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

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Abstract: Ketonisation of pentanoic acid was carried out over cobalt-molybdenum and its supported catalysts in the gas-phase using fixed-bed reactor at 320-420°C and atmospheric pressure. Bulk Co-Mo and its supported catalysts were active in the ketonisation of pentanoic acid. 20%Co-Mo/Al₂O₃ showed the best catalytic performance in comparison to other supported catalysts. It gave 95% 5-nonanone selectivity at 91% of pentanoic acid conversion at 308°C and ambient pressure for 5h time on stream (TOS). 20%Co-Mo/Al₂O₃ catalyst was stable for 15h TOS with small catalytic deactivation. All catalysts used in this study were characterized by different techniques such as TGA analysis, BET surface area and porosity, the catalysts acidity was measured in this work by using FTIR spectroscopy.

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

1. Introduction

Ketonisation reaction achieved large part of biorenewable fuels and several applications of catalytic reactions that observed receiving gain interest for it [1-5]. The heat of biomass in the absence of oxygen to create of bio-oil from small chain of carboxylic acids as good materials for the application of ketonisation knows as pyrolysis method. In this case, several carboxylic acids have been used for this purpose. Ketonisation reaction needs high temperature and that leads to make this reaction impractical. Therefore, ketonisation reaction was developed by using different kind of catalysts. Up to now, catalytic reaction mechanisms and suitable catalyst properties have not exactly known, but the active site as Lewis acid might be important in this reaction. It has been reported that Lewis acid sites on the surface of catalysts are require to form carboxylate as an intermediate species in the ketonisation reaction mechanisms [5, 6].

Ketonisation of carboxylic acids catalyzed by many metal oxides and mixed metal oxides as well as other catalysts such as heteropoly acids [7] and zeolites [8] in the gas phase has been investigated in the temperature range of 200-500°C [9-17]. Ketonisation mechanisms and the nature of catalytic active sites are not clear so far even many significant researches has been done during over three decades since the

first ketonisation of acetic acid carried out using calcium acetate to produce acetone [8].

Glinski et al. [18] tested MnO₂, CeO₂ and ZrO₂ supported on Al₂O₃, SiO₂ and TiO₂ catalysts in the ketonisation of heptanoic acid in the gas phase in the temperature range 300-450°C. It has been found that, at low temperature MnO₂ catalyst showed the best catalysts performance comparing to CeO₂ and ZrO₂. Regarding to supported catalysts, all catalysts were active in the ketonisation reaction, but MnO₂/Al₂O₃ was the most active one at 400°C, it gave 95% of 7-tridecanone yield. For CeO₂/Al₂O₃ and ZrO₂/Al₂O₃ they gave 82% and 24% of 7-tridecanone yields respectively. In another work, ketonisation of propionic acid to form 3-pentanone over CeO₂ and CeO₂-based composite oxides in the gas phase were investigated in the temperature range of 300-425°C for 5h TOS. It has been reported that, the conversion of acid increased with increasing the temperature, but ketone selectivity was decreased [19]. CeO₂ which has 40.1 m²/g specific surface area was active catalyst in the ketonisation of propionic acid; it gave 93.8% of 3-pentanone selectivity at 51.0% of acid conversion. The mixed oxide of CeO₂-Mn₂O₃ which has 38.4 m²/g specific surface area showed better catalytic activity in the ketonisation reaction. It gave 97.4% of 3-pentanone selectivity at 73.9% of propionic acid [14].

Fresh catalyst of CeO_2 which calcined at low temperature has been tested in ketonisation of acetic acid at low temperature of 230°C , with constant mass of catalyst. This temperature was lower than the typical temperatures that used in the ketonisation of carboxylic acids over many different catalysts structures and properties which have been previously reported. The results showed that greater acetone yields achieved by using CeO_2 catalyst that calcined at low temperature [5].

Steam reforming of acetic acid to form acetone in the presence of steam using 1-bed steam reforming catalyst and 2-bed catalytic system has been investigated. In the single bed hydrogen was produced, however, 2-bed catalytic system, ketonisation of acetic acid was taken place. 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 were used as catalyst without adding in the reforming reaction. Co-supported catalyst showed stable catalytic performance with even less coke deposition. The catalytic stability was improved by using 2-bed catalytic steam reforming of acetic acid to acetone and the coke deposition was decreased in the comparison to 1-bed steam reforming catalysts [20].

The ketonisation of carboxylic acids, acetic and propionic has been studied using different catalysts. In this case, zinc and chromium mixed catalysts as bulk and supported tested in ketonisation acetic, propionic and pentanoic acid and these catalysts were active in the ketonisation reactions [21]. For the ketonisation of pentanoic acid, series of Zn/Cr atomic ratio 1:30 to 30:1, ZnO and Cr_2O_3 tested in the ketonisation of pentanoic acid. All catalyst showed good catalytic performance but Zn-Cr (10:1) was the most active catalyst at 380°C and ambient pressure in the comparison with ZnO and Cr_2O_3 . It gave 82% of 5-nonanone selectivity at 86% of acid conversion. For more investigations, Zn-Cr (1:10) studied at different temperature from 300 – 400°C . The study showed that, the activity increased with increasing the temperature over 380°C , that because might be some coke deposited on the surface of catalyst and some of active sites might be blocked by coke [19-22].

Cobalt and molybdenum bulk and supported catalysts were tested in the deoxygenation of propionic acid in the gas-phase and atmospheric of N_2 and H_2 at 200 – 400°C . Co-Mo Supported catalyst on alumina showed the best catalytic activity under N_2 to form 3-pentanone, this catalyst gave 67% of 3-pentanone selectivity at 65% of propionic acid conversion (44% of ketone yields) in comparison with the same reaction conditions under H_2 which gave 16% 3-pentanone at 100% of propionic acid conversion (16% of ketone yields). For further testing, the catalyst stability was tested for 15 h time on stream using nitrogen atmosphere and the catalyst showed stable performance with small decrease in the catalytic activity after 10h time on stream, it might some coke has been deposited on the catalyst surface [22].

Recently, Co-Mo bulk and supported catalysts on Al_2O_3 , TiO_2 and SiO_2 were tested in the ketonisation of acetic acid in the gas phase from 200 – 400°C using 0.2g of catalyst, 1 bar

pressure, 2 vol% of acid and 20 mLmin^{-1} of N_2 flow rate. Both of bulk and supported catalysts were active in the reaction. Co-Mo bulk catalyst showed durable catalytic activity for 4h TOS. The catalyst gave 91% acetone selectivity at 86% of acetic acid conversion at 380°C . However, at the same reaction condition 20%Co-Mo/ Al_2O_3 was the best one in the ketonisation of acetic acid reaction in comparison with bulk and other supported catalysts. It gave 95% of acetone selectivity at 96% of acetic acid conversion (91% of acetone yields). In the case of catalytic stability, both bulk and 20%Co-Mo/ Al_2O_3 supported catalysts were more stable than the bulk one at 380°C for 12h TOS with no any deactivation noted during the reaction [23].

In the current work, bulk Co-Mo and 20%Co-Mo impregnated on Al_2O_3 , TiO_2 and SiO_2 were tested in gas phase ketonisation of pentanoic acid to form 5-nonanone in the temperature range 320 – 420°C , 20 mLmin^{-1} , 2 vol% of acid and 0.2g of catalyst. The catalysts were characterized using different techniques such as BET surface area and porosity, TGA and FTIR-pyridine adsorption for measuring both Brønsted and Lewis acid sites on the surface of bulk Co-Mo catalyst.

2. Experimental

2.1. Chemicals and Materials

In this study, all chemical were purchased from Sigma Aldrich and used without any further purification. Acetic acid was $\geq 99.5\%$ pure. Aerosil 300, Titanoxid P25 and Aluminiumoxid C were from Degussa. The distilled water was used for preparation and washing the catalysts.

2.2. Catalyst Preparation

The amount of Cobalt hydrates acetate ($\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$) and amount of molybdenum phosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$) were dissolved separately in a minimum of distilled water and then mixed together in one beaker. The mixture were evaporated by a rotary evaporation at 65°C , and dried at 110°C overnight. For Co-Mo supported catalysts preparation, the catalysts were prepared by impregnation method. 20% of Co-Mo was impregnated on Al_2O_3 , SiO_2 and TiO_2 . In this case, the same materials that used in the preparation of bulk catalyst were dissolved in minimum of distilled water and added to Al_2O_3 , SiO_2 or TiO_2 . After that, the mixture was stirred for 3h, evaporated, dried over night at 110°C in the oven. Finally, the catalysts were calcined at 400°C for 2h under N_2 atmosphere [22, 23].

2.3. Catalyst Characterisation

In this work, catalysts surface area and porosity were measured by the BET method using Micromeritics ASAP 2010 instrument. The diffuse reflectance infrared Fourier transform spectra (DRIFTS) has been used for measuring the catalytic acidity. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA 7 instrument under nitrogen flow for measuring the amount of water in the

catalysts.

2.4. Catalyst Testing

The reaction was carried out in a quartz glass fixed-bed reactor which was located in a vertical tubular furnace and fed from the top. To control reaction temperature, the Eurotherm controller using a thermocouple placed in the center of catalyst bed. 0.2 g of powder catalyst was loaded with the reactor and pretreated at the reaction temperature under 20 ml/min of N₂ or H₂ flow for 1h. The reaction was conducted at 320-400°C, and ambient pressure, 20ml/min N₂ flow rate, 4.0 g h mol⁻¹space time and 2 vol % pentanoic acid concentrations. At regular time intervals, the downstream gas flow was analyzed by the on-line GC ((Varian 3800 instrument with a 30 m × 0.32 mm × 0.5 μm Zebron ZB-WAX capillary column and a flame ionization detector (FID)) which was calibrated for each component. The conversion of acid and selectivity of each product are calculated from equations (1) and (2) respectively:

$$\text{conversion}(\%) = \frac{[\text{acid}]_o - [\text{acid}]_i}{[\text{acid}]_o} \times 100 \quad (1)$$

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

3. Results and Discussion

3.1. Catalyst Characterisation

The nature of acid sites and texture of surface are, pore volume and pore diameter have been investigated previously [22]. Here, it can be seen that 20%Co-Mo/Al₂O₃ showed the best catalytic performance in the ketonisation of pentanoic acid has 97 m²/g surface area with 0.12 cm³/g pore volume and 49 Å as an average pore diameter and that similar to results reported previously [22, 23]. Figure 1 shows that there are three bands, the first one at 25-180 attributed to loss of physisorbed water contents. The second band is at 180-490°C is assigned to the structure water contents. The third band is at 490-700°C is assigned to the decomposition of catalyst's Keggin structure [22-26]. Bulk Co-Mo and catalyst were characterized by Thermogravimetric analysis (TGA) and FTIR using pyridine adsorption as previously reported by Hossein Bayahia [22, 23]

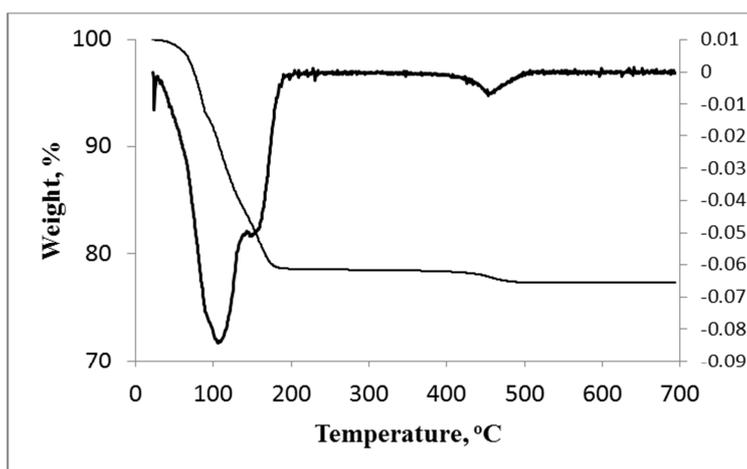


Figure 1. TGA for 20%Co-Mo/Al₂O₃.

Figure 2. shows that 20%Co-Mo/Al₂O₃ catalyst had H3 hysteresis loop of an adsorption isotherm and monodal pore size distribution as it clear of the peak at 35.79 Å pore diameter as Figure 3 shows.

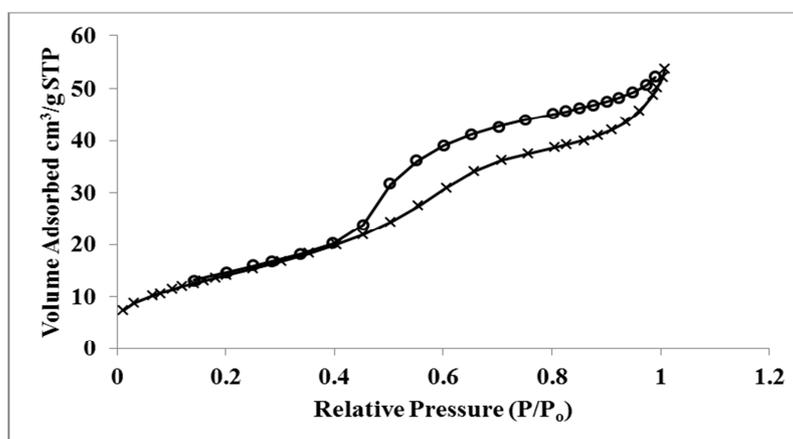


Figure 2. N₂ adsorption-desorption on 20%Co-Mo/Al₂O₃ at 77 K. The catalyst was pre-treated at 250°C in vacuum.

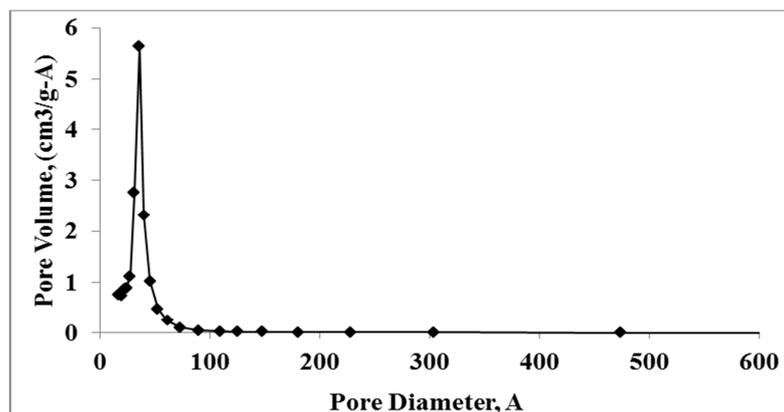


Figure 3. Pore size distribution curve for 20%Co-Mo/Al₂O₃ B/JH method. The catalyst was pre-treated at 250°C in vacuum.

3.2. Catalyst Performance

3.2.1. Bulk Co-Mo Catalyst

The results observed that gas-phase ketonisation of pentanoic acid over the bulk Co-Mo in the range of temperature of 320-420°C are presented in the table 1. From these results it can be seen that the bulk catalyst was active in the ketonisation reaction and the catalytic activity depends significantly on the temperature. Catalytic activity increased by increasing the reaction temperature. At 380°C the catalyst

showed the best catalytic activity, it gave 91% of 5-nonanone selectivity at 80% of acid conversion. The hydrocarbons products were formed as by-products and their amounts were increased by increasing the temperature. It can be noted that, there are some unknown products that slightly increased with increasing the temperature. The unknown products might be isopropanol or propanol and propanal. 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 N₂ flow rate, and 2 vol% of acid, 5h TOS.

^b might be isopropanol, propanol or propanal; CO and CO₂ not included.

3.2.2. Supported Co-Mo Catalysts

Catalytic activity was improved by Supporting 20%Co-Mo on γ -Al₂O₃, SiO₂ and TiO₂. Both Al₂O₃ and TiO₂ showed better catalyst performance in comparison with SiO₂ in the ketonisation of pentanoic acid in the gas-phase to form 5-nonanone (Table 2). It can be seen that, Co-Mo supported catalysts possessing significant amount of Brønsted and Lewis acid sites that can be the reason of their activity in addition to themselves activity in the ketonisation reaction [22, 23]. However, SiO₂ has been found inactive at lower temperature than 400°C (Table 2), but it showed that it was active at higher temperature as previously reported [23]. Interestingly, 20%Co-Mo/Al₂O₃ showed the best catalytic activity at 380°C, it gave 95% of ketone selectivity at 91% of acid conversion.

For further catalytic investigations, 20%Co-Mo/Al₂O₃ was

tested for long term of ketonisation of pentanoic reaction; the catalyst shows that stable catalytic performance for 15 h TOS with a small drift of catalyst conversion from 91% at the first hour of reaction to 83% at the constant ketone selectivity (Figure 4). Similar results has been reported for ketonisation of acetic and propionic acids in the gas-phase using the same catalyst of Co-Mo bulk and its supported catalysts that prepared by Hossein Bayahia [22, 23]. In the case of catalytic deactivation, there are several reasons such as poisoning, fouling, thermal degradation and so on [23, 27]. The deactivation of 20%Co-Mo/Al₂O₃ might be caused by the coke that can be deposited on the surface of catalyst and blocked the active sites [23]. The amount of coke measured by C, H analysis and it has indeed found in the catalyst and amounted 2.7wt%.

Table 2. Ketonisation of pentanoic acid over Co-Mo/supported catalysts.a.

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

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)		
			5-nonanone	Hydrocarbons	Unknown ^b
TiO ₂	380	70	55	32	13
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 N₂ flow rate, and 2 vol% of acid, 5h TOS.

^b might be isopropanol, propanol or propanal; CO and CO₂ not included.

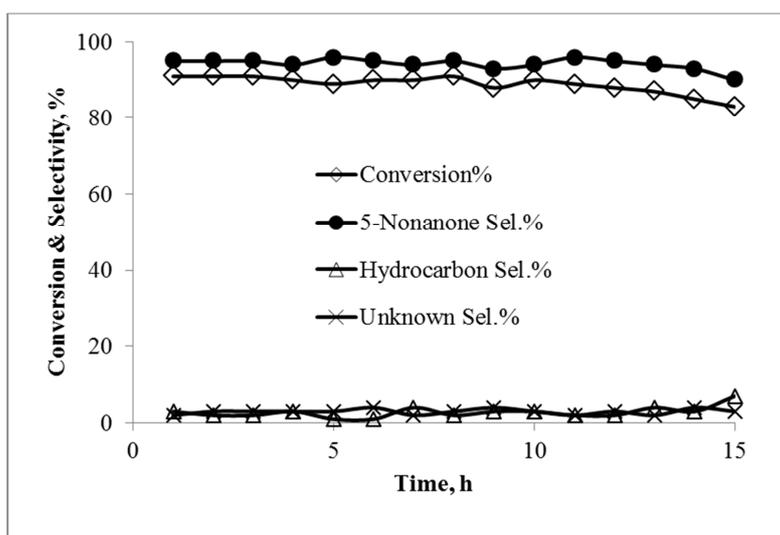


Figure 4. Catalytic stability of ketonisation of pentanoic acid over 0.2 g of 20%Co-Mo/Al₂O₃ for 15 h TOS at 380°C, 20 mL/min N₂, 2 vol% of pentanoic acid, 4.0 h g mol⁻¹ space time.

4. Conclusion

Bulk Co-Mo has been demonstrated as an active catalyst and durable catalyst for the ketonisation of pentanoic acid in the gas-phase at 320-400°C and atmospheric pressure to form 5-nonanone. For improving catalytic performance, the bulk catalyst of Co-Mo was supported on SiO₂, γ -Al₂O₃ and TiO₂. Among of these catalysts, 20%Co-Mo on γ -Al₂O₃ presented the best catalytic performance in the ketonisation of pentanoic acid to form 5-nonanone. This catalyst gave 95% of 5-nonanone selectivity at 91% pentanoic acid conversion at 380°C for 5 h TOS. 20%Co-Mo/Al₂O₃ was stable for 15 h TOS with a small deactivation in the catalytic activity. Bulk and supported catalysts were characterized by different techniques such as BET surface area and porosity, TGA analysis and DRIFTS of pyridine adsorption for measuring catalysts acidity.

Conflicts of Interest

The author declares that he has no competing interests.

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