Catalytic Activity of Cobalt-Molybdenum in Gas-Phase Ketonisation of Pentanoic Acid

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Abstract: Ketonisation of pentanoic acid over bulk cobalt-molybdenum and its supported catalysts in the gas-phase was investigated using a fixed bed reactor under atmospheric pressure at 320-420°C. Compared to other supported catalysts, 20% Co-Mo/Al2O3 demonstrated the best catalytic performance and stability giving to give 95% 5-nonanoe selectivity at 91% pentanoic acid conversion at 308°C and ambient pressure for 5 h time on stream (TOS).However, its stability was e for 15 h TOS with small catalytic deactivation. In this study, catalytic characterization was determined using TGA and BET surface area analyses while acidity was measured using FTIR spectroscopy.

Keywords: Ketonisation, Pentanoic Acid, Co-Mo Catalysts, Supported Catalysts, 5-Nonanone

1. Introduction

Ketonisation reaction is a major component in bio-renewable fuels processes and its application in several catalytic reactions is rapidly gaining interest [1-5]. **Biomass** pyrolysis (decomposition in oxygen-deficient conditions) produces bio-oil from small chain carboxylic acids and is an example of the application of ketonisation. For this purpose, several carboxylic acids have been used. Since ketonisation reaction requires high temperature to produce significant conversions various catalysts have been developed so that the reaction can occur at lower temperatures. Until now, catalytic reaction mechanisms and suitable catalyst properties have not exactly been identified. However, Lewis acid site might be of importance in this reaction. It has been reported that to form intermediate species such as carboxylate in the ketonisation reaction mechanisms, Lewis acid sites on the surface of catalysts are required [5, 6].

Ketonisation of carboxylic acids catalyzed by heteropoly acids [7], zeolites [8] and various metal and mixed metal oxides in the gas phase at temperatures of 200-500°C has been investigated [9-17]. Albeit several significant researches since the first ketonisation of acetic acid using calcium acetate to produce acetone over the last three decades, ketonisation mechanisms and the nature of catalytic active sites remain unclear [8].

Glinski et al. [18] analysed MnO_2, CeO_2 and ZrO_2 supported on Al_2O_3, SiO_2 and TiO_2 catalysts in the gas phase ketonisation of heptanoic acid at 300-450°C. Previous reports have shown that at low temperatures, MnO_2 showed the best catalysts performance compared to CeO_2 and ZrO_2. Although supported metal and metal oxide catalysts were active in the ketonisation reaction, , MnO_2/Al_2O_3 was the most active at 400°C to give 95% of 7-tridecanone yield. Meanwhile, CeO_2/Al_2O_3 and ZrO_2/Al_2O_3 gave 82 and 24% of 7-tridecane yields, respectively. In another study, the formation of of 3-pentanone from ketonisation of propionic acid over CeO_2 and its composite oxides in the gas phase were investigated at 300-425°C for 5h TOS. The results of that analysis showed that with increasing temperature, acid conversion also increased , but with a corresponding decrease in ketone selectivity [19]. As the active catalyst, CeO_2, with specific surface area of 40.1 m^2/g gave 93.8% of 3-pentanone selectivity at 51.0% acid conversion. However, the mixed oxide catalyst, CeO_2-Mn_2O_3 with 38.4 m^2/g specific surface area, exhibited better activity in the ketonisation reaction. It yielded 97.4% of 3-pentanone selectivity at 73.9% acid conversion [14].

At 230°C, fresh CeO_2 catalyst calcined at low temperature was tested in the ketonisation of acetic acid, with a constant mass of catalyst. Previous reports have shown that this temperature was lower compared to the typical temperature

range used in ketonisation of carboxylic acids over varying catalysts structures and properties. The results showed that greater acetone yields were obtained with CeO_2 catalyst that calcined at a low temperature [5].

The formation of acetone by steam reforming acetic acid with 1-bed steam reforming catalyst in a 2-bed catalytic system was investigated. Hydrogen was produced in the single bed while ketonisation of acetic acid occurred in the 2-bed catalytic system. Co-based system reforming catalyst under steam atmosphere was also tested in the steam reforming reaction. $MgAl_2O_4$, ZnO, CeO_2 and activated carbon (without addition) were used as catalyst in the reforming reaction. Co-supported catalyst showed stable catalytic performance with even less coke deposition. Catalytic stability improved with the use of 2-bed catalytic steam reforming of acetic acid to form acetone and coke deposition decreased in comparison to 1-bed steam reforming catalysts [20].

The ketonisation of propionic, acetic and carboxylic acids and using different catalysts have been studied. In a previous study, Zn-Cr catalysts as bulk and supported was used in the ketonisation of acetic, propionic and pentanoic acids and they were reported to be active in the reactions [21]. For the ketonisation of pentanoic acid, series of Zn/Cr atomic ratio 1:30 to 30:1, ZnO and Cr_2O_3 were tested. Although, all the catalyst showed good catalytic performance, Zn/Cr in the ratio 10:1 showed the most activity at ambient pressure and 380°C as compared with ZnO and Cr_2O_3. At 86% acid conversion rate, Zn/Cr in the ratio 10:1 yielded 82% 5-nonanone selectivity . Furthermore, Zn-Cr (1:10) was studied at different temperatures ranging from 300-400°C and the results indicated increased catalytic activity at increased temperature of over 380°C. This could have been due to some coke deposition on the catalyst's surface which might have blocked some of its active sites [19-22].

At conditions of 200-400°C and under N_2 and H_2 atmospheres, the gas-phase ketonisation of propionic acid over Co-Mo bulk and supported catalysts was studied. Supported on alumina, Co-Mo catalyst indicated the most catalytic activity under atmospheric N_2 to form 3-pentanone. At 65% propionic acid conversion (44% ketone yields), the catalyst gave 67% 3-pentanone selectivity compared to 16% 3-pentanone at 100% propionic acid conversion (16% ketone yields) at similar temperature but under atmospheric H_2 . Furthermore, catalyst stability was tested for 15 h TOS under nitrogen atmosphere indicating stable performance but with reduced catalytic activity after 10 h TOS probably due to coke deposited on its surface [22].

Over Co-Mo bulk and supported catalysts on oxides of alumina (Al_2O_3), titanium (TiO_2) and silicon (SiO_2), , the ketonisation of acetic acid in the gas phase was analyzed under conditions of 1 bar pressure and 200-400°C using 0.2 g catalyst, , 2 vol% acid and N_2 flow rate of 20 mLmin^{-1}. Both forms of the catalyst (bulk and supported) showed significant activity in the reaction. For the formation of acetone from acetic acid ketonization, Co-Mo bulk catalyst showed durable catalytic activity for 4 h TOS to give 91% selectivity at 86%

acid conversion at 380°C. However, under similar reaction conditions (in the ketonization of acetic acid), 20% Co-Mo/Al_2O_3 was the most active in comparison with bulk and other supported catalysts to give 91% acetone yields. With regards to catalytic stability, bulk and supported Co-Mo/Al_2O_3 indicated more stability compared to its bulk form at 380°C for 12 h TOS with no deactivation noted during the reaction [23].

The current research analyses the ketonisation of pentanoic acid in the gas phase with bulk Co-Mo and 20% Co-Mo impregnated on oxides of alumina, titanium and silicon to form 5-nonanone at 320-420°C, 20 mLmin^{-1}, 2 vol% of acid and 0.2 g catalyst. Different techniques were used to characterize the catalysts. They included BET surface area and porosity while TGA and FTIR-pyridine adsorption were used to measure Lewis and Brønsted acid sites on bulk Co-Mo catalyst surface.

2. Methodology

2.1. Chemicals and Materials

The chemicals used for this study were purchased from Sigma Aldrich without further purification. They include acetic acid ($\geq$ 99.5% purity), Titanoxid P25, Aerosil® 300, and Aluminiumoxid C (Degussa). Catalysts were prepared and washed with distilled water.

2.2. Preparation of Catalysts

Cobalt (II) acetate tetrahydrate (Co $(CH_3CO_2)_2.4H_2O$) and molybdenum phosphoric acid ($H_3PMo_{12}O_{40}.13H_2O$) were dissolved separately in distilled water and then mixed together in a beaker. The mixture was evaporated by a rotary evaporator at 65°C, and then dried overnight at 110°C. The preparation of 20% Co-Mo supported catalysts was done via impregnation on TiO2, Al_2O_3, and SiO_2. Similarly, the bulk catalysts were also prepared by dissolution in distilled water and then added to Al_2O_3, SiO_2 and TiO2. After stirring for 3 h, the reaction mixture was , evaporated, and oven-dried overnight at 110°C . Lastly, calcination of the catalysts occurred at 400°C for 2 h under N_2 atmosphere [22, 23].

2.3. Catalyst Characterisation

Porosity and surface area of the catalysts were evaluated using the BET method on Micromeritics ASAP 2010 instrument. Measurements for catalytic acidity was obtained with the diffuse reflectance infrared Fourier transform spectra (DRIFTS). The Perkin Elmer TGA 7 analyser under nitrogen atmosphere, was used for thermogravimetric analysis (TGA) to measure the amount of water in the catalysts.

2.4. Catalyst Testing

A quartz glass fixed-bed reactor placed in a vertical tube furnace that is fed from the upper part was used for this reaction. At the middle of the catalyst bed, a thermocouple set up on a Eurotherm controller was placed to control the

reaction temperature. The powdered catalyst (0.2 g) was loaded in the reactor while pretreatment occurred at the reaction temperature under 20 ml/min N_2 or H_2 flow for 1h. The reaction was carried out at 320-400°C under ambient pressureN_2 gas flow rate of 20 ml/min, 4.0 g h mol^{-1}space time and 2 vol % pentanoic acid concentrations. The Varian 3800 GC was used on Zebron ZB-WAX capillary column of dimensions 30 m × 0.32 mm × 0.5 μm at regular intervals to analyse downstream gas flow and)). The equations (1 and 2) below were used to determine acid conversion and selectivity of each product:

$$conversion(\%) = \frac{[acid]o-[acid]}{[acid]o} \times 100 \qquad (1)$$

$$selectivity\ of\ product\ (\%) = \frac{yield\ of\ product}{conversion\ of\ acid} \times 100 \qquad (2)$$

3. Results and Analysis

3.1. Catalyst Characterisation

Previous investigations have reported on pore volume and diameter, nature of Brønsted and Lewis acid sites and surface area texture [22]. The results of the current study indicated that 20% Co-Mo/Al$_2$O$_3$ characterized by 97 m^2/g surface area, pore volume and average pore diameter of 0.12 cm^3/g and 49 A, respectively, exhibited the best catalytic performance in pentanoic acid ketonisation. These results are similar to those reported in previous studies [22, 23]. Figure 1 shows that there are three bands; the first band at 25-180°C indicates the loss of physisorbed water while the second band at 180-490°C indicates the structure of water contents. The third band, at 490-700°C, indicates the decomposition of catalysts with the Keggin structure [22-26]. Similar to a previous study by Bayahia, thermogravimetric analysis (TGA) and FTIR using pyridine adsorption were performed to characterize Bulk Co-Mo catalyst [22, 23].
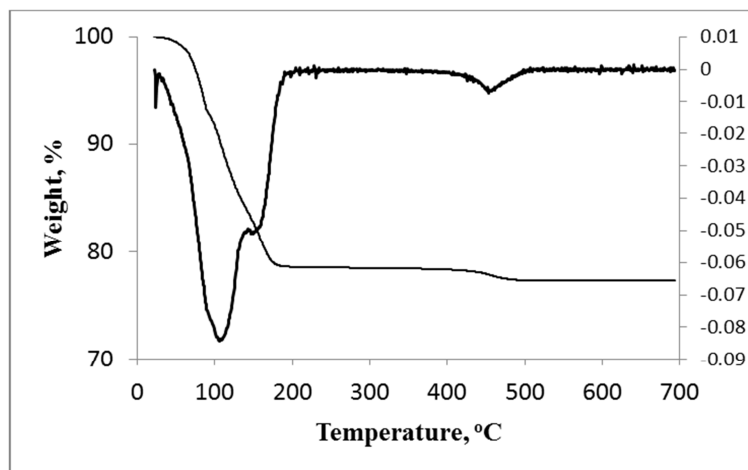

Figure 1. *TGA for 20%Co-Mo/Al$_2$O$_3$.*

Figure 2 shows that 20% Co-Mo/Al$_2$O$_3$ catalyst had H3 hysteresis loop of an adsorption isotherm and monomodal pore size distribution at the peak with 35.79 Å pore diameter as shown in Figure 3.
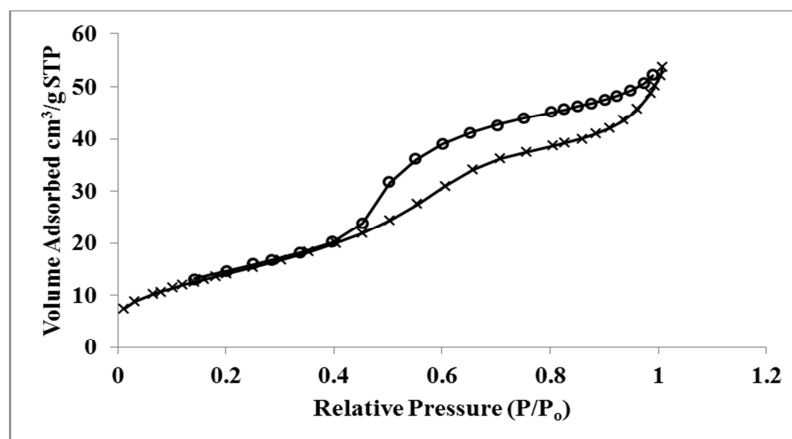

Figure 2. *N$_2$ adsorption-desorption on 20%Co-Mo/Al$_2$O$_3$ at 77 K. The catalyst was pre-treated at 250°C in vacuum.*
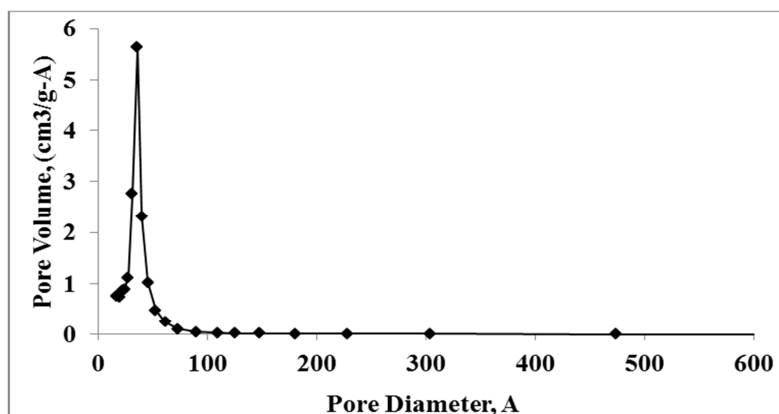
Figure 3. *Pore size distribution curve for 20%Co-Mo/Al$_2$O$_3$ BJH method. The catalyst was pre-treated at 250°C in vacuum.*

3.2. Performance of Catalysts

3.2.1. Bulk Co-Mo Catalyst

Table 1 shows the ketonisation of pentanoic acid in the gas phase over bulk Co-Mo catalyst at 320-420°C. These results indicate significant catalytic activity of the bulk catalyst in the ketonisation reaction and its positive correlation with temperature. Hence, with increased temperature, catalytic activity increased. Thus, the best catalytic activity was shown

at 380°C to give 91% 5-nonanone selectivity at 80% acid conversion. The amount of hydrocarbons formed as by-products increased with increasing temperature. However, there were some unknown products (probably, isopropanol or propanol and propanal) that also slightly increased in amount with increasing temperature. The amount of carbon monoxide and carbon dioxide were not monitored.

Table 1. *Ketonisation of pentanoic acid over bulk Co-Mo catalyst[a].*

Temperature (°C)	Conversion (%)	Selectivity (%)		
		5-nonanone	Hydrocarbons	Unknown[b]
320	17	96	2	2
350	29	93	3	4
380	80	91	5	4
400	87	79	13	8
420	93	74	17	9

[a] 1 bar pressure, 0.2 g of catalyst, 20 mLmin^{-1} N$_2$ flow rate, and 2 vol% of acid, 5h TOS.
[b] Probably isopropanol, propanol or propanal; CO and CO$_2$ not included.

3.2.2. Supported Co-Mo Catalysts

Catalytic activity improved with supported 20% Co-Mo on γ-Al$_2$O$_3$, SiO$_2$ and TiO$_2$. Both Al$_2$O$_3$ and TiO$_2$ showed better catalytic performance in comparison with SiO$_2$ to form 5-nonanone from the pentanoic acid ketonisation in the gas-phase (Table 2). It was found that Co-Mo supported catalysts possess significant amount of Brønsted and Lewis acid sites which explains their activity in the ketonisation reaction [22, 23]. However, SiO$_2$ was shown to be inactive at temperatures <400°C (Table 2). However, it was shown to be active at higher temperatures as previously reported [23]. Interestingly, at 380°C, 20% Co-Mo/Al$_2$O$_3$ exhibited superior catalytic activity to give 95% ketone selectivity at 91% acid conversion.

Furthermore, 20% Co-Mo/Al$_2$O$_3$ was used in the long term

ketonisation of pentanoic reaction to investigate its catalytic activity. Stable catalytic performance was exhibited by the catalyst for 15 h TOS with a slight reduction in catalyst conversion from 91% at the first hour of reaction to 83% ketone selectivity (Figure 4). Similar results were obtained in acetic and propionic acids ketonization in the gas-phase using the same catalyst [22, 23]. On the other hand, catalytic deactivation may be due to several reasons such as poisoning, fouling and thermal degradation etc [23, 27]. Therefore, the deactivation of 20%Co-Mo/Al$_2$O$_3$ might have occurred due coke deposition on the catalyst's surface thus, effectively blocking its active sites [23]. C, H analysis was used to determine that the amount of coke found on the catalyst measured 2.7 wt%.
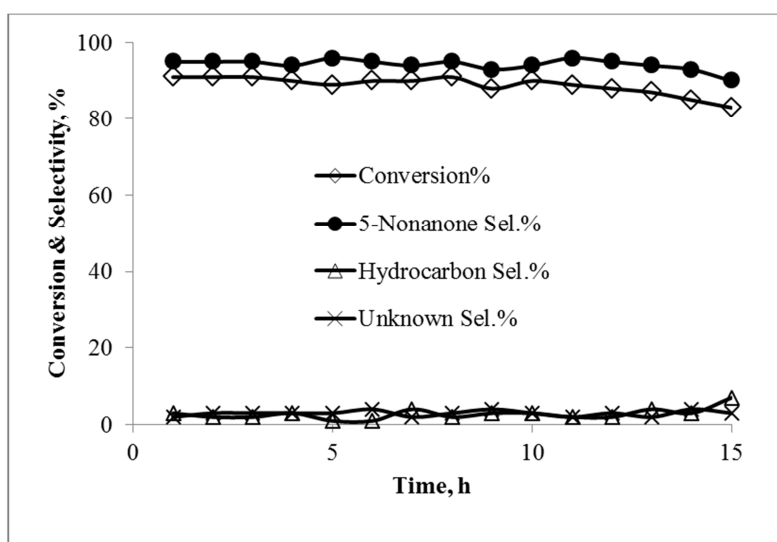
Table 2. *Ketonisation of pentanoic acid over Co-Mo/supported catalysts.*

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)		
			5-nonanone	Hydrocarbons	Unknown[b]
SiO$_2$	380	0	0	0	0
Al$_2$O$_3$	380	33	90	4	6
TiO$_2$	380	70	55	32	13

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)		
			5-nonanone	Hydrocarbons	Unknown[b]
20%Co-Mo/SiO$_2$	380	47	98	2	0
20%Co-Mo/TiO$_2$	380	72	93	5	2
20%Co-Mo/Al$_2$O$_3$	320	51	98	2	0
20%Co-Mo/Al$_2$O$_3$	350	64	96	3	1
20%Co-Mo/Al$_2$O$_3$	380	91	95	4	1
20%Co-Mo/Al$_2$O$_3$	410	96	78	16	6

[a] 1 bar pressure, 0.2 g of catalyst, 20 mLmin^{-1} N$_2$ flow rate, and 2 vol% of acid, 5h TOS.
[b] might be isopropanol, propanol or propanal; CO and CO$_2$ not included.

Figure 4. *Catalytic stability of ketonisation of pentanoic acid over 0.2 g of 20%Co-Mo/Al$_2$O$_3$ for 15 h TOS at 380°C, 20 mL/min N$_2$, 2 vol% of pentanoic acid, 4.0 h g mol^{-1} space time.*

4. Conclusion

Bulk Co-Mo has been shown to be an active and stable catalyst in pentanoic acid ketonisation in the gas-phase at 320-400°C under atmospheric pressure to form 5-nonanone. Supported on SiO$_2$, γ-Al$_2$O$_3$ and TiO$_2$, the catalytic performance of bulk Co-Mo was improved. Of these catalysts, 20% Co-Mo supported on γ-Al$_2$O$_3$ showed superlative catalytic performance in to give 95% selectivity at 91% pentanoic acid conversion at 380°C for 5 h TOS. Its stability lasted for 15 h TOS with small deactivation in its catalytic activity. Several techniques were employed to characterize both forms of catalysts. They include Brunauer-Emmett-Teller (BET) surface area and porosity analysis while TGA analysis and DRIFTS of adsorbed pyridine were used to measure the acidity of the catalysts.

Conflicts of Interest

The author declares that competing interests do not exist.

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