Original Paper

Kinetic conversion of carbon dioxide in Supported Tungsten Carbide Catalysts and Oxide Catalysts for the Reverse Water Gas Shift Reaction

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Abstract

The reverse water-gas shift reaction (RWGS) had a critical stage in the conversion of abundant carbon dioxide into chemicals or hydrocarbon fuels and has attracted widespread interest as a renewable fuel assembly system in unconventional ways. Interest has been in industrial applications such as the catalytic activity, carbon dioxide conversion, kinetics, and efficacy levels of tungsten carbide-supported catalysts and carbide oxide catalysts for the production of RWGS reaction. Additionally, carbide oxides have the ability to enhance RWGS and develop high-performance catalysts in RWGS. The RWGS reaction was ($CO_2 + H_2 \leftrightarrow CO + H_2O$; $\Delta G° = 27.94$ kJ/mol) an exothermic reaction that exhibits equilibrium conversion with temperature.

Introduction

A reverse water gas shift (RWGS) reaction had been seen for the first time in 1780 by Felice Fontana. At the time, Fontana showed that a combustible gas is produced when steam is passed through a bed of incandescent coke [1]. Furthermore, Mond and Langer discovered and reported for the first time in the literature on the RWGS reaction [2] in 1888. The first industrial application of this reaction happened in 1913 for the production of synthesis gas, as a part of the Haber-Bosch process of ammonia manufacture [3]. In addition, the RWGS reaction was one of the fundamental reactions which occur during supercritical water gasification. RWGS reaction [4, 5, 6] is an equilibrium reaction and the CO_2 conversion to CO is depending on temperature. There are very specific studies on reactions at temperatures above 873 K, thus to obtain a high conversion effective reactions need high temperatures. The CO_2 conversion to CO by hydrogenation catalytic is recognized as a very promising process. In industry, synthesis gas containing hydrogens and CO can be used to prepare CH_3OH as well as long-chain hydrocarbons via the Fischer-Tropsch synthesis. Therefore, the RWGS reaction was an important option for carbon monoxide production [6]. The WGSR reaction plays a major role in integrating gasification techniques with the hydrogen production and recovery unit; it is also considered a general industrial reaction in the production of chemicals and hydrogen. The effluent stream of the gasifier, mainly hydrogen, carbon monoxide, and carbon dioxide at high-pressure reach to 30 atm and temperatures reach to 400-1000ºC, would be directed

water-gas shift reactor along with steam where reaction (Equation 1) will take place, which increases the hydrogen yields [7].

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H = -40.6 \text{ KJ/mol} \qquad (1)$$

The RWGS reaction was an exothermic, equilibrium-limited reaction that exhibits decreasing conversion with increasing temperature. The temperatures below 600 °C catalyze the WGSR reaction as this study show. A catalyst is required under these conditions because of the lower reaction rate at low temperatures. However, recent developments in high-temperature materials have resulted in hydrogen separation membranes, reviving interest in RWGS reactions. The permeation of hydrogen through the walls of a membrane reactor enables the attainment of high conversion of carbon monoxide and steam to H_2 and CO_2 [8].

Materials and Methods

Preparation of activated carbon (AC)
In this study, the date palm fronds (PDF) were cut into small pieces of about 1-2 cm, washed with water, and subsequently dried under the sun. These steps were followed by the crushing and sieving of the particles to a mesh size of 1-4 mm. The palm pieces were then washed with hot water and further subjected to heat from the sun to remove any moisture content. Thereafter, the samples were wrapped in aluminum foil and carbonized at 400°C for 2 hours in an evaporating dish at a heating rate of 30°C/min. The resulting char was soaked in potassium hydroxide (KOH) solution with a ratio of 1:2 (w/w%) respectively for 24 hours. The sample was then activated at power 360-630W. The activated product was then cooled to room temperature and washed with 0.1M hydrochloric acid and afterward with hot distilled water [9, 10].

Preparation of tungsten carbide
In this study, the prepared carbon would be used in microwave induce alloying to the prepared tungsten carbide. The effect of KOH concentration was used in preparing the catalyst, tungsten hexacarbonyl powder was mixed with the appropriate amount of the activated carbon [7, 8]. There are several common methods used to prepare tungsten carbide catalysts and the one which was mostly used the involved reaction of solid precursor, either as metal or oxide with gas-phase containing reducing agent or carbonizing agent [9]. In this study, tungsten carbide catalyst was prepared using tungsten hexacarbonyl

and activated carbon as precursors. In preparing the catalyst, tungsten hexacarbonyl powder [$W(CO)_6$] (1g for all samples) was mixed with the appropriately activated carbons AC(1:2). The prepared sample was put together in a glass Petri dish. Thus, a glass Petri dish was placed on the hot plate, then set the ice bath on the lid and turned the heat on very low for 1 h, and to force the carbonyl to sublime evenly onto the activated carbon. Finally, the catalyst was put through heat treatment in the microwave-induced with a power of 360-630 watts. The duration of microwave exposure ranged from 2-5 mins under nitrogen gas. This activation takes about 4 hours until remove all moisture of the catalyst is. The tungsten carbide prepared was labeled as in Table 1. The previous study by Salma and Issa, 2020 describes the use of a continuous flow reactor cell in carrying out an RWGS reaction by different reactive mixtures of CO_2 and H_2 via WC, at temperatures from 100 to 400°C [11, 12].

Table 1: Experimental variable for tungsten carbide supported on activated carbon

W(CO)₆/AC Activation Method			
Impregnation Ratio (in gram)	Energy (Watt)	Sample Code	Time hours
1gW(CO)₆:2gAC (1:2)	360-630	WC	4

Results& Discussion
Kinetics of the RWGS reaction
The importance of support catalysts was increasing decades later. The support also functions to influence the catalytic properties of the supported metal catalysts through geometric or electronic effects. In this study, the WC effects provide catalytic characteristics of supported catalysts for the RWGS reaction. The high electron-donating property of metallic WC in contact with the ion site is caused by the Tungsten carbide-Support Interaction (WC-SI) effect, which generates new sites for CO production over the WC catalyst. Additionally, the WC-SI effect selectively weakens the binding of the C-O bond and O-bond intermediates at the tungsten-oxide interface, thus leading to the high selectivity toward CO in the RWGS reaction. For WC-supported catalysts, a result of its treatment in a $CO_2:H_2$ environment at 100-400°C. The high coverage of the adsorbates (WO_x) on the support induces oxygen vacancy formation, driving the migration of the WO_x-functionalized support onto the metal. This WC encapsulation state was more stable against re-oxidation by H_2O in the RWGS reaction process. Therefore, modulation of

Table 2: The data RWGS reaction kinetics obtained from the K values calculated at different temperatures.

Temp (ºC)	Temp (ºK) (K = °C+273)	1/temp (K^{-1}) $\times 10^{-3}$	Time (sec)	k =1/time (sec^{-1})	In k= In (1/time)
100	373	2.68	40	0.025	-3.69
150	423	2.36	45	0.022	-3.81
200	473	2.11	50	0.020	-3.91
250	523	1.91	55	0.018	-4.00
300	573	1.75	60	0.017	-4.09
350	623	1.61	65	0.015	-4.17
400	673	1.49	70	0.014	-4.25

the chemical state of the metal species by the WC-SI was more important for the regulation of the observed CO selectivity in the RWGS reaction. For the WC catalyst, the WO_3 and WO_2 interface structures can be generated by the electron transfer WC on its surface through the WC-SI effect, which can boost the adsorption and activation performance of reactant CO_2 and H_2 molecules for RWGS reaction.CO_2 hydrogenation was a thermo-dynamically favorable process ($\Delta G° = -27.94$ kJ/mol). However, the reaction requires a suitable

Table 3: The kinetic data for activation energy ($\Delta G°$) of reverse water gas shift (RWGS) reaction

Catalyst	Temperature (ºC)	Activation energy $\Delta G°$ (kcal/mol)
WC	100-400	−27.94

catalyst to overcome the kinetic limitation associated with reducing CO_2 to CO (RWGS reaction). The reaction favors low temperatures and high pressures, although it attains equilibrium conversions at lower temperatures. Thus, lower temperature leads to the activation of catalysts through coke and sinter. To

Table 4: A time taken for the calculated rate reaction at varied temperatures

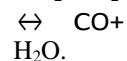| Temperature (ºC)	Time taken for the complete collection and measure gas (seconds)				Average time (seconds)	Reaction rate = (1/time) (seconds^{-1})
	Time taken to control and balance temperature	Time taken to collect gas				
		Initial	Final	Total time (Initial + Final)		
100	60	05	15	20	40	0.025
150	58	13	19	32	45	0.022
200	60	17	23	40	50	0.02
250	58	23	29	52	55	0.018
300	60	55	05	60	60	0.017
350	56	34	40	74	65	0.015
400	45	45	50	95	70	0.014

maintain the reactor at a relatively low temperature, proper cooling is required for the reactor.

The logarithm of k obtained depends on the temperatures; this layout is represented in Figure 1 and Tables (2–4). A scheme of the reaction rate versus temperature was created for this experiment

(Figure 1), in order to monitor the effects of temperatures on the plot of the reaction. It is clear that both under circuit operation of open and closed, CO formation rate increases with increasing temperature. This behavior is more pronounced in the potential negative cases. At negative potentials, the CO formation rate was dramatically enhanced, while by supplying the flow both of CO_2 and H_2 to the reactor chamber the rate was slightly decreased. Figure 1 showed the reaction rate at different temperatures. A negative rate of reaction indicates CO consumption via a reaction forward. As expected the reaction passed from the reverse to the reaction of forward with increasing temperatures of the product. It is possible to have negative activation energy ($\Delta G°$) because some reactions have negative (barrier-less).Chemical kinetics and dynamics have studied a reaction with negative activation energy showing an Arrhenius plot with a negative dependence on constant rate with temperatures. Therefore, the rate constant would decrease with increasing temperatures (Table 3). The implication for the thermodynamics (steady-state, time-independent) is that the products are at a lower energy (more stable) than the reactants (endothermic or endoergic reaction). Note that while the reaction of an endothermic can have a positive or zero barriers, a barrier-less reaction implies endothermicity (or less often a thermoneutral reaction, i.e. equal energies between products and reactants). However, an addition reaction is $CO_2 + H_2 \leftrightarrow CO + H_2O$. Thus, if the approach is too fast (high temperature), the product (CO and 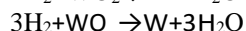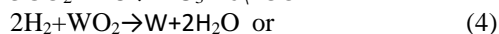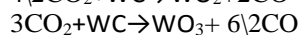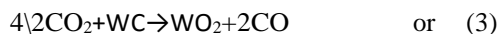H_2O) would be more likely to fall apart because there was simply too much energy for product stability. In this case, a cool third body or third inert reactant was needed to remove energy possibly with multiple collisions from the product (CO and H_2O) to prevent dissociation back to reactants CO_2 and H_2.

In Figure 2 (a,b): WC, the peak of CO appears very clear at temperatures from 250°C to 400°C. There were peaks constant at 100 to 250°C, while we observed clear change for peak from 300 to 400°C. The result showed adsorption of carbon monoxide (CO) when the region was between 2070−2080 cm⁻¹. The study of catalysts has been completed by adsorption of CO coupled to IR spectroscopy. The spectra of surface species arising from CO adsorption over the reduced catalysts are shown in Figure 2 (a,b). In the region 2000−2100 cm⁻¹, a main CO band appears split at about 2050 to 2080 cm⁻¹, the first component being more intense. Bands can be assigned to CO linearly adsorbed over reduced metal center. Where the form CO appeared on two peaks was close to each other. For CO_2 and H_2 mixture, the main reaction for carbon monoxide and water formation was (as shown in equation 2); Reverse Water Gas Shift Reaction (RWGS reaction).

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (2)$$
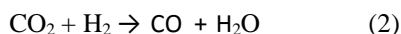
Mechanism of CO_2 formation in reverse water gas shift reaction over WC prepared catalyst

It indicates that W atoms provide active site to dissociate CO_2, while the reduction of oxidized W catalyst has to be faster than the oxidation process. Hydrogen was proposed to be only a reducing reagent without direct participation in the formation of intermediates in the RWGS reaction. The redox mechanism for the RWGS reaction has been simply modeled by following equations:

$$4\backslash 2CO_2 + WC \rightarrow WO_2 + 2CO \qquad or \quad (3)$$
$$3CO_2 + WC \rightarrow WO_3 + 6\backslash 2CO$$
$$2H_2 + WO_2 \rightarrow W + 2H_2O \quad or \qquad (4)$$
$$3H_2 + WO \rightarrow W + 3H_2O$$

Conclusions

A rate equation for a reverse water gas shift reaction is obtained based on a redox mechanism over WC catalysts. The rate reaction of the reverse water gas shift reaction was studied at low temperatures (373−673 K) conditions. The rate expression was characterized by the pre-exponential factor, 0.025 s⁻¹, and energy of activation, −27.94 kJ/mol for CO (RWGS reaction). The CO_2 hydrogenation has been simulated based on the kinetic equation of the carbon dioxide conversion to carbon monoxide (RWGS reaction) to find an optimum operating condition to form carbon monoxide from CO_2.

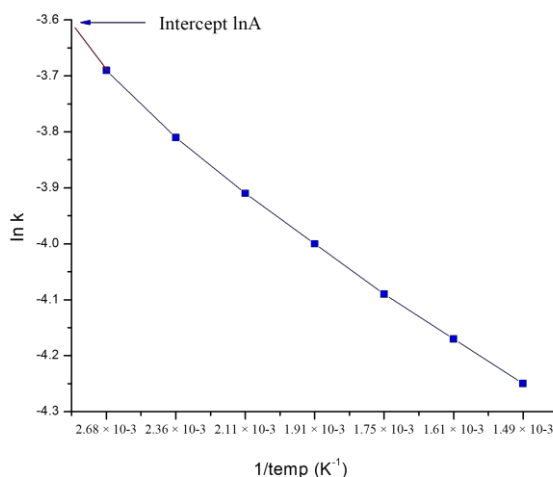The catalytic activity of this supported catalyst was investigated via hydrogenation CO_2 reactions.

Figure 1: Rate reaction analysis of RWGS activity
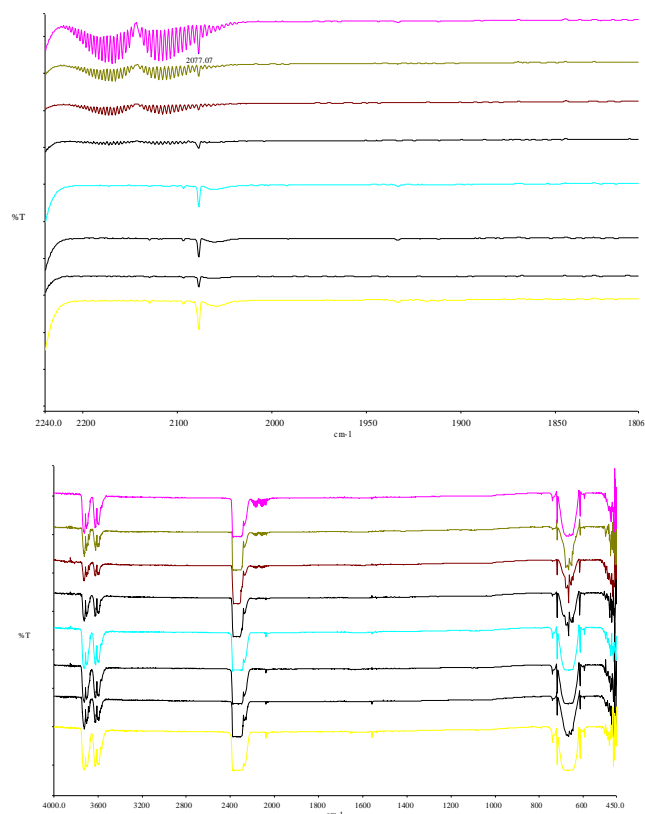

Figure 2 (a, b): IR spectra of CO_2 hydrogenation over catalyst WC at different temperatures

It is concluded that catalysts that prepared WC showed the best catalytic activity which resulted in the production of reverse water gas shift (RWGS) reaction. RWGS rate was found to provide an improved description of the RWGS kinetic data. These results indicated that by decreasing the catalyst

particle size, the activation energy of the RWGS reaction increased and as a result, the reaction rate decreased consequently. The main role of WO_3 and WO_2 was to provide active sites for the formation of CO (RWGS reaction) and adsorption of CO_2. Hydrogen which was dissociatively adsorbed on WC could be spilled over to WO_x to associate with CO_2, resulting in the formation of CO.

Conflict of interest

The authors declare that no conflict of interest exists.

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