Mohammed Bashir and Peter J. Derrick

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water and may view such an approach as solving the dual issues of fuel substitution and reduction of CO$_2$. Thus, the coupling of hydrogen generation from sustainable energies sources (Solar 175 / 509 GW) or wind (211/591.5 GW in 2019) may be an attractive approach, as this requires slightly less water than coal gasification. Due to the thermodynamic requirement of lower operating pressure and higher operating pressure, currently, there is no single operational approach, although some practice approaches (220 °C at 48 atm using copper) and zinc oxide/alumina are suggested for optimal performance.

Fig. 1. A: China Energy Production by Type and total consumption. (Source BP 2019 Statistical Review of World Energy data). B: Global carbon dioxide (CO$_2$) emissions (in kilotons) related to heat and energy production and amount of coal used by the energy sector in China that accounts for between 38–45 % of all coal consumed in the production of electricity. (Source: Statistics of China Power Industry, CEC, National Bureau of Statistics of China, NBSC; BP 2019 Statistical Review of World Energy for CO$_2$ emission data; [201]; and [202]). C: Summary of energy production every semi-decade from 1995 in China including exports. (Source: IEA, 2020). D: Diesel and gasoline consumption in China. (Source: 2019 BP Statistical Review of World Energy). E: Price of Brent Crude Oil ($/Barrell) and Asian Marker Coal ($/ton). Note 1 Ton of Coal Equivalent to Barrels of Oil Equivalent = 4.8: (Source: BP 2019 Statistical Review of World Energy). F: China Investment in renewable energy portfolio as outlined in the latest five-year plan in terms of Yuan investment (left) and percent investment (right). (Source: Globaltimes.CN; and [204]).
1. Introduction

The chief aim of the State Council through the issuance of the five-year plans was to meet current challenges [1], from positioning the republic to be a regional counterweight to Soviet Russia [2] to an international global economic superpower [3] can be seen through measurement of certain key performance indicators, chiefly amongst them was power generation [4], as it was recognized early on that independence from outside agencies necessitated sufficient industrial, mechanization which in turn required sufficient generation of electrical power [5]. As the five-year benchmarks were met, new challenges were perceived, and the five-year plans modified to reflect the current realities on the ground [6].

Policy formulations particularly in the energy sector are complex and vary across geographic locations and are spatiotemporal [7]. Recent policy integration has been both strategic in terms of economic resources but also took account of public welfare goods, materials allocation, and degree of environmental protection from key industrial sectors [8]. Therefore, to plan a country or region’s energy problems, the policy should be multidimensional and include a comprehensive evaluation efficiently and effectively from all stakeholders. Most international studies on China’s energy problems focus on country-to-country comparisons, but there are significant regional spatial differences in China [9]. Provinces differ significantly in resource endowment, energy structure, per capita gross domestic productions (GDP), production structure, and consumption pattern [10]. Therefore, current policies include an element of subsidiarity with a common matrix but varying paths to accomplish the national goals. Energy independence can be seen in Fig. 1A, where the total energy production was approximately 90% of need with an emphasis on renewables from 2006, which demonstrated that China was a global power in terms of energy production from fossil fuels because of its carbon dioxide (CO$_2$) [11]. China accounted for 9.23 gigatons, which is approximately 25% of the world total emissions in 2017 emissions mirrored global emissions (Fig. 1B, [12]), with the share of coal for energy utilized by the energy sector in China being constant from approximately 38–45% suggesting areas of improvements in terms of efficiency [13]. Of the 12,000 TW*h of electricity generation [14], approximately 50% was derived from coal and 8400 TW*h was consumed by secondary industries (4.5 MW/h per capita for commercial and residential versus 15 MW/h in the United States), suggesting a degree of under-capacity in these sectors and an overreliance on secondary industries, [15]. These figures also suggest that the continued production of electricity from coal is unsustainable, as exploitable mines become exhausted but also will affect the country’s import and export balance, as well as the environment (Lin, and Liu, 2010). China imports Oil and does not export energy (Fig. 1C).

From Fig. 1C, it can also be seen that the energy sector utilized a significant amount of generated energy up to 2012 [16]. when the economy shifted to a more digital or service type economy due to a slowdown in diesel consumption relative to gasoline consumption (Fig. 1D) [17]. This slowdown was in part due to the cost of coal extraction, which mirrors oil production costs suggesting that coal extraction for outer laying provinces whilst feasible was expensive to justify (Fig. 1E) [18]. This new policy change is reflected in the current five-year plan with a significant investment in renewables energy, as most of the cheap extractable coal in China has already been mined [19].

This policy shift towards renewables can be seen by an analysis of the current renewable energy investment outlined in the current (thirteen five-year plan) in renewables energy including wind, solar, biomass, geothermal, as well as nuclear and hydroelectric [20,21]. The new investment plan is also integrated with renewable energy consumption obligation weight factors, whereby electricity consuming entities purchase electricity derived from renewable energy sources [22]. Enterprises can purchase from two general brackets, renewable non-hydro or hydro by meeting the obligation weight or exceeding it, although they cannot meet it by swapping hydro for non-hydro, or through the purchase of the renewable energy green certificate [23]. These obligation weight parameters are set by the State Council and administered at the provincial level via the energy administrative departments and monitoring and evaluation by the state using the obligation burden estimated by the provincial administration region [24].

The advantage of the prescribed approach is that it enables the grid utilities to integrate the renewable energy consumption obligation as part of the marketization process, where energy needs are met via a mix of renewable energy sources [25]. The utilities can also act as a coordinator with local consumers and power exchange centers for on-time transfer of electricity derived from renewable energy sources [23].

2. China’s energy national conditions

2.1. Population and economic base

The above investment plan is based on the State Council assessment that, the population and economic conditions of various regions on the Chinese mainland in 2019 show that the Chinese economy is still in a sound financial position with project growth [26]. The condition of various regions in the mainland related to methanol is illustrated in Fig. 2A as well as important demographics in Table 1a. Although a generalization, the population of china is steady at around 1.4 billion which requires food and energy. The energy in terms of electricity and as liquid fuel for cars. This has resulted in large increases of carbon dioxide (CO$_2$), particulate matter (PM), and sulfur oxides (SO$_2$) being released into the environment. One solution is to convert CO$_2$ directly to methanol and use methanol as a fuel in methanol fuel cells, as a blend with gasoline or as a precursor to generating other synthetic materials utilizing CO$_2$ and H$_2$. The case for which this should be considered will briefly be made, followed by a policy rationale of current and future policies as they’re elated to energy and the environment and we will conclude with an extensive analysis of methanol hydrogenation and the catalyst and technologies utilized.

According to the above figure, the economic growth rate in various regions of China is maintained at 3–8.1%, the strategic emerging industries are maintained at 2.3–14.9%, and the natural population growth rate is between −1.8 and 12.3%. The growth rate and range span not only show that China’s energy problems cannot be viewed centrally but at the provincial level [27,28,29]. This suggests the methanol-based economy might assist China with the twin goals of energy independence and the lowering of carbon dioxide emissions. Global production of methanol is around 140 million tons (55 Billion USD) of which China contributes approximately 51%. China also consumes approximately 55% of the world methanol, therefore imports methanol. Of the entire continuum of methanol consumed approximately 40% chemicals & fuels; 20.5% in dimethyl ether (DME) fuels; and 37.5% for traditional precursors, In 2020, it was estimated that approximately 61.5% of chemicals & fuels; 16.5% in DME fuels; and 20.5% for traditional precursors [30]. Most of the methanol to olefins (MTO), and methanol to propylene (MTP), methanol to gasoline (MTG), Methanol to aromatics (MTA), Ethylene glycol (EG) with three or more plants in Inner Mongolia, Henan, Shaanxi, and Shandong, methanol can be synthesized from biomass, natural gas, coal, or ta sand, via synthesis gas. Syngas is often produced through the gasification of biomass, by catalytic reforming of the feedstock biomass to synthetic gas and then catalytic synthesis of methanol from the synthesis gas [31]. With fossil fuels, this can be accomplished by steam reforming, oxy reforming, or CO$_2$ reforming steps. In the first step that is auto thermal in nature, the endothermic steam reforming process and exothermic oxy reforming step are coupled to generate methanol.

Methanol (physical properties summarized in Table 1b) can also be generated by direct oxidation of methane, using catalytic gas-phase or liquid-phase oxidations or conversion of mono halogenated methane to methanol or using bioreactors with enzymes. Our favored approach is the chemical recycling of CO$_2$ to methanol [32].
As stated, earlier methanol can be used directly to generate electricity via direct methanol fuel cells. The fuel cells have electrodes, an electrolyte, and a membrane from which protons can migrate. The methanol feed is at the anode, whilst oxygen is taken at the cathode with platinum (cathode), platinum–tungsten-based (anode) catalyst (Eqn: 1 and Fig. 2B). The anode can abstract a proton from methanol. When operated between 60–130 °C enough electricity is generated to power storage batteries or small appliances. Oxidation of carbon dioxide to methanol is energetically unfavorable, as carbon has a formal oxidation charge of C\(^{4+}\) to CH\(_3\)OH, with a formal change of C\(^{2-}\), therefore requiring six electrons, requiring 228 kJ/mol. For photooxidation, the metal oxide bandgap (~3.2 eV) to the reduction potential of CO\(_2\) would be required [33].

\[
\text{Anode: } \text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \\
\text{Cathode: } 1.5 \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}
\]

**Overall Reaction:** CH\(_3\)OH + 1.5 O\(_2\) → CO\(_2\) + 2H\(_2\)O

Methanol can also be blended into gasoline to increase the octane number of gasoline and increase the energy efficiency of the internal combustion engine, or directly as a methanol fuel cell in fuel cell cars or methanol powered vehicles and even as a fuel for heating. Methanol to gasoline (MTG) or methanol to olefins (MTO) to produce plastics is another application. Lastly, methanol can be used to produce biodiesel via transesterification of vegetable oil or as a marine fuel.

The tables above shown that methanol has a higher energy density than methanol, is safer to transport than ethanol and gasoline, although itself is a potential poison. The hydrogenation of CO\(_2\) to methanol will be discussed in the concluding section. The current state of the economy within the framework of the current five-year plan will be described.

### 2.2. Geography and industrial endowments

Based on the geographical location, climatic conditions, agricultural
and industrial foundation, population distribution, and other factors, the development of the various provinces in the mainland has shifted from a managed command economy to the present more decentralized approach [34]. Particularly during the development leading up to and beyond the Beijing Olympics industrial technology and energy development has geared up to the utility of renewable energy at the level of the province away from petrochemical coal and petroleum to non-hydro renewables [35]. China’s northwest region is famous for its abundant coal, wind, light, and oil and gas resources. The southwest region is characterized by abundant water resources and other renewable energy resources [36]. The coastal areas are represented by nuclear energy and wind power [37].

The State Council has directed each province to meet the renewable energy portfolio obligation via a multimodal complementarity approach coordinated with regional energy providers. Here, harmonized regional development is placed in the context of green energy obligations, where energy input and greenhouse gases and particulate matter as outputs development, are managed, which are currently implemented by regions in Anhui, Henan, Hubei, and Shanxi which has led to a reduction of carbon dioxide relative to the 2018 benchmark shown in Fig. 3A for 2018 and 2010 in Fig. 3B [38,39].

### Table 1a
Summary of economic and population data and trends, using World Bank and OECD data sources.

| Province     | The Natural Population Growth Rate (%) | The Economic Growth Rate in Various Regions Of China (%) | The Strategic Emerging Industries (%) | Methanol Blend Standard |
|--------------|----------------------------------------|--------------------------------------------------------|---------------------------------------|--------------------------|
| Beijing      | 2.63                                   | 6.1                                                    | 5.5                                   |                          |
| Tianjin      | 1.25                                   | 4.8                                                    | 15.7                                  |                          |
| Hebei        | 4.71                                   | 6.8                                                    | 7.4                                   |                          |
| Shanxi       | 4.3                                    | 6.2                                                    | 7.4                                   | M5, M15, M45, M100       |
| Neimenggu    | 2.57                                   | 5.2                                                    | 2.3                                   |                          |
| Liaoning     | –0.8                                   | 5.5                                                    | M15                                   |                          |
| Jilin        | 0.36                                   | 3                                                      |                                        |                          |
| Heilongjiang | –0.69                                  | 4.2                                                    | M15                                   |                          |
| Shanghai     | 2.08                                   | 6.1                                                    | 3.3                                   | M45                      |
| Jiangsu      | 4.99                                   | 6.8                                                    | 9.8                                   | M15, M30, M50            |
| Zhejiang     | 6.45                                   | 7.5                                                    | 14.9                                  |                          |
| Fujian       | 6.8                                    | 7.6                                                    | 8.1                                   |                          |
| Jiangxi      | 7.37                                   | 8                                                      | 11.4                                  |                          |
| Shandong     | 4.27                                   | 5.5                                                    | M15                                   |                          |
| Henan        | 4.92                                   | 7                                                      | 13.7                                  |                          |
| Hubei        | 5.21                                   | 7.8                                                    | 11.3                                  | M15, M30                 |
| Hunan        | 5.11                                   | 7.6                                                    | 4                                     |                          |
| Guangxi      | 7.17                                   | 6                                                      |                                        |                          |
| Guangdong    | 8.08                                   | 6.2                                                    | 8                                     |                          |
| Hainan       | 8.5                                    | 5.8                                                    | 6                                     |                          |
| Chongqing    | 2.91                                   | 6.3                                                    | 11.6                                  |                          |
| Sichuan      | 4.04                                   | 7.5                                                    | 11.7                                  | M10                      |
| Guizhou      | 7.05                                   | 8.3                                                    |                                        | M15                      |
| Yunnan       | 6.87                                   | 8.1                                                    |                                        |                          |
| Xizang       | 10.64                                  | 8.1                                                    |                                        |                          |
| Shaanxi      | 4.43                                   | 6                                                      | 8.1                                   | M15, M25                 |
| Gansu        | 4.42                                   | 6                                                      |                                        | M15, M30                 |
| Qinghai      | 8.06                                   | 6.3                                                    |                                        |                          |
| Ningxia      | 12.29                                  | 6.5                                                    |                                        |                          |
| Xinjiang     | 10.57                                  | 6.1                                                    | 6.9                                   | M15, M30                 |

(Note: EG = ethylene glycol; 15 % gasoline blend = M15; MTA = methanol to aromatics; MTG = methanol to gasoline; MTO = methanol to olefins; and MTP = methanol to propylene. Source: National Bureau of Statistics of China; World Energy Council; Methanol Institute, Xu, et al. 2007; [199]; World Bank; and OCED).

### Table 1b
Physio-Chemical properties of common fuels.

| Property          | Gasoline | Diesel | Ethanol | Propane | CNS |
|-------------------|----------|--------|---------|---------|-----|
| Formulae          | C4–C12   | CR–C25 | C2H5OH  | C3H8    | CH4 (83–99 %) + C2H6 (1–13 %) |
| Molecular Mass    | 100–105  | 200    | 46.07   | 44.1    | 16.04 |
| Molar Carbon (%)  | 85–88    | 87     | 52.2    | 82      | 75   |
| Molar Hydrogen (%)| 441–80   | 13     | 13.1    | 18      | 25   |
| Molar Oxygen (%)  | 0        | 0      | 34.7    | 0       | 0    |
| Specific Gravity  | 0.72–0.85| 0.78   | 0.794   | 0.508   | 0.424 |
| Boiling Point (°F)| 80–437   | 356–644| 172     | –44–263 to 126.4 |
| Freezing Point (°F)| –40  | –40 to –173.2 | –305.8 to –296 |
| Flash Point (°F)  | –45      | 140–55 | 156     | –300   |
| Autoignition Temperature (°F) | 495-536 | 600    | 793     | 876    | 1076 |
| Research Octane Number | 88-98 | N/A    | 106.8   | 97      | N/A  |
| Heat of Vaporization (Btu/gal) | 900 | 710    | 2378   | 775     | 1441 |
| Specific heat (Btu/lb °F) | 0.48 | 0.4    | 0.57    | 0.34    | 0.45 |
| Specific heat (But/Ib °F) | 0.48 | 0.4    | 0.57    | 0.34    | 0.45 |
| Volumetric Energy Density (grams/litre) | 198 | 216    | 168     | 0.777   | 0.267 |

| Property          | Hydrogen | Biodiesel | Methanol | Water |
|-------------------|----------|-----------|----------|-------|
| Formulae          | H2       | C12 to C22 | CH3OH    | H2O   |
| Molecular Mass    | 2.02     | 292       | 32.04    | 18.02 |
| Molar Carbon (%)  | 0        | 77        | 37.5     | 0     |
| Molar Hydrogen (%)| 100      | 12        | 12.6     | 67    |
| Molar Oxygen (%)  | 0        | 11        | 49.9     | 33    |
| Specific Gravity  | 0        | 0.88      | 0.796    | 1     |
| Boiling Point (°F)| 423     | 599-662   | 149      | 212   |
| Freezing Point (°F)| –435    | 26-66    | –143.5   | 32    |
| Flash Point (°F)  | FG       | 212-228   | 52       | N/A   |
| Autoignition Temperature (°F) | 932 | 705-840 | 867     | N/A   |
| Research Octane Number | N/A | N/A      | 107     | 300   |
| The Heat of Vaporization (Btu/gal) | 1353 | 3340     | 8092    |       |
| Specific Heat (Btu/lb °F) | 2.42 | 0.6      | 0.9     |       |
| Volumetric Energy Density (grams/litre) | 71 | 214.5    | 99      |       |

(Note: Btu = the British thermal unit; CNS = 83–99 % of CH4 and 1–13 % of C2H6; °F = degrees Fahrenheit; FG = flammable gas; FAME = fatty acid methyl esters; gal = gallon; and lbs = pounds. Source: [182,183,200]; Engineeringtoolbox and Neutrium).

3. Several factors which affect China’s energy

3.1. Influence of structural adjustment in energy consumption

Based on the statistical analysis from the NBSC the reform related to the reduction of electricity price and the consumption of clean energy have not been met [40]. At present, the energy policies of China’s 13 provinces are related to coal and electricity, 13 regions are involved in the energy-saving renovation, 19 regions are involved in new energy transportation, and 12 regions have launched industrial ecological development plans for clean energy [41]. Seven provinces continued to emphasize energy reform, increase the consumption of renewable energy, optimize the energy structure, and adjust the proportion of clean energy mix, and seven regions focused on natural gas, summarized in Table 2a.
Fig. 3. A: Carbon dioxide emissions per ton of combusted petroleum, using data from the National Bureau of Statistics, China. B: Carbon dioxide emissions per million-ton unit using data from the National Bureau of Statistics, China.
Summary of reform project outlined in the current five-year plan; expenditure is shown in Fig. 1 f.

When comparing energy production and consumption at the provincial level through assessment of SOx, NOx, and CO2, some generalization can be stated starting from the 11th five-year plan to the 13th five-year plan to the 1990–2000 period, we can see clearly that the Chinese economy and energy production increased significantly. In 2000, China’s GDP was 10 billion yuan, and in 2017, it reached 100 billion yuan, a tenfold increase. At the same time, energy production and consumption increased from 2000 to 2017. During the 11th five-year plan, the proportion of energy intensity in GDP was 15.8%, which was lower than the 12% in 2005. The proportion of energy intensity in GDP decreased by 15.8% which is on target, with the greatest reductions occurring in Xinjiang, Shaanxi, Guangxi, Guangdong, and Fujian, with current reductions occurring in the South and Northwest provinces [51]. The provinces have to balance its balance to generate a gross domestic product to that of transitioning to low-carbon sources for energy, such as Beijing, Shanghai, and Guangdong focus will be on efficiency enhancements and development of solar, whereas Shandong, Inner Mongolia, Xinjiang, Ningxia, and Guizhou focus will be on carbon capture due to an abundance of fossil resources [52]. Since the gross domestic product (GDP) and economic resources of central and western provinces in China are lower, utilization of low carbon energy sources or carbon capture may be more appropriate pathways towards increasing both GDP and lowering CO2 emissions [53].

Recently, the central government issued a consultative document entitled “Opinions on accelerating the establishment of a green production and consumption regulatory and policy system through the national development and reform commission and the ministry of justice” on March 17, 2020. The opinion if promogulated will be administered by the ministry of justice, strengthening law-based energy governance [54]. The core purpose of the opinions is to promote clean energy development, increase policy support for distributed energy, smart power grid, energy storage technology, and multi-energy complementarity, and research and formulate standards, regulations, and support policies for the development of new energy sources such as hydrogen energy and marine energy [55]. The energy balance should incorporate the whole life cycle, via the industrial chain to evaluate whether the energy supply and consumption meet the requirements of green and clean development. This may be promoted by recent rises in the particulate matter which were stable with a slight increase in 2005 and then a large rise in 2015 [56].

The progressive decreases of NOx and SO2 during the 1990–2000 decade, increased in the early 2000s due to increased electricity generation and industrial production and infrastructure (45); and (46). These decreases in emission were related to the Beijing Olympics, cement production peak in April and October of 2005 of a modal value of 8.5 thousand tons of cement, with production declining from Jan-April [47]. Cement production then increased back to 10 thousand tons and crept up to about 22 thousand tons per year by and stayed constant except for a slight increase in 2014 [48] and a slight decrease in 2020 due to a slowdown in the Chinese economy due to the coronavirus [49].

Most of the emissions were from the generation of electricity from fossil fuel consumption, but emissions from heavy industries including the production of cement cannot be ignored [50]. In general CO2 emissions increased from west to east and north to south. Most reduction over the five-year plan (11th to 12th) decreased by 15.8 % which is on target, with the greatest reductions occurring in Xinjiang, Shaanxi, Guangxi, Guangdong, and Fujian, with current reductions occurring in the South and Northwest provinces [51]. The provinces have to balance its balance to generate a gross domestic product to that of transitioning to low-carbon sources for energy, such as Beijing, Shanghai, and Guangdong focus will be on efficiency enhancements and development of solar, whereas Shandong, Inner Mongolia, Xinjiang, Ningxia, and Guizhou focus will be on carbon capture due to an abundance of fossil resources [52]. Since the gross domestic product (GDP) and economic resources of central and western provinces in China are lower, utilization of low carbon energy sources or carbon capture may be more appropriate pathways towards increasing both GDP and lowering CO2 emissions [53].

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3.2. The economic influence of new spatial geography

In China’s “Completed of the thirteenth five-year plan and opening of the fourteenth five-year plan” period, we can see clearly that the Chinese
government is promoting “the coordinated development of Beijing-Tianjin-Hebei region”, [57,58] “the Yangtze River economic belt”, [59] “Yangtze river delta integration development” [60], “Guangdong-Hong Kong-Macao Greater Bay Area” [61] and “the Belt and Road” [62] new five regional development strategy, further formed the new pattern of linkage with whole areas, overall planning for regional and marine economic activities and coordinated development [63]. It shows that China’s new space geographic economic phenomenon more and more clear, enters the new coordinated development stage of regional economic coordination and ecological environmental governance, comprehensive energy-using past experiences [64]. The promulgation assumes all areas of the country continue to accelerate the development of renewable energy, strengthen local absorption capacity, reduce the amount of wastewater, wind, and light, and strive to build a highly clean energy supply system [26].

In Shanxi, Inner Mongolia, Xinjiang, Shaanxi, and Shandong green mining technologies are expected to gradually replace traditional industries. The integration of science and technology in the field of energy development, through information technology and the introduction of a circular economy mode of production, will provide employment and opportunities and displace the traditional energy-intensive industries [65]. Provinces in the upper and middle reaches of the Yangtze River and other central provinces are actively seizing the opportunity of natural gas and renewable energy sources to gradually release supply capacity to the central region to improve energy cleanliness [66]. The 11 provinces and cities of the “Yangtze river economic belt” strive for the promotion of the country, and enterprises have formed a benign mix of industrial transformation, environmental protection upgrading, government-enterprise cooperation, and the participation of private capital [67].

Some regions in the five regions have the self-circulation of energy production, supply, and elimination, while some regions are still dominated by external energy supply. For example, one-third of the Zhejiang province’s electricity comes from outside the region [68]. Also, China’s administrative governance has a special means, that is, the policy of poverty alleviation. This policy is not only poverty alleviation, but also has a great impact on energy production, supply, and consumption. For example, in Xinjiang and Ningxia province, the coal power supply, wind power supply, and natural gas supply have their consumption and absorption counterparts corresponding to the poverty-stricken provinces [69].

China’s urbanization process is still in the promotion stage, while urbanization plays an important role in China’s energy consumption. The study of energy consumption in the process of urbanization from a spatial perspective is conducive to the coordinated development of urbanization and energy consumption [70]. In China, the previous energy problems in the process of urbanization are relatively extensive, in the future development of urbanization, the energy-saving strategy will be included in the process of urban planning and layout, starting from the demand side, the construction of economical and intensive mode of energy use, a new type of urbanization construction of ecological efficiency, energy conservation, and environmental protection, it will be China’s new micro one of the symbols of the new space geographic economy [71].

3.3. The influence of energy technology integration

With the development of the Chinese government’s green and environmental protection law enforcement becomes legally enforceable [72], China’s energy science and technology ministries, also strengthened laws related to the mining of coal, oil and gas exploration technology, recovery of smelting technology, environmental protection, as well as aspects related to clean coal and efficient conversion utilization of feedstocks [73]. Similarly, other laws have affected energy generation from nuclear, photovoltaic, wind power, and other aspects, whether in the design, manufacturing, or operation and maintenance [74]. Much of the focus has been on renewable energy, designed to stimulate technological innovation in areas of smart grid, energy storage to enable a transition to renewables and foster a new digital economy [27]. The current Chinese market reforms (Table 2b) are designed to promote active research and development of new energy technologies and industries, particularly in green energy and transport [75]. Both state-owned enterprises and private investors are committed to seizing the commanding heights of a new round of green and low-carbon technologies [76].

China is also investing heavily into artificial intelligence, cloud computing, big data, industrial internet, new materials, the large-scale generation of blockchain, and the sinking digital marketplace where technology commercialization is matched with Angel investors has become one a major source of innovation and buy-ins [77]. With the development of first-line terminal sensing and control technology, the production efficiency of energy production and transportation will be significantly improved. According to artificial intelligence-based prediction, the efficiency in the manufacturing sphere will be improved by 5–10%. With the direct collaboration of machines, the large-scale intelligent transportation upgrade will be closer to people’s lives [78]. In the supply or consumption terminals, driverless new energy vehicles, intelligent traffic dispatching applications, the cross-regional industrial interconnection of energy production, and cross-type and proportionally dispatching of energy consumption have made steady progress [79].

3.4. The influence of the smart digital economy

As shown in Table 2b, much of the focus has been on the implementation of technical assistance to reduced CO2 emissions as PM, through a transition to sustainable energy sources and digitization of the industrial economy to an industrial internet economy mirroring moves by other countries such as the USA and Russian Federation [80]. The further integration of the industrial Internet and data has been widely applied in China’s domestic market, which brings new development opportunities and challenges to the energy industry [81]. Based on the traditional energy industry, the energy industry will achieve great improvement by solving the “five core problems”: (i) the transformation of energy digitalization, (ii) the collection of energy industry data, (iii) the value-added service technology of data comprehensive analysis, (iv) market demand, (v) and core products manufacturing & distribution [82].

China, driven by the five-year plan has targeted environmental pollution as a major obstacle to increased efficiency and cost savings and the need to reduce carbon emissions and energy consumption by 10 percent. With the direct collaboration of machinery, the large-scale intelligent transportation upgrade will be closer to people’s lives [78]. In the supply or consumption terminals, driverless new energy vehicles, intelligent traffic dispatching applications, the cross-regional industrial interconnection of energy production, and cross-type and proportionally dispatching of energy consumption have made steady progress [79].

Table 2b

| Law on Prevention and Control of Water Pollution | May 1984 |
| Environmental Protection Law | Dec 1989 |
| Law on Prevention & Control of Air Pollution | Aug 1995 |
| Law on Prevention and Control of Environmental Pollution by Solid Waste | Oct 1995 |
| Law on the Promotion of Clean Production | June 2002 |
| Law on Environmental Impact Assessment | Oct 2002 |
| Law on Energy Conservation | Oct 2007 |
| New Water Pollution and Prevention Control Law | May 2015 |
| Reform Plan for Ecological Environmental Damage Compensation System | Dec 2017 |
| Tax Exemption for New Energy Vehicles | Dec 2017 |
| Nuclear Safety Law | Jan 2018 |
| Number of Environmental-focused policies documents 2007-2015 | <10 |
| Number of Environmental-focused policies documents 2016-2019 | >30 |
| Total # of Policies Proposed (2007-2019) | 161 |
| Percent of Policies related to Environmental Taxation, Legal Enforcement | 45% (72) |
| Percent of Policies related to ‘Supply’ in terms of technical assistance | 44% (71) |
| Percent of Policies related to ‘Demand’ in terms of Procurement Modification | 11% (18) |

(Source: [207-209]; and [210]).
envisions a transition to digital environmental as a benefit as approximately 80% of all carbon dioxide emissions up to 2015 were from heavy industries [83]. The roll-out of artificial intelligence, industrial Internet, and blockchain, the combination of an energy revolution and digital revolution is one approach to transition to local and more responsive environmental to both supply-side but also demand economics [84]. The assumptions are that through the introduction of a smart digital economy, the energy system is increasingly digital and intelligent, especially the rapid development of clean energy represented by the production and supply of new energy and renewable energy, forming a new generation of energy digital technology economy. It is embodied in the multiple sharing of energy types, the mutual crossing of the main body’s source-network-load, the mutual promotion of energy consumption and information consumption, and real-time data reporting and anticipates that it will incorporate elements of cloud computing, embedded device reporting, robotics, just-in-time deliveries, and payment. Since this involves digital transactions, electrically operated devices with lower power demand the carbon footprint is anticipated to drop [85].

Under the policy influence of such technology, the raw materials, manufacturing technology, control technology, and management technology involved in the energy supply side, transportation network side, and consumption load side will all undergo qualitative changes such as in the field of agriculture [86]. At present, the technology has gradually realized the real-time identification of the supply and consumption state of different types of energy, the timely installation of various energy storage regulation technologies, the statistical analysis of the proven-network-load operating curve of each province, and the prediction and response of potential risks in advance [87]. In terms of top-level management and online supervision, online data collection, transmission, and cloud computing analysis will inevitably evolve to advance new intelligent automated operations, maintenance technologies, and most importantly, the supply chain [88].

All these new technologies, summarized in Fig. 5A will give birth to the Internet digital economy in the field of energy so that the energy economy is no longer the traditional asset-heavy economy, but both the traditional asset-heavy real economy and the digital asset economy. In the next five to 10 years, China’s energy sector will form a new type of business and a new model powered by energy numbers [89].

4. Energy trends observation in China

4.1. Policy guidance trend observation

According to the information released at several meetings of the financial and economic committee of the Chinese government in 2019, supply-side reform in the energy sector and the construction of an economy that emphasizes both green and quality will continue to be the keynote of the 14th five-year plan period [58]. With the dual promotion of the country and the market, the energy technology field will further form an industrial system upgrading that combines points, lines, and faces [90]. With the implementation of the “13th five-year plan” in the field of energy, how to build a high-quality green energy system reform transition, from sustained growth to more of a balanced holistic strategy in the “14th five-year plan” is the central policy question which will occupy managers and decision-makers, as China continues to update part of its energy planning portfolios and specific policies seven broad areas such as (i) energy production, (ii) energy consumption, (iii) energy technology and systems, (iv) energy development model, (v) the energy industry ecological, (vi) synchronous propulsion, and (vi) international cooperation [91]. These are related to key performance indicators summarized in Fig. 5B and C.

In Fig. 5C top-left panel is a decade summary of Vehicle production (black line) and Electricity Production (bold blue line), the top-right panel is Industrial Output (black line) and Manufacturing production (bold blue line). The bottom left panel is cement production (black line) and Steel production (bold blue line) and the bottom right-hand side panel is Mining production (black line) and Industrial Capacity Percent utilization (bold blue line). (Sources: National Bureau of Statistics of China, China Association of Automobile Manufacturers, World Steel Association, IMF and tradingeconomics.com). In the “14th five-year plan”, to maintain energy consumption more emphasis will be given to production and distribution from various energy sustainable sources, with a local mix of Solar PV, wind, it is anticipated that energy efficiency will improve requiring fewer coal-powered stations and thereby reducing carbon emissions and energy use costs, and promoting market-oriented energy trading of wind and solar companies even if electricity consumption continues to rise [92]. The State Council directives prioritize the production of clean and efficient utilization of petrochemical energy and the large-scale promotion of nuclear energy and renewable energy, building on from the best practices of the previous plan [93]. Based on the report card of energy conservation and emission reduction, the directive empowers the promotion of in-depth energy conservation and energy efficiency technologies. In terms of the reform of energy science and technology system, the directives also have set-aside funding, tax adjustments to further develop clean technologies and IoT integration such as the battery industry chain and the hydrogen energy industry chain is also continuously trying to adopt more flexible development policies and encourage the participation and development of various entities ([94,95]; and [96]).

4.2. The trend of environmental protection and emission reduction

With the continuous development of the new normal of China’s economy, China’s energy development has entered the “three lows” trend. Some of these are summarized in Figs. 5b and 5c. Energy development is characterized by ‘low growth rate, low increment, and low carbonization’, and the Chinese government’s continuous tightening of ‘constraints on the safe supply of resources, the protection of the ecological environment and the reduction of greenhouse gas emissions’ has been further strengthened (Fig. 5D-F). During the period of the 14th five-year plan period, the carbon intensity of Chinese provinces is expected to continue to decline significantly as electric vehicles and renewables kick-in.

The decline in energy intensity, combined with the substitution of renewable energy and natural gas for coal, led to an average annual decline in the carbon intensity of about 5.4 percent in all provinces during the 14th five-year plan period, and the average annual decline in carbon intensity is more than 4.0 percent in almost all provinces.

The Chinese government is still the same as usual, on the demand side strongly advocated and encouraged revolution, the energy consumption in response to an increase in demand for energy, economic growth, and urbanization through the upgrade of industrial structure development of high and new technology industries, low energy consumption through real-time pricing, peak shaving, demand response to the demand side of the energy management, enhance the energy market competition mechanism, revitalize the enterprise vitality, eliminate backward production capacity, improve the efficiency of energy production enterprise for production [97].

Whilst the policy directives are set forth at the State Council, the actual implementations are left to the individual provinces. For example, clean energy, or the proportion of non-water renewable energy is achieved by wind or solar power, in the form of an integrated energy system and where systems can complement each other, promote energy system step by step in the direction of clean, green, low carbon transformation [98]. In the comprehensive energy system, the traditional fossil energy such as coal power needs to be phased-out with wind power, photovoltaic power, and other renewable energy, and the proportion of renewable energy needs to be gradually increased, to reduce sufficient time for maturation of technologies and develop high storage capacities with cheaper operating costs [58].
Fig. 5. A: Summary of the concept of the internet of things (IoT) which couples, cellular communications with big data, transportation to business such as legal services, physical services (dry cleaning, delivery, car wash) to wearable diagnostic devices (lower panel icons) to the distribution of major companies in China such as SANY, Alibaba Cloud or Baidu (China Map top-right panel, Source: PBS.ORG). The total number of IoT cellular devices is shown in the lower-left panel (right-hand axis, line trend) versus investment in IoT technologies (left-hand side axis, column trend) from 2011 to 2018 (Sources: [184–189, 211]; Ericsson Mobility Report, June 2018; and [212]). The left middle and left top graphs are companies or sectors with over $100 revenue operating in the IoT economy (Source: PBS.ORG; Jude, 2012; and [213]). B: Top-Left panel is a decade summary of annual wages (open square) and Inflation (open circle). The top-right panel is the gross domestic product (gray columns) and the ratio of debt-to-GDP (closed square). The lower-left panel is the population (line) and unemployment rate (closed square). The bottom-right panel is Government ten-year Yields (black line) and the rate of exchange with the US Dollar (bold black line). (Sources: National Bureau of Statistics of China; [205, 214, 203]; and IMF). C: top-left panel is a decade summary of Vehicle production (black line) and Electricity Production (bold blue line), the top-right panel is Industrial Output (black line) and Manufacturing production (bold blue line). The bottom left panel is cement production (black line) and Steel production (bold blue line) and the bottom right-hand side panel is Mining production (black line) and Industrial Capacity Percent utilization (bold blue line). (Sources: [190–193]). D: Plot of change in electricity generation by Fuel Type in kilowatt/hour (left bars) and as a percent (right bars). (Source: International Energy Outlook, 2019). E: Summary of Electric Sales over the last decade (top-Left), CO2 Emission from Coal (top-Right), CO2 Emissions from Liquid-based Fuels (Lower left panel), and CO2 emissions from natural gas (lower right panel). (Sources: [216]; and Bloomberg NEF for EV Sales and [215] for fossil fuel CO2 emissions.). F: Summary of Fiscal expenditure on the entire economy over the last decade (black line figure), the ear-marked investments on renewables energy technologies (bold blue line), and adjusted inflation over the same period (closed circle). (Sources: IMF, World Bank, [217]; and National Bureau of Statistics of China; [177–181]) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
4.3. Optimization trend of wisdom energy-using

The industrial Internet has been widely used in the field of energy and has penetrated and affected the integrated development of the secondary and tertiary industries covered by energy [99]. Under the influence of blockchain technology based on the industrial Internet, the energy production relationship that can be reconstructed with the characteristics of decentralization in the digital economy era will gradually come to displace centralized systems and enhance redundancy [100]. This new technology of integrated development will probably reshape the status and interrelationship of various subjects in the field of energy production, change the form of product distribution, and become a new engine to drive the development of energy digital economy [101].

Today’s digital economy era based on blockchain softens the boundary between the producer, and end-user and the production materials no longer belong to a single party, as the ‘producer-consumer’ linage is not strictly descriptive. In the field of energy digital economy, blockchain is profoundly changing the management, trading, and operation of distributed energy, and demand-side users are gradually playing the dual roles of consumers and producers [102]. This aspect makes the energy supply-side and demand-side are the support of information technology, each data source, which changes the original traditional centralized energy distribution network and center, formed the new smart energy system construction direction, on the other hand, can complement each other, send parallel this new type of integrated energy storage mode to adapt to the market demand [103]. With the acceptance and promotion of the market, the energy and digital resources supported by cloud technology will get the opportunity of coordinated development. Surely, safety and reliability are still a problem that needs to be addressed before widespread adoption and replaced the traditional production workflow [104].

5. Methanol synthesis for cleaner fuel and lowering carbon dioxide

Methanol synthesis through CO2 hydrogenation offers an attractive way to generate a synthetic precursor molecule, a fuel substitute, and a mechanism to lower the global CO2 threshold [30]. The economy of such an approach depends on whether the price of electricity is cheaper from coal, natural gas, solar, nuclear, or wind and are on average more expensive than conventional approaches. The conversion of CO2 to methanol is also more expensive (~$650 per ton vs €400 per ton) than the syngas process, although the price difference is decreasing, like how the price decrease from solar sources [105]. The higher prices reflect the high stability of carbon dioxide and its associated activation (1072 kJ/mol) and water production as a side-reaction which can lead to the deactivation of metal catalysts such as copper. One approach to minimize these potential disadvantages is to utilize the reverse water gas shift reaction which is separated from the main methanol synthesis route and then combined in the reactor. One final advantage is that net carbon dioxide emissions from hydrogenation are lower than from syngas emissions (0.2-tons CO2 per ton CH3OH, versus 0.8-ton CO2 per ton CH3OH) [106]. The synthesis, operational parameters, and common catalyst configurations are summarized.

5.1. Carbon dioxide conversion to methanol

Methanol has several advantages as a fuel, due to its energy content 726.3 kJ/mol, although its heat of combustion per gallon is lesser than gasoline (57,520 Btu versus 116,090 for gasoline) [107]. Methanol is also a viable fuel substitute as their prices per gallon are similar with methanol being slightly cheaper ($1.50/gallon versus 1.71 for a gallon). Jan 2020), is a liquid at room temperature and has a lower freezing temperature than standard gasoline (~ 96 °C versus ~ 57 °C for n-octane, although the value will depend on other additives) [108]. Methanol having less carbon than gasoline combuts to only carbon dioxide and water, and has a lower flash point (14 °C versus 13.3 °C for n-octane, although in typical gasoline with additives the flashpoint may be negative (~ 43 °C) and in this regards is a safer fuel choice. Since gasoline can exhibit incomplete combustion products and particulate matter, inhalation of fumes from the combustion of gasoline is generally more toxic than for methanol [109].

Methanol is synthesized commercially by syngas using zinc/chromic based catalysts at 300 °C and 296 atm. Substitution of Zinc/Chromic by Cu/ZnO has enabled the synthesis to be favorable at lower pressures and temperatures (49 – 296 atm, 200 – 300 °C) [110]. The present method for synthesis is related to the use of syngas and CO2 over the Cu-ZnO/Al2O3 catalyst at 220 – 300 °C and 46 – 96 atm respectively [111]. Methanol seed material is carbon dioxide with carbon monoxide as surface oxygen, which is an attractive feature as it consumed CO2 and has been proposed as a potential avenue away from the carbon economy to more clear methanol and ethanol economies, whereby methanol synthesis is via hydrogenation of CO2 driven by solar or geothermal energy, at 250 °C and 29 atm. In catalyst design, the three major obstacles are thermodynamic, kinetic, and cost considerations [112].

5.2. Thermodynamic considerations

As CO2 is a stable molecule, high pressures, and temperatures around 250 °C are required to drive the reaction forward (Eqn: 2), although the heat of formation suggests the reaction is favored at lower temperatures [113].

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \Delta H_{298K} = -49.5 \text{ kJ/mol} \quad (2a)
\]

Therefore, the actual pressure and temperature regime is influence by the catalyst employed. Recently CO2 hydrogenation to methanol using a Cu/ZnO/Al2O3 catalyst was achieved at 49 atm and at 296 atm when using a Ni(CO)4 catalyst. One problem is water formation that leads to the deactivation of the catalyst, in addition to the use of hydrogen, which is greater than by syngas alone. Water can also act as an oxidant at higher temperatures and oxidize the metal to the metal oxide [114].

\[
\text{Cu} + \text{H}_2\text{O} \rightarrow \text{CuO} + \text{H}_2 \quad (2b)
\]

The water can be removed during the reaction, or CO introduced to reduce the metal oxide.

\[
\text{CuO} + \text{CO} \rightarrow \text{Cu} + \text{CO}_2 \quad (2c)
\]

This would regenerate the CO2 or H2 gas been used for the reduction of CuO to Cu. recently a new study showed that pre-addition of water suppressed the oxidation process, similar to the effects of water addition for CO selectivity by the reverse water gas shift reaction [115]. This reaction:

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \Delta H_{298K} = 41 \text{ kJ/mol} \quad (2d)
\]

is unfavored, thereby requiring higher temperatures to drive it, which also promotes the reverse water gas shift relative to hydrogenation of CO2 to methanol. The current approach focuses on liquid phase methanol synthesis rather than gas-phase methanol hydrogenation [116]. The major metal catalyst for methanol synthesis is based on copper, zinc oxide, and alumina [117].

5.3. Other metal catalysts

Silver as the active catalytic component with ZrO2 compared with Cu/ZrO2 at temperatures lower than 230 °C, with enhanced selectivity for CO2 hydrogenation, when added to Cu/ZnO with 100 % selectivity whereas the selectivity with Cu/ZrO2 was 95 % [118]. Although the selectivity of silver is greater its activity is not as high as with CuO/ZrO2 catalyst [119].

Palladium based catalysts at 119 atm and 350 °C n over La2O3
support, but with lower selectivity for the CO$_2$ hydrogenation reaction (~ 90%) [120]. Palladium (Pd) on in catalyst also gave superior results relative to Cu/ZnO/Al$_2$O$_3$ catalyst. Other supports evaluated were Pd on CeO$_2$ at 500 °C and multi-walled carbon nanotubes supposed Pd/ZnO or Pd/TiO$_2$ at 500 °C gave higher selectivity due to stronger interactions between the metal catalyst and the support surface [121]. In some of these studies, lower temperatures resulted in the production of methane, with indications that their selectivity for methanol may be greater than methanol [122].

Copper is the most widely used catalyst particularly when supposed by ZnO and is operated at higher temperatures than 250 °C, 52 atm [123]. By using ZnO on silica the methanol formation from H$_2$ and CO$_2$ can be increased, due to the availability of oxygen vacancies of zinc oxide, improving both stability and dispersion of the copper catalyst [124]. Therefore, the addition of support that enhances the stability of copper whilst increasing its dispersion generally leads to greater methanol selectivity [125].

The addition of Ga$_2$O$_3$ to Cu/ZnO led to better catalyst performance for hydrogenation of CO$_2$ to methanol, where the Ga$_2$O$_3$ facilitate the reduction fo Cu, increasing the activity, suggesting that the interaction of Cu with ZnO support is greater than with the SiO$_2$ support. Whilst methanol is generated using copper alone, the addition of a promoter like Ga$_2$O$_3$ or support such as CeO$_2$ or ZnO, because of the latter offer the probability of greater dispersion of Cu on the support and thereby greater catalytic surfaces for the hydrogenation reaction to take place, relative to copper alone, in addition to stabilizing effect of the support material for the copper (I) species [126].

This reflects the complexity of the system in terms of catalyst half-life, selectivity, and activity, resulting in Cu/ZnO/Al$_2$O$_3$ or Cu/ZrO$_2$ as being the default choice for the hydrogenation reaction [127]. The oxidation state of the metal catalyst is critical, it is generally observed that the zero-valent species are more stable and active.

Other support systems evaluated were silica, alumina, and zirconia, due to the availability of accessible oxygen sites and ion exchange pricing multiple reactive surfaces for the hydrogenation reaction. Therefore, the correct choice of promoter and support can lead to greater activity, for example, Cu/ZrO$_2$ over Cu/ZnO [128].

Zirconia can form some crystalline forms that are transformed at various pH, with the tetragonal form of zirconia is the most stable at basic pH environments, while at neutral pH the monoclinic form of zirconia is the most stable [129]. Lastly, the calcination temperature can also influence the allotropic, with the tetragonal form being most stable under 500 °C, but the monoclinic being formed at higher temperatures [130]. The monoclinic zirconia (mZrO$_2$) is more active than the tetragonal allotrope (tZrO$_2$), due to greater interactions of the tetragonal form with intermediates than the monoclinic form [131]. Doping with silver ion has also been shown to enhance activity via stabilization of the tZrO$_2$ form, suggesting that Cu/ZrO$_2$ is a better catalyst than Cu/ZnO. The addition of ZrO$_2$ or ZnO generally increased the activity of the Cu catalyst by increasing the stability of the Cu ion, but the rate was unchanged with ZnO but not ZrO$_2$ with doped Ag$^+$ [119]. This difference between ZnO and ZrO$_2$ appears to be due to the stabilizing effect of ZrO$_2$ on Ag$^+$ that is lacking with ZnO.

The pH-dependence for the hydrogenation reaction may be related to the mechanism of co-precipitation for Cu/ZnO/Al$_2$O$_3$ due to aging, where hydroxide ions are release increasing the pH. The increase of pH can be countered by the addition of CO$_2$, and a constant pH improves catalyst performance [132].

$$\text{Cu(OH)}_2 + 3\text{Cu(OH)}_2 + 2\text{CO}_2 \rightarrow 2\text{Cu}_2\text{O}
\text{CO}_3 \ (s) + 2\text{OH}^- + 2\text{H}^+ (3a)$$

$$\text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{H}^+ + \text{CO}_3^{2-} \quad (3b)$$

$$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \quad (3c)$$

Thus, methanol selectivity is highly dependent upon the Cu surface, morphology, and the phase of ZrO$_2$ [133], summarized in Table 3a.

### Table 3a

| Catalyst | SBET (m$^2$/g) | CO$_2$ Conversion (%) | CH$_3$OH Selectivity (%) | CH$_3$OH Yield (%) |
|----------|----------------|-----------------------|--------------------------|--------------------|
| CuO/ZnO/ZrO$_2$ | 26.32 | 15.81 | 23.31 | 3.69 |
| TiO$_2$/CuO | 33.69 | 20.24 | 27.15 | 5.5 |
| ZnO/Al$_2$O$_3$ | 37.77 | 16.1 | 25.29 | 4.07 |
| ZnO/Al$_2$O$_3$ | 42.72 | 40.7 | 41.17 | 16.76 |

The introduction of CO$_2$ in the aging process has several advantages, which are control of composition [134], maintenance of constant pH [135], increased in pore volume to promote gas diffusivity and increase surface area to promote catalysis [133] in addition to strong interactions between Cu and specific stable phase of ZrO$_2$ [129]. The above studies with glycine or co-precipitation suggest that crystallinity and activity of the copper catalyst are counter to each other, where the dopant atom (e.g. Ag) serves as a site for nucleation Cu crystallization [136]. The extent of crystallization, in turn, depending on the degree of dispersion of the dopant or alloyed metal or metal substitution (e.g. La for Cu) [133], with activity being correlated with Cu active sites [137] and selectivity being correlated with basic sites on the catalytic surface [138], as shown in Table 3b.

As observed in earlier studies, the addition of Ga$_2$O$_3$ as a catalyst promoter increased activity, could be used instead of substitution of the metal catalyst itself, the promoter could enhance the catalyst to support structure or stabilize the metal catalyst itself by acceptance of an electron or promoting the reduction of the active metal [127].

As stated, earlier gallium oxide enhanced the activity of copper-based catalysts via oxidation of copper (0) to copper (I), thereby maintaining a constant ratio between each zero-valent and mono species increasing the catalyst half-life [126].

Niobium oxide (Nb$_2$O$_5$) as support has also been used and has been shown to exhibit excellent activity and selectivity in the hydrogenation reaction fo CO and CO$_2$ for methanol production [139]. As this is an acidic oxide, it can also be used as a promoter. It is thought that the oxide increases Cu dispersion, enhancing surface area sites better Cu stability against water, and enhanced activity with CO$_2$ hydrogenation [140].

Zinc oxide has been used as a catalyst in the CO$_2$ hydrogenation reaction, and as a promoter for Cu by increasing its dispersion, thereby slowing potential agglomeration on the active copper catalyst when supported by alumina [141]. The zinc oxide is basic and can counteract the activity of the alumina support. This has been shown to slow down the conversion of methanol to dimethyl ether [126]. The interaction between Cu and ZnO is thought to occur via interaction interactions Cu$^+$–O–Zn, where the zinc oxide can adsorb H$_2$ species and promote a stable intermediate (methoxy oxide) which is ultimately converted to methanol upon hydrogenation [142]. It should be noted that with syn-gas based synthesis, the feed gas may have trace amounts of sulfur that can position that active catalyst surface, ZnO is thought to be able to
abstract the sulfur forming ZnS and thereby lessening the deactivation of the Cu species [143]. The Zn was also able to adsorb with species such as H₂CO, increasing the rate of methanol synthesis [144].

5.4. Support materials

The role of the catalyst support is the dispersal of the active metal, but also to avoid sintering or aggregating the metal particles. The acidity or basicity of the support will affect catalyst performance [148].

Silica has high thermal stability and good dispersion capacity and has been used as a support material using CO₂ and H₂. Some first two and second-row transition metals were evaluated on silica supports, at 250 °C and 49 atm resulting in higher selectivity of methane for Ni, Co, and CO on Pt [124]. For methanol selectivity, Cu, Ag, Fe, and Pd were greater and may diver higher activities due to the greater surface area of silica relative to ZnO. Silica can also transform silica hydroxide in the presence of steam, resulting in a search for substitutes such as alumina [146].

Alumina has been used as a support for methanol by CO₂ hydrogenation using Cu/ZnO. However, over a prolonged operation that methanol yields have decreased, which could be lessened by the addition of Cu/ZnO/Al₂O₃ [143].

Zirconia has been used as a support with Cu (ZuO) which gave good selectivity and stability that could be increased by the addition of Al₂O₃ as a Cu/ZnO/ZrO₂/Al₂O₃ system. The higher thermal stability of ZrO₂-Al₂O₃ and selectivity of CuO/ZrO₂ may be the reason or the improvement. Also, the Cu/ZnO/ZrO₂ system was found to be more tolerant to water poisoning during methanol synthesis than Cu/ZnO/Al₂O₃ [115].

Recently carbon nanotubes or fibers have been used due to the high surface area and thermal stability of carbon and the ability to adsorb hydrogen via H-adsorption sites. Catalyst particles dispersed onCNT support gave more active sites than on activated carbon, resulting in increased hydrogenation of methanol [121]. Low rates were observed for Pd/CNT suggesting that Pd atoms required to be activated for the hydrogenation reaction to proceed and require a nearby metal oxide. Nanocarbon fibers have also been used and can promote the hydrogenation to methanol from CO₂ at lower temperatures [147].

5.5. Mechanism of methanol synthesis

Whilst the macro-level mechanism is known in that CO₂ adsorption on metal oxide and H₂ on metal, with the formation of intermediates being the rate-determining step in methanol synthesis through CO₂ hydrogenation on copper [148]. The active species appears to be Cu(0), although other studies also suggest that Cu(I) stabilized on the catalyst (Cu(0)) surface also assists with CO₂ adsorption and has a bearing on methanol selectivity as well as activity [127]. This stabilization may also assist with the formation of the intermediate formate (HCOO⁻) through interactions with atomic oxygen and carbon dioxide resulting in hydrogenation to dioxyxymethylene (HCOOH). The intermediate undergoes further hydrogenation to methyl hydroperoxide (H₂COOH) which dissociates to formaldehyde (H₂O) and hydroxide (HO) [144]. The hydrogenation of formaldehyde to hydroxymethyle (CH₃O), methylene alcohol (CH₂OH), and methyl alcohol (CH₃OH). Other plausible intermediates are carbonyl (HOCO) which form methanol upon additional hydrogenations and were observed using copper catalysts and mass spectrometry of the byproducts, with the methanol originating intermediate identified as formate, derived species [149].

Also, studies on Cu/ZnO/Al₂O₃ show that after adsorption of oxygen and carbon dioxide, carbonate (CO₃⁻) and formate (HCOO⁻) are generated as intermediates, with the carbonate being converted to formate upon additional hydrogenation, forming a methoxy species (CH₃O⁻) and methanol on the final reduction step (CH₃-OH) [150]. Using Pd/Ga/Al₂O₃ only these two species were identified when CO₂ was reduced to methanol, whilst the major species are formate, minor species often identified are varied such as carbonylate (HOOCH) and methylene peroxide (CH₂OO) [151]. The formate is coordinated with the surface metal oxide axially with an adjacent adsorbed carbon dioxide and hydrogen from the metal, with the monodentate formate being unstable at temperatures over 200 °C and is transformed into formic acid (HCOOH) upon a reaction with the newly formed formate [152]. Upon further hydrogenation, a dihydroxyhydroxyl carbonyl (H₂O–OH-C-O) is generated with upon hydrogenation yields formic acid, which in turn undergoes dehydration to product methylene peroxide (CH₂OO) [153]. The unstable methylene peroxide is converted to the methoxy species through reaction with adsorbed hydrogen (H₂) and to methanol upon reduction. The application of bimetallic catalysts such as Cu/ZnO and Cu/ZrO₂ suggest a dual mechanism operating on each catalyst surface, whereby CO₂ hydrogenation occurs on the metal surface with adsorbed hydrogen (H₂) and carbon dioxide adsorption on the metal oxide, with molecular hydrogen adsorption occurring on the copper atoms. Upon adsorption the hydrogen molecules dissociate to form atomic hydrogen and are transported from the Cu surface to the ZrO₂ surface where CO₂ is adsorbed by spillover, to reduce adsorbed CO₂ to formate, methyl species and reduction to methanol [154].

In cases of metal oxide supports, the optimal ratio is not uniform, for example for Cu on ZnAl₂O₄, the Cu:Zn ratio of 0.72 was found to yield the greater activity, whilst for Al/Zn the ratio was 0.5, which reflects sites for synthesis and sites for coordination via monodentate or bidentate formate hydrogenation to methanol via a methoxy intermediate [196–198]. With copper substitution by La, the range for a higher activity for LaMn₁₋ₓCuₓO₃ (0 ≤ x ≤ 1) mod with a modal value of 0.5. The range like with Ag⁺ stabilization that activity is related to the dispersion of Cu⁺ species that is inhibited by the reduction of Cu⁺ to Cu⁰, which is no longer stabilized by Mn in the perovskite [155]. The synthesis of methanol from layered double hydroxides consisting of Zn and Cu offered a high capacity for CO₂ adsorption and alterations of the electronic properties through doping with Ga or Al. Carbon dioxide is converted to CO and methanol with high selectivity being observed for [Zn₁₋ₓCuₓAl(OH)₃]₂(CO₃)₂·mH₂O. A higher ratio of Ga promoted selectivity towards methanol and higher Al towards CO [156].

5.6. Bulk synthesis: reactor design considerations

The catalyst in the forms of beads or pellets can be fixed to the surface in the form of fixed bed reactors, or suspended in a solvent which allows for thermal motion, a form of a slurry reactor which may be charged and then discharged (‘digital’) or steady-state (‘analog’) configuration [128]. In general, fixed-bed reactors are applied to gas phase reactions, where hydrogenation of carbon dioxide to methanol occurs, from 200 °C to 8 atm, using Cu/ZrO₂/ZnO catalyst. Higher conversion may be achieved by switching over to a different catalyst such as CuZnGa or a co-precipitated Cu-Zn-Zr with gel-oxide to provide greater active surface sites relative to co-precipitation with sodium carbonate and coordination with citric acid [157]. The activity of methanol synthesis is related to the number of exposed sites on the Cu surface, whilst selectivity was related to the number of basic sites on the support. The introduction of an electron-receptive atom may improve activity as was demonstrated by the introduction of fluorine on CuZnAl catalyst for CO₂ hydrogenation to methanol [158]. The advantages of a fixed bed configuration are that gas and metal interaction does not require prior mixing, diffusion of reactants does not occur, and the higher volumetric loading of the catalyst and easier to upscale to higher quantities [159]. The deactivation of the catalyst at higher temperatures over time is one disadvantage [160], which may be overcome with new catalysts such as Mo₂O₅ coated by nitrogen and sulfur co-doped carbon (NSC) that as functional after almost 100 h of operation on steam [161]. It was further demonstrated that Cu/Mn catalyst exhibited a selectivity of approximately 49 % at 250 °C for 400 h on steam, and might indicate that a bifurcated reactor design be implemented with separate hydrogen (H₂) and water (H₂O) feed to pre-select the optimal ratio [162].
In a slurry reactor, the reaction is carried out in a liquid phase, such as the operating temperature can be reduced to promote the thermodynamic reaction to the right. In this manner, the catalyst deactivation observed at elevated temperatures can be minimized. The selectivity and activity of CO$_2$ hydrogenation to methanol was found to be greater with a slurry reactor than a fixed bed reactor design [163]. As the reaction occurs in solution, the rate of heating, over-temperature, the temperature gradient can be better controlled with greater precision than with a fixed bed reactor design. In a slurry, the metal catalyst can be dispersed in the form of a powder rather than pellets and are configured in three type configurations. type 1 configuration is used for batch reaction stirred autoclaves, type 2 pump stirred, and type 3 reactant gas used to stir the mixtures [164]. In the slurry, the excess heat is absorbed by the solvent, such as tetrahydroquinoline (C$_6$H$_{11}$N), which can be operated at less than 425 °C and 138 atm (Sun, et al. 2002). The role of solvent is important, as well as co-additives in determining final operating temperature, pressure, activity, and selectivity [165].

### 5.7. Parameter optimization

As hydrogenation to CO$_2$ to methanol is exothermic, thermodynamically, lower temperatures are favored. In practice, higher temperatures are utilized to give the gas and intermediate enough kinetic energy to interact and higher temperatures yield higher activity, up to where the equilibrium constant decreases with increasing temperature [166]. The maximum temperature at which the equilibrium constant will decrease depending on the catalyst type, form, and support material but is from 220–250 °C [150]. This is due to the occurrence of side reactions or the reverse water gas shift reaction, which appears to have faster reaction kinetics than methanol synthesis concerning temperature [167].

To illustrate the difference between reverse water gas shift reaction [168] and methanol synthesis, the most common reaction conditions are summarized in Table 3c (for reverse water gas shift reaction) and 3D (methanol synthesis) (Table 3d).

#### 5.7.1. Effect of temperature

At elevated temperatures, methanol (Eqn: 4) can degrade to carbon monoxide and hydrogen

$$\text{CH}_3\text{OH} \rightarrow \text{CO} + \text{H}_2 \Delta H 298.90 \text{kJ/mol} \tag{4}$$

suggesting an upper limit of 250 °C, above which CO$_2$ is in part converted to CO lessening the methanol yield [169]. The methanol synthesis via hydrogenation also appears to be more sensitive to temperature fluctuations than the reverse water gas shift reaction as can be seen by comparison of operating condition variance between the two (Tables 3a versus 3b variables) reactions [170]. At 350 °C, the probability of methane formation is high. Similarly, the selectivity of methanol decreased from approximately 38% at 220 °C to 2% at 300 °C [171]. Therefore, the optimal temperature appears to be between 220–250 °C but is highly dependent on the catalyst [172].

#### 5.7.2. Effect of pressure

While the thermodynamic yield favors lower temperatures, the thermodynamic calculations point to higher pressures for the reduction reaction, with the reverse water gas shift reaction would decrease at higher pressures [173]. Higher pressures also favor oxygenated byproducts such as dimethyl ether, with additional safety concerns of chambers at very high pressure. Most pressures are from 18 atm to 50 atm using Cu/Zn/Zr/Al/Zr fibrous catalyst or Cu/Al$_2$O$_3$ or Cu/ZnO/Al$_2$O$_3$ catalysts in a slurry reactor at 250 °C [174].

#### 5.7.3. Effect of feed gas composition

The stoichiometric reaction indicates one mole of carbon dioxide to three molecules of hydrogen (H$_2$) gas, thus a ratio of (H$_2$ : CO$_2$) of 3 is favored for CO$_2$ hydrogenation to methanol [175]. In reactor practical applications it has been demonstrated that at higher pressure, the reaction is controlled thermodynamically with a ratio of CO$_2$ : H$_2$ of > 10, but at lower pressures, it is kinetically controlled (ratio < 10), with a suboptimal ratio between 3–10 depending on the final pressure (Shen et al. [54]). Computational calculations at a fixed pressure (28 atm) but at varied temperatures (200–280 °C) or fixed temperature (240 °C) but at varied pressures (9–89 atm) show a linear relationship between H$_2$: CO$_2$ ratio and methanol yield (Kim, et al. 2003). In a slurry reactor, an increase of the H$_2$: CO$_2$ ration from 2-5 resulted in higher CO$_2$ conversion due to the availability of hydrogen to promote hydrogenation and methanol synthesis [176].

### 6. Conclusion

A problem could also be viewed as an opportunity to be solved. In the current situation of the global epidemic, digital technology plays an irreplaceable role in social life and is also exerting a profound impact in the field of energy. The Chinese government is making efforts to promote technological upgrading in the energy sector through policies and the market, especially in the integration of energy expertise and digital technology, as well as energy conservation and environmental protection technology and digital technology, to create an energy ecology based on local conditions, wisdom and comprehensively in energy-

| Table 3c: Summary of activation energies, and reaction conditions for reverse water gas shift reaction. |
|---|
| Catalyst | $E_a \text{kJ/mol}$ | CH$_3$OH RWGS | T (°C) | Pressure (atm) | Feed gas |
| Cu/ZnO | 64 | 121 | 0.98 | H$_2$/ CO$_2$ |
| Cu/ZrO$_2$ | 50 | -93 | 16.78 | CO$_2$ |
| CZA (Cu/ZnO/Al$_2$O$_3$) | 54.5–104 | 109-125 | 14.8–49.3 | H$_2$/ CO$_2$ |

| Table 3d: Summary of reaction conditions for the methanol synthesis reaction. |
|---|
| Catalyst | Temperature (°C) | CH$_3$OH Activity (g/Kg.h) | CO$_2$ Conversion (%) | Ref. |
| Ag/ZnO/ZrO$_2$ | 219.7 / 78.9 | 15 | 2 | [218]. |
| Cu(ZnGa) | 249.3 / 29.6 | 40 | 5.48 | [219]. |
| Microwave Assisted Synthesis | | | | |
| Cu/B$_2$O$_3$/ZrO$_2$ | 249.3 / 19.7 | 57 | 16 | [127]. |
| Cu/Ga$O_3$/ZrO$_2$ | 249.3 / 19.7 | 62 | 13.7 | [220]. |
| Cu/Zn$O/ZrO_2$ | 249.3 / 29.6 | 131 | 1 | [221]. |
| Cu$Zn$/Al/Zr-F | 249.3 / 49.3 | 390 | 22 | [222]. |
| Cu/ZnO | 240 / 29.6 | 240 | 17 | [223]. |
| Cu/ZnO/ZrO$_2$ | 249.3 / 19.7 | 20 | 11 | [220]. |
| Cu/ZrO$_2$ | 249.3 / 29.6 | 116 | 1 | [220]. |
| Cu/ZnO/Al$_2$O$_3$ | 249.3 / 40.5 | 55 | 18.2 | [224]. |
| Cu/ZnO/Cu$O/ZrO_2$ | 249.3 / 19.7 | 137 | 15 | [225]. |
| Cu$Zn$/ZrO$_2$ | 249.3 / 19.7 | 31 | 12 | [223]. |
| MgO/Al$_2$O$_3$ | | | | |
| Cu$Zn$/Zr/Al$_2$O$_3$ | 249.3 / 49.3 | 10 | 23 | [226]. |
| La$Cu$/Cu/ZnO | 249.3 / 49.3 | 80 | 8 | [227]. |
| Pd/Si$O_2$ | 249.3 / 40.5 | 9.86 | 3 | [228]. |
| Pd/ZnO/Al$_2$O$_3$ | 249.3 / 29.6 | 24 | 4.4 | [121]. |
| Pd/ZnO/CNTs | 249.3 / 29.6 | 37 | 6.3 | [121]. |
using, and security with science and technology.

One technological approach is carbon dioxide hydrogenation to methanol via homogeneous catalysis, which was inefficient due to lower catalyst recovery and regeneration. Consequently, heterogeneous catalysis has been adopted using a reverse water gas shift reaction, whereby carbon dioxide and hydrogen gases are converted to carbon monoxide and water by the water gas shift reaction and the resulting gas mixture of CO/CO2/H2 is channelled into a slurry reactor after removing water. The recent introduction of Cu/ZnO based catalysts indicates higher selectivity and activity to methanol than prior approaches due to operation near-optimal thermodynamic conditions such as low temperature and moderate pressures and remove off heat due to efficient heat removing solvent. Whilst direct CO2 hydrogenation to methanol is a new technology, advances in a catalyst, reactor design, and operational at lower temperatures are pushing these technologies to be competitive with electricity generation from fossil fuels, with the catalyst being based around Cu, such as Cu/ZnO, NiB2O3 or GeO2, with carbon nanotubes as support. Due to the exothermic profile of the reaction, low temperature and high pressure will favor methanol selectivity over methane or other by-products, due to depression of the reverse water gas shift reaction and methanol decomposition. The stoichiometric ratio of H2:CO2 is 3 is also favored for the hydrogenation reaction, but practical applications have a ratio of 3–10.

Author contribution

Dr. Gao conceived the thrust and wrote the first draft. Dr. Liu did Figs. 1, 4 and 5 and the section on catalysis. Lastly, Dr. Bashir contributed to the analyses of emission data, catalytic technologies, Fig. 3, and references and copyright.

Declaration of Competing Interest

Two of the authors are from TAMUK (Dr. Sajid Bashir and Jingbo Liu) and Dr. Liu is also a Guest Editor. However the manuscript will still go through the peer-review process.

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