Gas-phase ketonization of acetic acid over Co–Mo and its supported catalysts

Hossein Bayahia

The Department of Chemistry, Faculty of Science, Albaha University, Albaha, Saudi Arabia

ABSTRACT
Ketonization of acetic acid was carried out in the gas phase over bulk and supported cobalt–molybdenum catalysts using a fixed-bed reactor. The conditions of the reaction were: 0.2 g of catalyst, 200–400°C, 1 bar pressure, 2 vol% of acetic acid and 20 mL min$^{-1}$ of nitrogen flow. Bulk and supported catalysts were prepared and calcined at 400°C in N$_2$ flow for 3 h to obtain metal oxides. Both bulk and supported catalysts were tested in the ketonization reaction of acetic acid to form acetone. They have been found active catalysts in this reaction. The catalytic activity was enhanced further by supported catalysts. 20% Co–Mo/Al$_2$O$_3$ catalyst showed superior catalytic performance in the ketonization of acetic acid, with 95% of acetone selectivity at 96% of acetic acid conversion at 380°C, 1 bar and 20 mL min$^{-1}$ of N$_2$ flow. These materials were characterized by thermogravimetric analysis, nitrogen sorption and FTIR using pyridine adsorption.

1. Introduction

Biomass is an important renewable feedstock [1]. In addition, it is important in replacing fossil fuels which can increase global warming [2]. The estimated energy that can be obtained from raw biomass materials will be 150–450 EJ/year by 2030 [3]. It is estimated that 20% of that will be used for transportation and 25% for producing useful chemicals. It really plays the role as the source of useful chemicals and fuels [4,5]. The heating of biomass in the absence of oxygen to create small organic acids such as acetic acid is known as Biomass fast pyrolysis. Acetic and other acids would be good candidates for ketonization applications [5–8]. Ketonization of carboxylic acid is the reaction that two molecules of carboxylic acid can be reacted with loss of CO$_2$ and H$_2$O to give ketones [9–17]. Its importance lies in its practical potential. This has been since the pyrolysis decomposition of metal salts [17]. Then the ketonization was improved by forming ketones from carboxylic acids in the gas phase using solid materials as catalysts. It has been found that different metal oxides and their supports have been used in the ketonization of carboxylic acids [9,18–21]. Recently, acetic acid ketonization to produce acetone was investigated using many metal oxides such as MnO$_2$/Al$_2$O$_3$, CeO$_2$/Al$_2$O$_3$ and ZrO$_2$/SiO$_2$ [22,23]. However, zeolite and crystalline silicalite [24] and Co–Mo [25] and their supported catalysts are also used in the ketonization of propionic acid.

The ketonization of pentanoic acid was carried out using Zn/Cr mixed oxide catalyst in the gas phase (300–480°C). In this work, all catalysts were active. However, Zn–Cr (10:1) showed the best catalytic performance for formation of 5-nonanone. Zn–Cr (10:1) gave 82% of 5-nonanone selectivity at 86% of pentanoic acid conversion at 450°C. The concentration of acid was 2 vol% acid and 20 mL min$^{-1}$ of N$_2$ flow rate [9]. Additionally, these catalysts also showed good catalytic activity in the ketonization of acetic and propionic acids in the gas phase at 380°C, 2 vol% of acid and 20 mL min$^{-1}$ of flow rate of N$_2$ as previously reported by Hossein Bayahia et al. The catalysts showed good conversions of acetic and propionic acids and good selectivity of acetone and 3-pentanone [21].

Glinski et al. [22] tested 20 metal oxides. It has been reported that 20% Ce/Al$_2$O$_3$ and 20% Mn/Al$_2$O$_3$ were the most active catalysts in the ketonization of acetic acid. Both of them gave 97% of acetone yield at 350°C. Regarding to molybdenum and cobalt catalyst, 10% CoO/SiO$_2$ was active in the ketonization of acetic acid in the range of temperature 300–400°C. It has been reported that catalytic activity increased by increasing the ketonization temperature. In this case, CoO/SiO$_2$ showed the best acetone yield at 450°C which was 68%. In the current work, the combination of Co–Mo and its supported catalyst on alumina gave better catalytic performance. The bulk Co–Mo and 20% Co–Mo/Al$_2$O$_3$ gave 78% and 91% of acetone yield respectively in comparison to 10% CoO/SiO$_2$ which gave only 50% of the yield of acetone. It has been also reported that MoO$_3$/SiO$_2$ was not active at 300–450°C. Co–Mo catalyst was active in desulfurization of thiophene as previously reported [25,26]. To the best of our knowledge, Co–Mo and its supported...
catalysts have not been reported for ketonization of acetic acid so far. These catalysts have been used for ketonization of propionic acid as mentioned in this work by Hossein Bayahia [27].

Hossein Bayahia [27] has been reported that Co–Mo and Co–Mo/Al2O3 were active in the ketonization of propionic acid in the gas phase at 200–400°C. Supported catalyst showed better catalytic performance in comparison to bulk one. The results showed that supported catalyst gave 67% 3-pentanone selectivity at 65% conversion of acid. The catalyst showed stable catalytic performance for at least 15 h time on stream.

Here, Co–Mo bulk catalyst and its supported catalysts on Al2O3, SiO2 and TiO2 have been tested in the ketonization of acetic acid in the gas phase using 0.2 g of catalyst, 20 mL min−1 and 2 vol% of acetic acid in the temperature range from 300°C to 400°C and ambient pressure.

2. Experimental

2.1 Chemical and materials

In this work, all chemicals were from Sigma-Aldrich with high purity. Al2O3 was received from Degussa. Distilled water was used in the preparation of catalysts.

2.2 Catalysts preparation

Cobalt–molybdenum catalyst was prepared and characterized according to the literature [27–29]. In a minimum amount of distilled water, cobalt acetate and 12-molybdophosphoric acid H3PMo12O40·13H2O were dissolved at room temperature. After that, the mixture of acetate and acid was homogenously stirred for at 3 h. The mixture was rotary evaporated at 35–45°C and then dried at 110°C overnight. The supported catalysts were prepared by wetness impregnation. Typically, a known amount of Co–Mo bulk catalyst was added to suitable amount of supports, Al2O3, SiO2 and TiO2 and dissolved in a minimum of distilled water. The mixture was stirred for 3 h at room temperature, dried at 110°C overnight to remove the physisorbed water. Finally, the catalysts were calcined at 400°C for 2 h in air to remove water [27].

2.3 Catalyst characterization

In this study, some techniques have been used for characterizing of Co–Mo and Co–Mo/Al2O3 supported catalyst that used in the ketonization of acetic acid in the gas phase. Catalyst surface area and porosity were measured by nitrogen sorption (Micromeritics ASAP2010 instrument). Thermogravimetric analysis (TGA) and catalytic acidity were measured by DRIFTS of pyridine adsorption using a Nicolet Nexus FTIR spectrometer, as reported previously [27].

2.4 Catalyst testing in the gas-phase ketonization of acetic acid

The ketonization of acetic acid was carried out using a quartz fixed-bed reactor (9 mm internal diameter) connected to online GC analysis (Varian 3800 instrument with a 30 m × 0.32 mm × 0.5 μm Zebron ZB-WAX capillary column and a flame ionization detector). Additionally, a 60 m × 0.32 mm GS-GasPro capillary column was hydrocarbon analysis. 0.2 g of catalyst was packed. Then the reaction was carried out using 2 vol% of acetic acid concentration at 20 mL min−1 N2 flow and 4.0 g h mol−1 space time (where W is the weight of catalyst) and F is the total molar flow rate (mol h−1)). Initially, the catalysts were pretreated at the reaction temperature, pressure and N2 flow rate for 1 h. The reaction was carried out for 4 h and the products were analysed at hourly intervals. Then acid conversion, selectivity and yield of ketone were calculated. For the best catalytic reaction condition, the stability of catalytic reaction was tested for long term.

The selectivity of the products was calculated as a percentage of acetic acid that had been converted into products. In this case, 100% of acetone selectivity means that 1 mole of acetic acid converted to form half mole of acetone. Both CO and CO2 were not quantified and they were not included in the selectivity of ketonization reaction.

3. Results and discussions

3.1 Catalyst characterization

Catalysts surface area and porosity of SiO2, Al2O3, TiO2, Co–Mo and its support on Al2O3, SiO2 and TiO2 are presented in Table 1. It can be seen that BET surface area, pore size and pore diameter are different. From the results, the surface area of Co–Mo was 45 m² g−1, with 0.06 cm³ g−1 of pore volume and 23 Å pore diameter, whereas the values for 20% Co–Mo/Al2O3 catalyst were 97 m² g−1, 0.12 cm³ g−1 and 49 Å respectively.

Infrared adsorption of H3PMo12O40·13H2O and Co1.5–Mo/Al2O3 supported catalysts were measured at 1060, 990, 960, and 950 cm−1. The vibration of P=O, M=O, and M=O appeared at 1080–1150 cm−1 might be assigned to the Keggin structure [20,21]. The vibration of P–O, M–O, M–O–M and M–O–M appeared at 1080–1060, 990–960, 1130–1230 cm−1 and 1200–1300 cm−1.

| Catalyst | BET surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Pore diameter (Å) |
|-----------|---------------------------|----------------------|------------------|
| SiO₂      | 296                       | 1.15                 | 156              |
| Al₂O₃     | 164                       | 0.22                 | 53               |
| TiO₂      | 56                        | 0.25                 | 18               |
| Co–Mo     | 45                        | 0.06                 | 23               |
| Co–Mo/Al₂O₃ | 97                       | 0.12                 | 49               |
| Co–Mo/SiO₂ | 203                      | 0.18                 | 51               |
| Co–Mo/TiO₂ | 132                      | 0.25                 | 44               |

*Note: Table 1. Catalyst characterization.

aBET surface area.

bSingle point total pore volume.

cAverage BET pore diameter.
900–870 and 810–760 cm$^{-1}$ respectively (where M is Co or Mo [27–31]).

TGA results for H$_3$PMo$_{12}$O$_{40}$·13H$_2$O and Co$_{1.5}$PMo$_{12}$O$_{40}$·13H$_2$O are shown in Figures 2 and 3 respectively. There are two thermal areas for Co–Mo bulk catalyst as Figure 2 shows. The peak of 50–240°C is attributed to loss of physisorbed water or hydration water contents. However, the peak at 240–450°C is assigned to the decomposition of the catalyst’s Keggin structure [27–31]. Figure 3 shows that surface water can be removed at around 180°C corresponding to the removal of physisorbed water that depends on the hydration water number in the catalyst. At around 190°C, it can be seen that further weight lost can be attributed to further water loss. At ~640°C, the catalyst is decomposed.

Catalytic acidity by using pyridine adsorption was measured for the Co–Mo bulk catalyst and the best supported catalyst is Co–Mo/Al$_2$O$_3$. There are two bands at 1440–1450, which can be attributed to Lewis acid sites. The band at 1490 cm$^{-1}$is attributed

![Figure 1. IR results for (a) H$_3$PMo$_{12}$O$_{40}$·13H$_2$O and (b) Co$_{1.5}$PMo$_{12}$O$_{40}$·13H$_2$O [27].](image1.png)

![Figure 2. TGA analysis for H$_3$PMo$_{12}$O$_{40}$·13H$_2$O [27].](image2.png)

![Figure 3. TGA analysis for Co$_{1.5}$PMo$_{12}$O$_{40}$·13H$_2$O [27].](image3.png)
to pyridine that adsorbed on both Lewis and Brønsted acid sites as well as H-bonded pyridine. In addition, the band at 1540 cm\(^{-1}\) (Figure 4) is attributed to Brønsted acid site [9,27,32–34]. It can be seen that both Co–Mo bulk and 20% Co–Mo/Al\(_2\)O\(_3\) catalysts have Lewis and Brønsted acid sites as previously reported [27]. The amount of Lewis acid sites is higher than the amount of Brønsted. Catalytic acidity results can be seen in Figure 4.

3.2 Catalytic performance for ketonization of acetic acid

3.2.1 Co–Mo bulk catalyst performance for ketonization of acetic acid

In this study, Co–Mo bulk catalyst showed good performance in the ketonization of acetic acid at 300–400°C with 0.2 g of catalyst used. Acetic acid conversion increased with increasing reaction temperature, but the selectivity was slightly decreased. Table 2 shows that the conversion of acetic acid was 39% at 300°C. However, it increased to 86% at 380°C and to 91% at 400°C. Catalyst selectivity decreased with increasing temperature.

In this case, the selectivity was 91% at 380°C (78% acetone yield) and decreased to 76% (69% acetone yield) which are in the agreement with results that reported previously [27].

3.2.2 Co–Mo supported catalyst performance for ketonization of acetic acid

SiO\(_2\), Al\(_2\)O\(_3\), TiO\(_2\) and 20% Co–Mo supported catalysts were tested in the ketonization of acetic acid at 380°C and optimum conditions. It can be seen that, support catalysts showed low activity in the ketonization of acetic acid as their testing results are shown in Table 3. 20% Co–Mo/Al\(_2\)O\(_3\) catalyst showed the best catalytic performance in comparison to other Co–Mo supported catalysts. It gave 95% of acetone selectivity at 96% acetic acid conversion as shown in Table 3. These results are in good agreement with results reported for Zn–Cr/Al\(_2\)O\(_3\) [21]. This may be due to the higher dispersion of Co–Mo on the alumina support in comparison to other supports [21,27].

The ketonization of acetic acid over 20% Co–Mo/Al\(_2\)O\(_3\) supported catalyst was investigated using different temperatures. The catalyst was tested at 300–400°C. The results show that the catalytic ketonization of acid increased with increasing temperature. At 380°C, the catalyst gave 95% of ketone selectivity at 96% acid conversion. At higher temperature, the catalyst showed 100% conversion, but the selectivity decreased with increasing temperature (Table 4). Coke might be deposited on the surface of catalyst and because of that, the catalyst showed decreasing selectivity. These results are in good agreement with the results reported for ketonization of pentanoic acid over Zn–Cr oxide catalyst in the gas phase by Al-Ghamdi et al. [9] and that reported for ketonization

Table 2. Ketonization of acetic acid over Co–Mo bulk catalyst in the gas phase (0.2 g, 2 vol% of acid, and 20 mL min\(^{-1}\) of N\(_2\) flow, 4.0 h g mol\(^{-1}\) space time).

| Catalyst | Temperature (°C) | Conversion (%) | Acetone | Hydrocarbons | Unknown |
|----------|-----------------|----------------|---------|--------------|---------|
| Co–Mo    | 300             | 21             | 98      | 0            | 2       |
| Co–Mo    | 330             | 39             | 97      | 1            | 2       |
| Co–Mo    | 350             | 69             | 93      | 3            | 4       |
| Co–Mo    | 380             | 86             | 91      | 4            | 5       |
| Co–Mo    | 400             | 91             | 76      | 4            | 8       |

Table 3. Ketonization of acetic acid over supports and 20% Co–Mo/support catalysts in the gas phase (0.2 g, 2 vol% of acid and 20 mL min\(^{-1}\) of N\(_2\) flow at 380°C, 4.0 h g mol\(^{-1}\) space time).

| Catalyst | Conversion (%) | Acetone | Hydrocarbons | Unknown |
|----------|----------------|---------|--------------|---------|
| SiO\(_2\) | 21             | 91      | 7            | 2       |
| Al\(_2\)O\(_3\) | 45           | 87      | 9            | 4       |
| TiO\(_2\) | 99             | 53      | 38           | 9       |
| 20% Co–Mo/Al\(_2\)O\(_3\) | 96       | 95      | 3            | 2       |
| 20% Co–Mo/SiO\(_2\) | 60         | 98      | 2            | 0       |
| 20% Co–Mo/TiO\(_2\) | 71         | 95      | 4            | 1       |
of propionic acid in the gas phase over Co–Mo and Co–Mo/\textit{Al}_2\textit{O}_3 by Hossein Bayahia [27].

4. Catalyst stability

Both the bulk and supported catalysts were tested for long term for ketonization of acetic acid in the gas phase at optimum conditions for 10 and 12 h time on stream respectively as shown in Figures 5 and 6. The bulk and supported catalysts exhibited stable catalytic performance over chosen time without any notable catalytic deactivation. 20% Co–Mo/\textit{Al}_2\textit{O}_3 catalyst gave the best catalytic performance (95% selectivity at 96% conversion) in comparison to bulk and other supported catalysts were used in this study. The conversion decreased slightly to 94% with the selectivity to acetone largely unaffected. The small drift in conversion was probably caused by catalyst coking which is amounted as 2.4% of carbon content. The catalytic deactivation can be caused by poisoning, fouling and thermal degradation of catalyst [35].

Previously, it has been reported that Co–Mo bulk and 20% Co–Mo/\textit{Al}_2\textit{O}_3 both were stable catalysts for long term in the ketonization of propionic acid at similar conditions in this study. There was very small catalytic deactivation observed after 18 h TOS [27]. Similar results have been recorded in this study as it can be seen in Figures 5 and 6.

5. Conclusion

We have shown that Co–Mo and their supports are active catalysts in the ketonization of acetic acid in the gas phase at the temperature range 300–400°C with an ambient pressure using flow rate of \textit{N}_2. 20% Co–Mo/\textit{Al}_2\textit{O}_3 catalyst showed the best catalytic performance at 380°C in the comparison to the bulk one. The catalyst surface area does not play a significant role in catalytic activity. We believe the higher dispersion of Co–Mo on \textit{Al}_2\textit{O}_3 enhanced the catalytic performance in the ketonization reaction and this catalyst was the best catalyst for this reaction. Both Co–Mo bulk and 20% Co–Mo/\textit{Al}_2\textit{O}_3 supported catalyst showed stable catalytic activity without any notable deactivation during the reaction time around 10 and 12 h TOS respectively.

Acknowledgements

Albaha University is gratefully acknowledged. Special thanks from Dr. Hossein Bayahia to Professor Ivan Kozhevnikov, the University of Liverpool and Professor Ahmed Aoiuissi, King Saud University for all their helps and direction to success. Sincere thanks to Dr. Joel McGlone, the University of Liverpool (United Kingdom) for helping to proofread this paper.

Disclosure statement

No potential conflict of interest was reported by the author.
References

[1] Pandey A, Larroche C, Ricke SC, et al. Biofuels: alternative feedstocks and conversion processes. Burlington: Academic Press; 2011.

[2] Wang W, Niu M, Hou Y, et al. Catalytic conversion of biomass-derived carbohydrates to formic acid using molecular oxygen. Green Chem. 2014;16:2614–2618.

[3] Huber GW, Iborra S, Corma A. Synthesis of transport fuels from biomass: chemistry, catalysts, and engineering. Chem Rev. 2006;106:4044–4098.

[4] Serrano-Ruiz JC, West RM, Dumesic JA. Catalytic conversion of renewable biomass resources to fuels and chemicals. Annu Rev Chem Biomol Eng. 2010;1:79–100.

[5] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels. 2006;20:848–889.

[6] Snella RW, Shanks BH. Ceria calcination temperature influence on acetic acid ketonization: mechanistic insights. Appl Catal A. 2013;451:86–93.

[7] Diebold JP. A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-oils, 1999 NREL/SR-570-27613.

[8] Weingarten R, Tompset GA, Conner WC, et al. Design of catalysts for gas-phase ketonization of pentanoic acid. J Catal. 2011;279:174–182.

[9] Bayahia H, Kozhevnikova EF, Kozhevnikov IV. Ketonisation of carboxylic acids over CeO$_2$-based composite oxides. Appl Catal A: Gen. 1995;128:209–217.

[10] Bayahia H, Kozhevnikova EF, Kozhevnikov IV. Ketonisation of carboxylic acids over Zn–Cr oxide in the gas phase. Appl Catal B. 2015;165:253–259.

[11] Gliński M, Kijerski J. Catalytic ketonization of carboxylic acids synthesis of saturated and unsaturated ketones. React Kinet Lett. 2000;69:123–128.

[12] Bayahia H. PhD thesis, the University of Liverpool, 2015.

[13] Bayahia H, Kozhevnikova E, Kozhevnikov I. High catalytic activity of silicalite in gas-phase ketonisation of propionic acid. Chem Commun. 2013;49:3842–3844.

[14] North J, Poole O, Alotaibi A, et al. Efficient hydrodesulfurization catalysts based on Keggin polyoxometalates. Appl Catal A. 2015;508:16–24.

[15] Alsalme AM, Alzaqri N, Alsaleh A, et al. Efficient Ni–Mo hydrodesulfurization catalyst prepared through Keggin polyoxometalate. Appl Catal B. 2016;182:102–108.

[16] Bayahia H. Deoxygenation of propionic acid in gas phase over cobalt molybdenum catalyst. Asian J Chem. 2016;28:2745–2748.

[17] Aoussi A, Apblett AW, Al-Othman ZA, et al. Direct synthesis of dimethyl carbonate from methanol and carbon dioxide using heteropolyoxometalates: the effects of cation and addenda atoms. Trans Met Chem 2010;35:927–931.

[18] Chen GC, Hsu CS, Mochida I. Chemistry of diesel fuels, applied energy technology series. New York: Taylor and Francis; 2000;140.

[19] Alotaibi MA, Kozhevnikova EF, Kozhevnikov IV. Deoxygenation of propionic acid on heteropoly acid and bifunctional metal-loaded heteropoly acid catalysts: reaction pathways and turnover rates. Appl Catal A. 2012;448:447–488.

[20] Benissa H, Davey PN, Khimyak YZ, et al. Heteropoly compounds as catalysts for hydrogenation of propionic acid. J Catal. 2008;253:244–252.

[21] Alsalme AM, Wiper PV, Khimyak YZ, et al. Solid acid catalysts based on H$_3$PW$_{12}$O$_{40}$ heteropoly acid: acid and catalytic properties at a gas–solid interface. J Catal 2010;276:181–189.

[22] Al-Wadaani F, Kozhevnikova EF, Kozhevnikov IV. Pd supported on ZnII–CrII mixed oxide as a catalyst for one-step synthesis of methyl isobutyl ketone. J Catal 2008;257:199–205.

[23] Al-Wadaani F, Kozhevnikova EF, Kozhevnikov IV. Zn(II)–Cr(III) mixed oxide as efficient bifunctional catalyst for dehydroisomerisation of α-pinene to p-cymene. Appl Catal A. 2009;363:153–156.

[24] Argyle MD, Bartholomew CH. Heterogeneous catalyst deactivation and regeneration: a review. Catalysts. 2015;5(1):145–269.