Alcohol synthesis from syngas over $K_2CO_3/CoS/MoS_2$ on activated carbon

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Supported K_2CO_3/Co–MoS_2 on activated carbon was prepared by a co-impregnation technique and has been characterized by X-ray diffraction (XRD) and BET. Active ingredients ranged from 39 to 66% and included molysulfide and cobalt sulfide. XRD analysis indicates that cobalt and molybdenum sulfides are found in the Co_3S_4 and Co_9S_8 phases. These catalysts were performance tested in a fixed-bed reactor under higher alcohol synthesis conditions, 2000–2400 psig and 270–330 °C. Active chemicals on the carbon extrudates decreased the surface area dramatically, as measured by BET. Surprisingly, at the high level of active chemicals, alcohol productivity and selectivity were decreased. An increase in the reaction temperature led to a decrease in the selectivity of methanol and an increase in selectivity of hydrocarbons. Total alcohol productivity was also increased as gas hourly space velocity (GHSV) was increased. Co_9S_8 may play a role in the catalyst aging process. In prolonged reaction periods (140 h), sulfur is lost from the surface, possibly as H_2S. The quantity of Co_9S_8 on the surface appears to increase as the catalyst ages.

KEY WORDS: alcohol synthesis from syngas; $K_2CO_3/CoS/MoS_2$; activated carbon

1. Introduction

In the catalyst industry, it is widely recognized that higher alcohols can simultaneously be generated with methanol from synthesis gas by an appropriate alkali-modified MoS_2 [1]. A process to convert synthesis gas to alcohols over Mo-based catalysts was developed by Dow and Union Carbide [2]. The role of alkali is to slow or to suppress the hydrogenation ability of surface alkyl species to form alkanes as well as to increase the active sites for alcohol formation [3,4]. Activated carbon has also been used as a catalyst support with a porous structure, averaging about 1000 m^2/g [5].

Quarderer and Cochran [6] and Kinkade [7] investigated many catalysts related to the Fischer–Tropch process to make alcohols, and particularly described the alkali promoted Mo-based catalyst under moderate alcohol synthesis conditions, a pressure range of 10340–20680 kPa (1500–3000 psig), and a temperature range of 240–325 °C. Potassium carbonate was the alkali of choice in promoting MoS_2-based catalyst. The level of potassium was varied from zero to 10 wt% of the total catalyst. The total alcohol productivity of the catalyst on a CO_2 free basis was 0.138 kg/kg-cat h at 260 °C and 1200 psig with a gas hourly space velocity (GHSV) about 1300 h^{-1} [6]. The total alcohol and hydrocarbon selectivities were 85.5 and 14.4%, respectively. The authors reported that the alcohol yield was a function of temperature and pressure.

Murchison [8] tested molysulfide on both alumina and carbon and showed that the carbon support was superior to alumina. The activated-carbon-supported catalyst showed alcohol selectivity about six times higher than that from the alumina-supported catalyst. The productivity of ethanol and higher alcohols was increased by the addition of H_2S to the synthesis gas feed although system response to the addition/deletion of H_2S to the feed was slow. He also found that the addition of CoS to the catalyst, at a 0.5 molar ratio of Co/Mo, provided the same performance as the addition of H_2S. This was not confirmed in long term testing. Murchison presented XRD patterns for a CoMo sulfide catalyst with and without Co_9S_8. However, the catalyst preparation procedure and testing conditions are not fully disclosed.

The surface composition of the cobalt–molybdenum catalyst depends strongly on the preparation procedure [9]. It has been proposed that Co_9S_8 can be generated in Co–MoS_2 catalyst, depending on the atomic ratio of Co/Mo and preparation method. Cobalt may exist in two major phases that have very different catalytic properties (Co_9S_8 and Co–Mo–S). Co_9S_8 contributes little to the catalyst for alcohol production, and it is stable under typical reaction conditions. Inamurra and Prins [10] examined the role of Co in unsupported Co–MoS_2 catalyst by XRD for both impregnation and co-precipitation methods. Co_9S_8 was observed at a Co/Mo atomic ratio of 0.43 when the impregnation method was used. Whereas Co_9S_8 was observed at a Co/Mo atomic ratio of 1 when the co-precipitation method was used.

In the present investigation, supported $K_2CO_3/CoS/MoS_2$ catalysts on activated carbon were prepared by a co-impregnation technique at two levels of active chemicals, 39 and 66%. The productivity and selectivity of products have been investigated at both levels as a function of temperature and GHSV. Fresh catalysts were characterized by BET surface

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area and X-ray diffraction (XRD). An XRD analysis was also made following an extended performance testing period of 140 h in a fixed-bed reactor for a low level of active chemicals. The aging process of the catalyst may be related to the loss of sulfur from the surface and the development of Co_9S_8 over the life of the catalyst.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared at two levels of active ingredients, by a co-impregnation procedure with a molar ratio of Co/Mo ratio of 0.5. The low-end catalyst contained 39% active ingredients and the high-end catalyst contained 66% active ingredients. The low-end catalyst is designated as Low_AI and the high-end is designated as High_AI. Catalysts used in the present work are shown below. Compositions are as follows:

Low_AI $K_2CO_3/CoS/MoS_2$/activated carbon = 39% CoMoS;
High_AI $K_2CO_3/CoS/MoS_2$/activated carbon = 66% CoMoS.

Catalysts were prepared by a co-impregnation method which consisted of an aqueous mixture of ammonium molybdate tetrahydrate (AMT) ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), potassium carbonate ($K_2CO_3$), and cobalt(II) sulfide (CoS). This mixture was prepared by adding 9 g of AMT in 60 g of 20 vol% ammonium sulfide solution $(NH_4)_2S$ at 65–70 °C, and then K_2CO_3 (1.26 g) and CoS (2.32 g) were added to the solution. For the Low_AI catalyst, fifteen grams of 3 mm activated carbon extrudates were heated to 115–120 °C for 30 min in a glass dish to remove moisture in the carbon. The mixture described above was stirred vigorously at 65–70 °C and was impregnated on the activated carbon in a drop-wise fashion until the carbon was thoroughly wetted. The catalyst was air-dried at ambient temperature under a hood. This impregnation procedure was repeated until one-half of the solution was added to the carbon extrudates. The semi-dry impregnated extrudates were calcined under a nitrogen atmosphere. The calcination was conducted in a furnace by ramping the temperature at a rate of 2 °C/min to 450 °C and holding for 2 h. After calcination, the remainder of the solution was heated to 65–70 °C and impregnated on the catalyst using the same procedure. The catalyst was calcined for the second time using the same procedure. High_AI catalysts were prepared by co-impregnation using the same procedure.

2.2. Analytical equipment

Surface areas of the catalysts were determined by a Quantasorb Surface Area Analyzer (QSAA). The measurement was based on the single point BET method. A mixture of helium and nitrogen was passed through the catalyst sample holder at −195.78 °C (using liquid nitrogen), and nitrogen was adsorbed physically on the surface of the catalyst.

XRD analyses were performed by Siemens Energy and Automation, Inc. (Madison, WI). An X-ray diffractometer (Siemens Analytical X-ray System Inc., D5000) was used to obtain the diffraction patterns of the catalysts. No grinding or other type of sample preparation was done prior to the data collection. A 10 s count time was chosen and the analysis was performed at 2θ values from 5° to 92°.

A Hewlett–Packard model 5890 gas chromatograph (GC) equipped with a Carboplot P7 column and a thermal conductivity detector (TCD) was used for the identification and quantification of gaseous products leaving the reactor.

A Hewlett–Packard model 5972A gas chromatograph/mass spectrophotometer equipped with a Poropak-Q column was used for the identification and quantification of liquid products.

Moisture in the product was measured by a Karl Fischer (aquametry) apparatus.

2.3. Reactor and catalyst performance testing

A single-pass, fixed-bed reactor was designed for catalyst performance testing. See figure 1. It consisted of a 316 stainless-steel tube (ID = 7.747 mm and $L = 317.5$ mm), a furnace, mass-flow-meter, a pressure control device (dome regulator) which controlled the pressure up to 2700 psig. A back-pressure regulator was used to reduce the pressure to atmospheric. The low pressure gas stream passed through a wet test meter before being vented to the atmosphere. The reactor furnace had three heating zones and their temperatures are individually controlled by a CAMILE data acquisition and control system. A valve between the back-pressure regulator and wet test meter was used to adjust the flow rate. The reaction zone (Z_1–Z_2) was sandwiched between two layers of Pyrex beads, the preheat zone and the exit zone. Condensable products were cooled and drained at periodic intervals. Non-condensable products were vented to the atmosphere through a wet test meter.

3. Results and discussion

3.1. Surface area

CoMoS/K catalysts on carbon supports were characterized by BET surface area. Prior to impregnation, the carbon extrudates had a BET surface area of 1050 m^2/g. After co-impregnation, surface areas for the two catalysts were significantly reduced and are as follows:

carbon extrudates	1 050 m^2/g,
Low_AI	422 m^2/g,
High_AI	307 m^2/g.

These numbers show that surface areas were decreased by 60.0% (628 m^2/g) for Low_AI catalysts and 70.8% (743 m^2/g) for High_AI catalysts. These reductions may have an impact on performance.

3.2. Performance of Low_AI catalyst

Table 1 shows alcohol productivity, selectivity, liquid and gas product compositions, and CO conversions (CO_2 free)

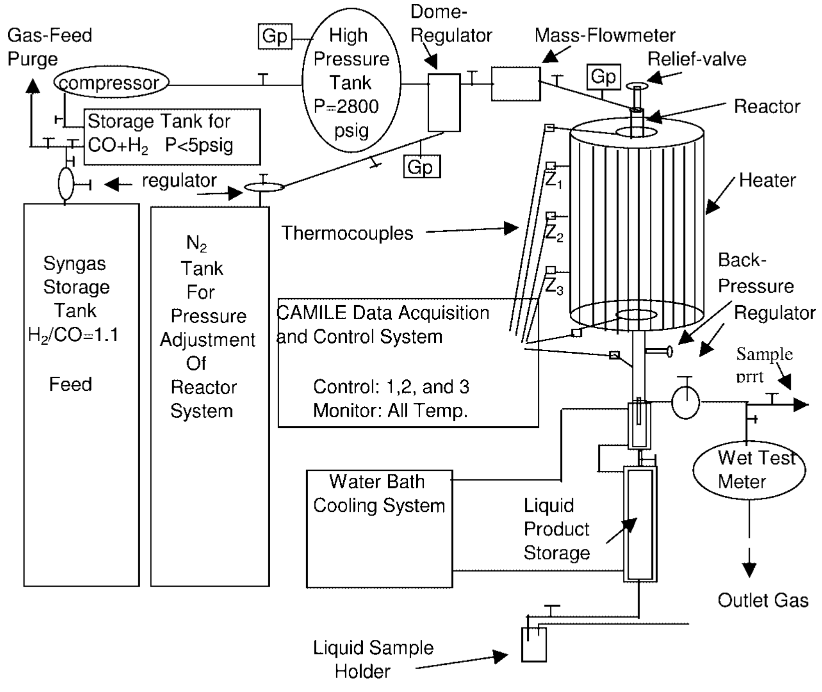

Figure 1. Schematic of the reactor system for alcohol synthesis operation.

Table 1
Results of Low_AI catalysts (weight of catalysts = 4.7 g)

	Run 1	Run 2	Run 3
Reactor temperature (°C)	270	270	290
Reactor pressure (psig)	2100	2100	2000
GHSV (1/h)	1879	2546	1744
Feed ratio H_2/CO	1.1	1.1	1.1
Alcohol productivity (kg/kg-cat h)	0.25	0.25	0.39
Liquid product composition (wt%)			
Methanol	64.80	61.10	72.74
Ethanol	26.20	27.00	20.56
1-propanol	4.10	4.70	3.67
1-butanol	1.20	1.40	0.68
Water	3.80	5.90	2.98
Gas product composition (mol%)			
H_2	50.55	50.56	48.00
CO	47.10	47.25	46.70
CH_4	0.60	0.51	1.64
CO_2	1.77	1.70	3.65
C_2H_6	0.00	0.00	0.00
C_3H_8	0.00	0.00	0.00
Alcohol selectivity			
Methanol	52.47	49.03	53.68
Ethanol	29.51	30.14	21.10
1-propanol	5.31	6.03	4.33
1-butanol	1.68	1.94	0.87
Total	88.97	87.14	79.98
Hydrocarbon selectivity			
CH_4	11.04	12.85	20.02
Conversion of CO mol% exclusive CO_2	13.54	10.40	14.01

Table 2
Results of High_AI catalysts (weight of catalysts = 9.5 g)

	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Reactor temperature (°C)	300	300	310	290	330	330	330
Reactor pressure (psig)	2000	2400	2400	2400	2400	2400	2400
GHSV (1/h)	1836	1638	1692	1542	1980	1152	4032
Feed ratio H_2/CO	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Alcohol productivity (kg/kg-cat h)	0.18	0.20	0.20	0.14	0.22	0.15	0.32
Liquid composition (wt%)							
Methanol	64.60	62.28	62.07	66.60	52.12	42.80	61.58
Ethanol	24.33	26.60	27.73	23.75	30.67	36.40	26.54
1-propanol	5.00	5.87	6.28	4.29	10.64	12.50	6.43
1-butanol	0.61	0.99	1.03	0.75	1.50	2.04	0.96
Water	5.44	4.85	3.14	5.15	5.65	6.94	5.15
Gas composition (mol%)							
H_2	47.09	49.03	48.31	49.51	47.00	48.08	48.92
CO	43.71	47.14	46.17	48.51	44.50	45.65	47.74
CH_4	2.86	2.86	3.98	1.26	6.12	4.53	2.36
CO_2	6.14	0.96	1.07	0.71	1.23	1.16	0.97
C_2H_6	0.21	0.00	0.47	0.00	1.00	0.58	0.00
C_3H_8	0.00	0.00	0.00	0.00	0.20	0.00	0.00
Alcohol selectivity							
Methanol	38.60	42.14	35.33	51.03	23.20	24.50	37.78
Ethanol	20.22	25.04	21.95	25.31	19.00	28.93	22.65
1-propanol	4.78	6.35	5.72	5.26	7.57	11.44	6.31
1-butanol	0.63	1.16	1.01	1.00	1.15	2.02	1.02
Total	64.23	74.69	64.01	82.60	50.92	66.89	67.76
Hydrocarbon selectivity							
CH_4	31.31	25.31	29.11	17.40	34.47	26.40	32.24
C_2H_6	4.46	0.00	6.88	0.00	11.26	6.75	0.00

as a function of temperature (270–290 °C) and GHSV over the Low_AI catalyst. The total alcohol selectivity decreased from a nominal 89% at 270 °C to a nominal 80% at 290 °C. However, this 20 °C increase in reaction temperature, at constant pressure, led to an increase in the quantity of both methane and carbon dioxide.

3.3. Performance of High_AI catalyst

Table 2 shows the alcohol productivity, selectivity, liquid and gas product compositions, and CO conversions (CO_2 free) as a function of temperature, pressure, and GHSV over High_AI catalysts. It was surprising to note that at the higher level of active chemicals, 66 *versus* 39%, the High_AI catalyst showed a decrease in total alcohol productivity and selectivity. C_{2+} hydrocarbons were not detected in the gas product stream for Low_AI catalysts, but C_{2+} hydrocarbons were detected when High_AI catalyst was being used.

3.4. Steady state conditions

It is not unusual for a catalyst to require a break-in period to stabilize its output and this is the case for cobalt/molysulfide catalysts. This induction period is characterized by rapidly changing parameters of selectivity and productivity in the first few hours of operation. Figure 2 illustrates the change of selectivity and CO conversion on cobalt molysulfide catalyst at 2400 psig and 300 °C, as a function of time from the beginning of the run. It is clear from the data that an extended period of operation is required to achieve steady state conditions; constant CO conversion, constant alcohol production, constant alcohol selectivity. Data show that the selectivity to alcohols continued to increase through 20 h of operation. However, the slope between 15 and 20 h was relatively mild indicating an approach to steady state. Other parameters also showed an approach to steady state. In the present study, catalysts were conditioned for an appropriate period prior to data collection.

3.5. Pressure effect

Figure 3 shows the pressure effect on alcohol productivity, CO conversion, and product selectivity for High_AI catalyst. When the pressure was increased from 2000 to 2400 psig at 300 °C and GHSV $= 1600–1800\ h^{-1}$, the total alcohol selectivity and productivity was increased from 64.2 to 74.7% and 0.18 to 0.20 kg/kg-cat h, respectively. Higher pressure at a constant temperature favors the formation of higher alcohols [6].

3.6. Temperature effect

Figure 4 shows the selectivity to products, CO conversion, and alcohol productivity for the catalysts as a function

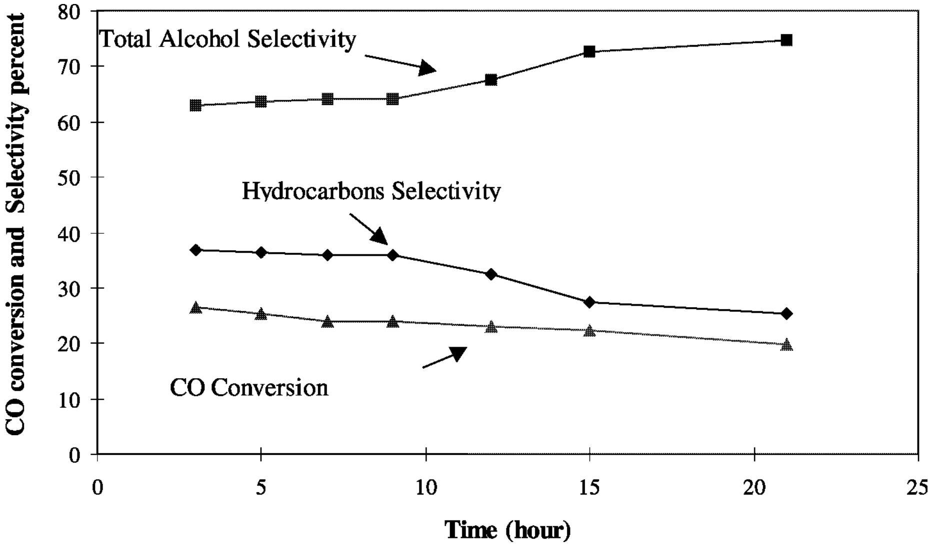

Figure 2. Selectivity and CO conversion *vs.* time for High_AI catalyst at $T = 300\,^{\circ}\mathrm{C}$ and GHSV = 1638 h^{-1}.

of temperature. Methanol was the dominant product at each of the three temperatures in the range of 290–310 °C. An increase in the reaction temperature led to an increase in selectivity for hydrocarbons and an increase in selectivity of methanol. Ethanol selectivity was changed little over the temperatures studied.

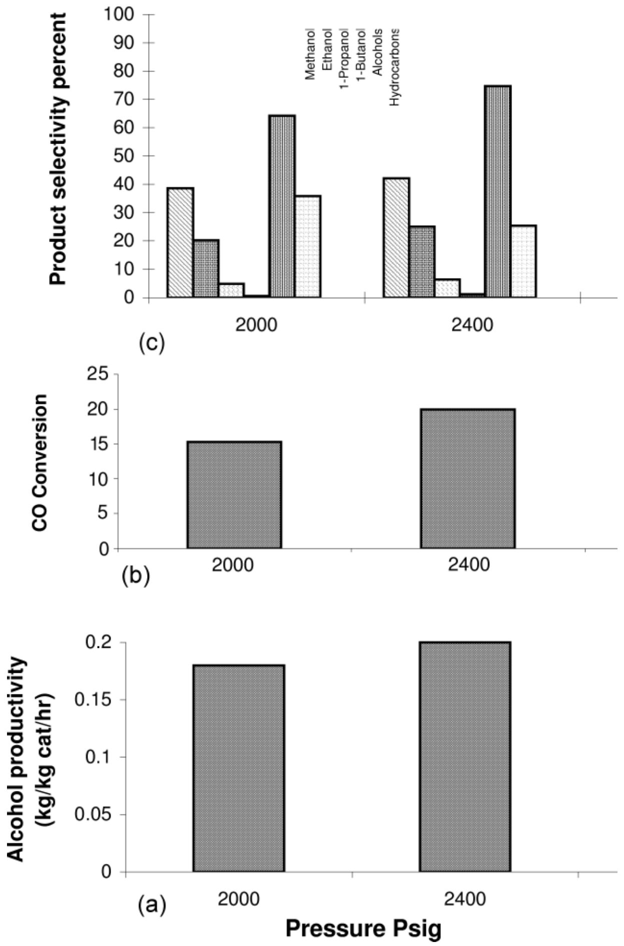

Figure 3. Pressure effect on alcohol productivity (a), CO conversion (b), and selectivity (c), at $T = 300\,^{\circ}\mathrm{C}$ and GHSV = 1600–1800 h^{-1} for High_AI catalysts.

3.7. GHSV effect

The High_AI catalyst also was examined as a function of GHSV at 2400 psig and 330 °C. The productivity, CO conversion, and selectivity results are illustrated in figure 5. This figure shows that the alcohol productivity was increased as GHSV was increased in favor of total alcohol. However, CO conversion was decreased as GHSV was increased. Apparently, the C_{2+} alcohol selectivity was decreased and methanol selectivity was increased with an increase in GHSV [8].

3.8. Catalyst characterization by XRD

Figure 6 shows the XRD pattern for Low_AI catalyst which was tested in the fixed bed reactor. The XRD peaks of Co_3S_4 were observed by sharp peaks at $2\theta = 31.5^{\circ}$ ($d_{\mathrm{spacing}} = 2.84$), $2\theta = 50.5^{\circ}$ ($d_{\mathrm{spacing}} = 1.81$), and $2\theta = 55.5^{\circ}$ ($d_{\mathrm{spacing}} = 1.65$). There are also two small sharp peaks at $2\theta = 29.8^{\circ}$ ($d_{\mathrm{spacing}} = 2.99$) and $2\theta = 52^{\circ}$ ($d_{\mathrm{spacing}} = 1.76$) which are associated with the Co_9S_8 phase. The presence of these small sharp peaks is consistent with the work of Inamura and Prins [10]. Figure 7 shows the XRD pattern for Low_AI catalyst which was obtained after the catalyst was tested for HAS in the reactor for 140 h. It is interesting to note that the sharp peaks, which represent the Co_3S_4 phase, were not observed after the catalyst was tested in the reactor. On the other hand, the small peaks, which represented the Co_9S_8 phase, were increased. This may suggest that the Co_3S_4 phase of the $K_2CO_3/CoS/MoS_2$ supported on activated carbon was gradually changed to a Co_9S_8 phase during the reaction period:

$$3Co_3S_4 + 3H_2 \rightarrow Co_9S_8 + 3H_2S \qquad (1)$$

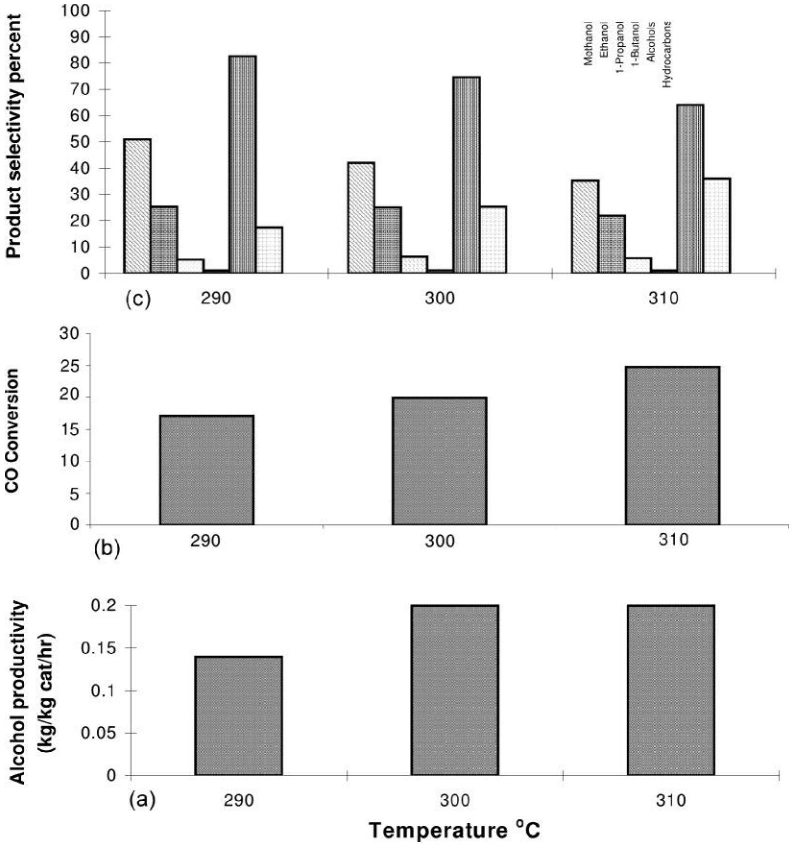

Figure 4. Temperature effect on alcohol productivity (a), CO conversion (b), and selectivity (c), at $P = 2400$ psig and GHSV $= 1542$–1692 h^{-1} for High_AI catalyst.

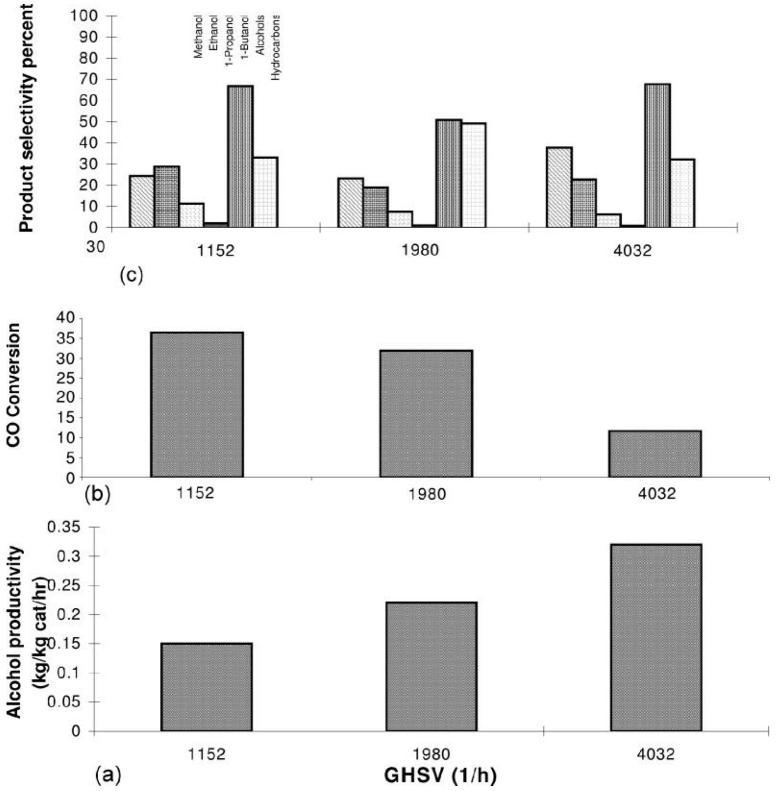

Figure 5. GHSV effect on alcohol productivity (a), CO conversion (b), and selectivity (c), at $T = 330\,^{\circ}\mathrm{C}$ and $P = 2400$ psig for High_AI catalyst.

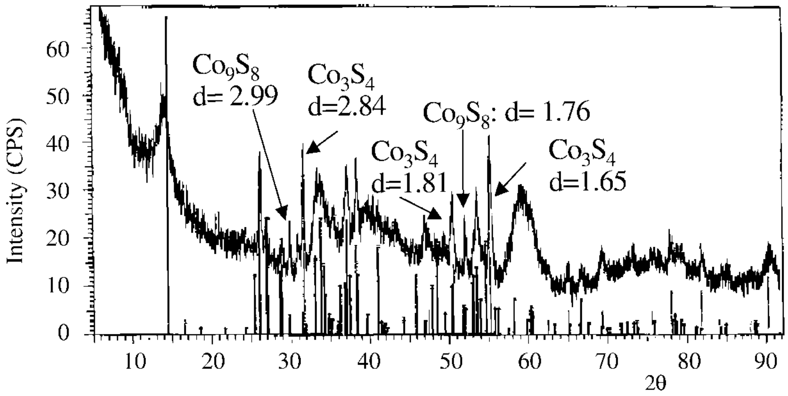

Figure 6. XRD pattern for Low_AI catalyst before reaction.

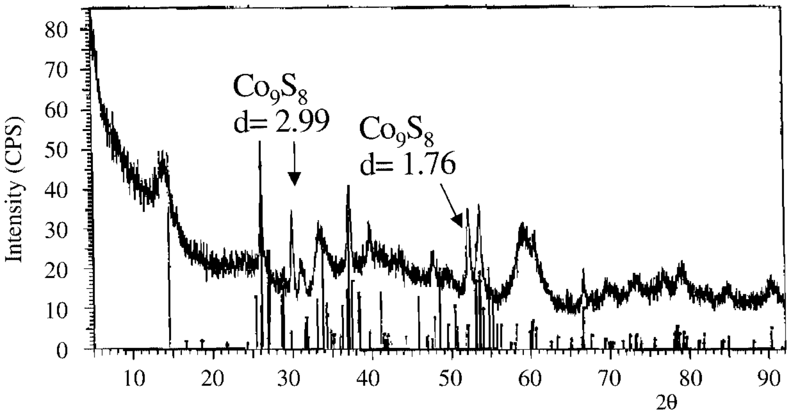

Figure 7. XRD pattern for Low_AI catalyst after reaction.

As a result of this change, the catalyst loses sulfur by hydrogenation and the sulfur is removed as H_2S from the surface of the catalyst. Murchison [8] reported that a catalyst with substantial amounts of Co_9S_8 behaved similar to molysulfide promoted with K_2CO_3 only. A possible explanation for aging of the catalyst is the loss of S from the catalyst and the formation of Co_9S_8 on the surface. The addition of small amounts of H_2S has been shown to maintain productivity. Therefore, one explanation of catalyst aging may be that the less effective Co_9S_8 continues to grow. Additional researches with longer runs are needed to determine the details of this observation. Further investigations of this catalyst by BET surface area measurement also indicate that due to aging, the surface area was decreased from 422 m^2/g (before the test) to 336 m^2/g (after the test).

4. Conclusions

The K_2CO_3/CoS/MoS_2/activated carbon catalyst produced linear alcohol. The active-chemical content on the catalyst influenced the alcohol productivity at a given temperature and pressure. The High_AI catalyst provided lower alcohol productivity than the Low_AI catalyst. High GHSV favored methanol formation over this catalyst and increased total alcohol productivity. After a prolonged exposure to synthesis gas, the agglomeration of Co_9S_8 phases on the surface of the catalyst was increased, which could result in a reduction of the HAS production or the requirement of H_2S in the feed.

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