

Zinc-Chromium oxide catalyst for gas-phase ketonisation of pentanoic acid

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Abstract: Oxides of Zinc and Chromium mixed catalyst with different atomic ratios of Zinc and Chromium were tested in the ketonisation of pentanoic acid in the gas phase. These catalysts were active to form 5-nonanone, at 300 – 400 °C and ambient pressure. It was found that Zn-Cr with an atomic ratio (10:1) gave the best catalytic performance in comparison with other oxides with higher or lower atomic ratio of Zn and Cr mixed oxides, ZnO and Cr₂O₃. In this test, Zn-Cr (10:1) gave 82% of selectivity for 5-nonanone as the main product at 86% of conversion of the acid at 350°C. The catalyst showed stable performance at the best selected conditions with a small decrease in acid conversion. For catalyst characterization, BET surface area and porosity technique, X-ray diffraction and DRIFTS of pyridine adsorption were used.

Keywords: Ketonisation; Pentanoic acid; Zinc-Chromium oxide catalyst; 5-Nonanone, gas-phase.

Introduction

The conversion of carboxylic acid to ketones, CO₂ and H₂O is known as the ketonic decarboxylation or ketonisation of carboxylic acid¹⁻⁶ as shown in the following equation:



Additionally, the ketonisation reaction is an environmentally benign clean reaction since it gives rise to ketones without and by-product pollutants^{7,8}.

The first ketonisation reaction was carried out in 1858 for the production of acetone from calcium acetate⁸. Ketonisation of acetic to produce acetone first took place in 1895 as the first industrial application⁹.

The Ketonisation reaction is a significant upgrading reaction by converting the biomass and achieving partial deoxygenation. Bio-oil compounds can be formed from fast pyrolysis of biomass and that is an example of upgrading of biomass-derived oxygenates. It is a promising reaction due to its importance in industrial processes of upgrading of biomass-derived oxygenates. It is a promising reaction due to its importance in industrial processes¹⁰.

Stonkus et al.¹¹ used Cr-Zn-Mn mixed oxide catalyst in the ketonisation reaction of some aliphatic acids in the vapor phase in temperature ranging between 300-400 °C. In this reaction and, under

optimum condition of 325 °C, the maximum yield of ketones was obtained.

Several bulk and supported mixed oxide catalysts were used in the ketonisation of carboxylic acid in both liquid and gas phase reactions. Strong proton sites catalyst such as heteropoly acid catalyst were active in the ketonisation of propionic acid. Ru/TiO₂ catalyst has been tested in the liquid phase ketonisation of carboxylic acids and showed good catalytic activity⁸.

Bulk Co-Mo and Co-Mo/ Al₂O₃ catalysts were used in the deoxygenation of propionic acid in the gas phase in the presence of N₂ and H₂. Co-Mo/Al₂O₃ and the catalysts showed a very good performance in the presence of N₂ at 200-400 °C to form 3-pentanone. This catalyst gave around 44% of 3-pentanone and only 16% of 3-pentanone which were obtained in the presence of H₂ at the same conditions¹².

Hexanoic acid ketonisation was carried out using the fermentation of sugars to produce high carbon numbers as diesel bendable as 6-undecanone over magnesium and manganese oxides and zirconia catalysts. It was found that the zirconia catalyst was more active than the other catalysts used. It gave 92% of ketone selectivity at 72% of acid conversion¹³. For pentanoic acid ketonisation to form 5-nonanone over Ceria-zirconia at 350°C, it was seen that the ketonisation reaction was thermodynamically favorable at 250°C. This reaction was carried out using the same catalyst at 350°C and,

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it was reported that the catalyst was active in the ketonisation of pentanoic acid to form 5-nonanone with 60% of yield ¹⁴.

It has been reported that 90% of 5-nonanone with lower ketones such as 2-hexanone and 3-heptanone were produced from an aqueous γ -valerolactone (GVL) over Ce-Zr catalysts using single reactor. The same reaction was carried out over 0.1% Pd/Nb₂O₅ and this catalyst was selective for producing pentanoic acid ¹⁵.

Carboxylic acids such as butanoic, pentanoic and hexanoic acids were tested in the ketonisation reaction over Ceria-Zirconia catalyst in the range of temperature between 548 and 623 K. The results showed that the reactivity of ketonisation reaction decreased when increasing the length of the acids carbon chains ¹⁶. These catalysts have also been reported as being active in ketonisation reactions, producing fuels by the upgrading of biomass-derived intermediates ¹⁷.

Crystalline silicalite zeolite¹⁸ and Zn-Cr ¹⁹ and its support have been used in the ketonisation of acetic and propionic acids in the gas phase at 300-450 °C ^{18,19}. Strong proton site catalyst such as heteropoly acid was an active catalyst in the ketonisation of propionic acid in the gas phase ²⁰.

In the current work, ketonisation of pentanoic acid was carried out using 0.2 g of zinc-chromium mixed oxide with different atomic ratio of Zn/Cr which was prepared by co-precipitation method in the range of 300-400 °C, 20 ml min⁻¹ of N₂ flow and 2 vol% of acid.

Experimental Section

Chemicals and materials

The chemical and solvent used in this research work were purchased from sigma Aldrich with no further purification. For the reaction and calibration, pentanoic acid (99.0%), 5-nonanone (>99.0%), Zn(NO₃)₂·6H₂O, Cr(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O were used.

Catalyst synthesis

Pure oxides of chromium, zinc and mixed oxides of zinc and chromium oxides were prepared by co-precipitation method as previously discussed in literature ^{19,21-23}. In this method, chromium and zinc nitrates were dissolved in distilled water. After that, 10 wt% aqueous ammonia was added to 0.2 M of mixture metal nitrates solution. The mixture was stirred at 70 °C until pH = 7 was achieved ^{18,21-23}. At 70 °C, after 2-3 hours the result was filtered and washed with distilled water until it became ammonia-free. The presence of ammonia will contaminate the system at the expense of the desired product. Next, the obtained material was air-dried at 120 °C overnight. Finally, the precipitated material was calcined at 300 °C for 3h in the presence of N₂ flow ²⁴.

Catalyst characterisation

For catalyst characterization, various techniques were used such as nitrogen adsorption-desorption to determine the surface area, X-ray Diffraction and DIFTR- Pyridine adsorption. The procedure for adsorbing pyridine was carried out by grounding the sample of catalyst with KBr as following; firstly, the mixtures were ground and pretreated up to a temperature of 150°C and kept constant for 1 h. For the removal of pyridine, the sample was exposed to pyridine vapor at room temperature for 30 minutes and then heated at 150 °C. Finally, DFTIR spectra were recorded for all samples used in this work ^{18,24}.

Catalyst testing

The reaction of ketonisation of pentanoic acid in the gas phase was carried out using 0.2 g of catalyst, 20 mL/min of N₂ flow, ambient pressure, and 2% vol of acid in the quartz fixed-bed reactor. Prior to the reaction, the amount of catalyst used has been pre-heated to the reaction condition for 1 h. The product was analyzed by using online GC to calculate acid conversion and ketone selectivity and yield. The amount produced of CO₂ was not quantified and not included in the product selectivity calculation.

Result and Discussion

Catalyst characterization

Catalyst surface area and porosity are presented in Table 1. BET results show that pure chromium with the highest surface is in comparison to zinc oxide and zinc-chromium mixed oxides.

Fig.1. shows nitrogen adsorption-desorption isotherm for the best catalyst which is bulk Zn-Cr (10:1) oxide catalyst. This catalyst is mesoporous (between 2 to 50 nm pore diameter) with IV isotherm type. Zn-Cr (10:1) mixed oxide catalyst showed an adsorption isotherm with an H3 hysteresis loop and a mononodal pore size distribution with pore diameter at 94 Å ¹⁹.

Table 1. Catalyst characterisation.

Catalyst ^a	S _{BET} ^b [m ² g ⁻¹]	Pore vol. ^c [cm ³ g ⁻¹]	Pore size ^d [Å]
Cr ₂ O ₃	241	0.28	45
Zn-Cr(1:30)	230	0.35	56
Zn-Cr(1:20)	227	0.36	54
Zn-Cr(1:10)	216	0.33	57
Zn-Cr(1:6)	196	0.35	56
Zn-Cr(1:1)	140	0.13	71
Zn-Cr(10:1)	46	0.11	89
Zn-Cr(20:1)	15	0.02	85
Zn-Cr(30:1)	12	0.02	88
ZnO	14	0.03	97

^a Zinc chromium fresh catalyst, calcination condition (300°C and N₂ flow for 3 h); ^b BET surface area; ^c single point total pore volume; ^d average BET pore diameter.

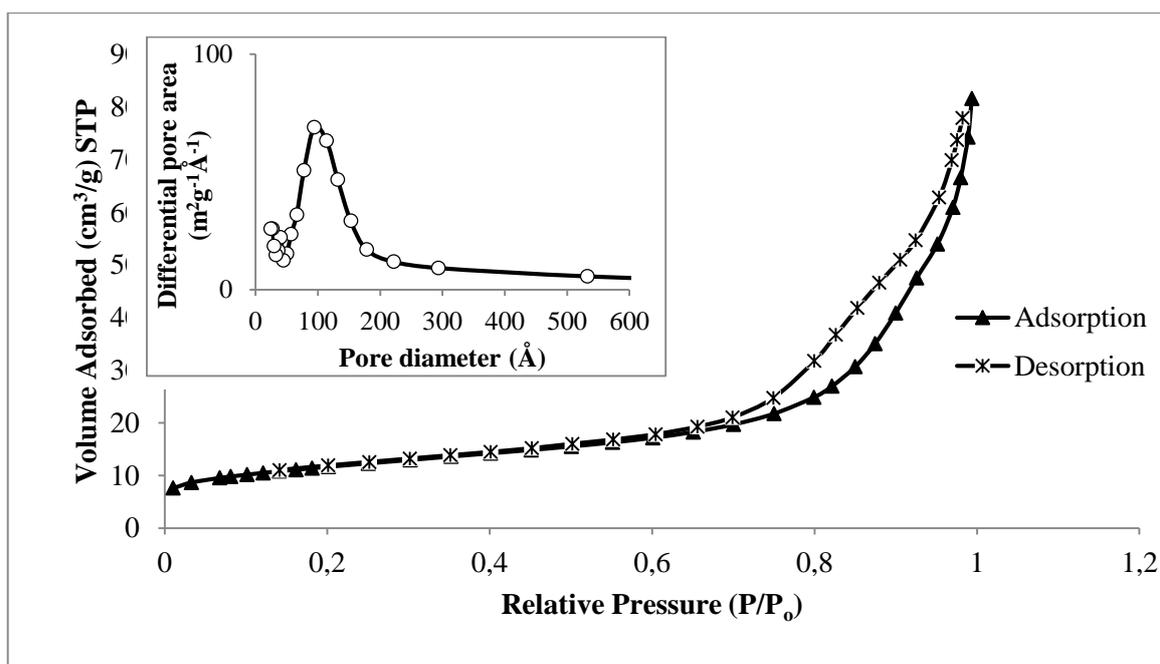


Figure 1. Fresh Zn-Cr (10:1) nitrogen adsorption and desorption isotherm.

X-ray diffraction of zinc-chromium catalyst

X-ray diffraction for pure zinc and chromium and zinc-chromium mixed oxide catalysts calcined at 300 °C in the presence of N₂ shows that rich zinc catalyst is crystalline. However, rich chromium

catalyst is amorphous as shown in Fig. 2.

It has been reported by Hossein Bayahia et. al.¹⁹ that Zn-Cr mixed oxides calcined at > 350 °C exhibited Cr₂O₃ and ZnCr₂O₄ spinel crystalline phase.

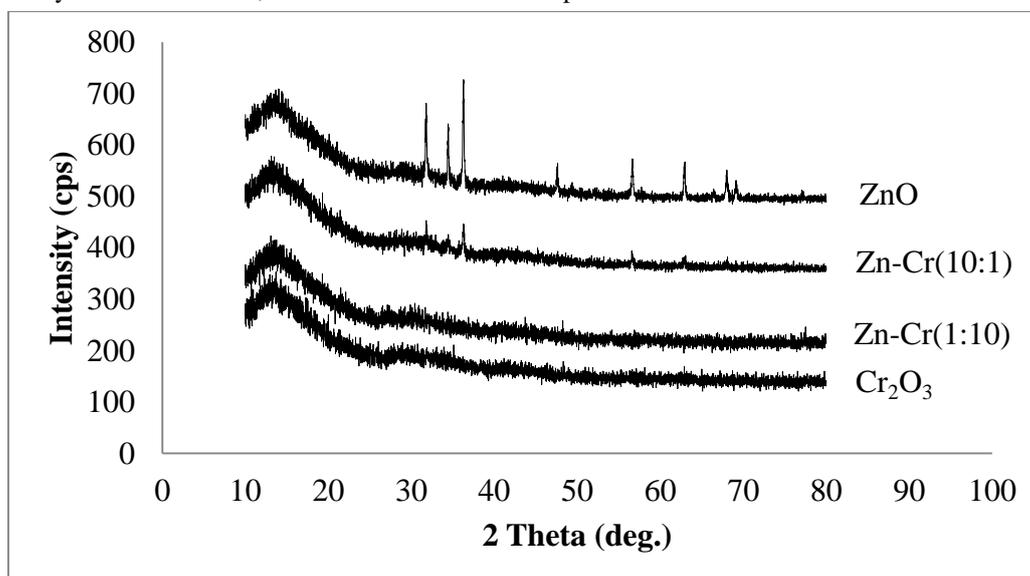


Figure 2. X-ray diffraction for the zinc-chromium catalyst.

Catalyst acidity

The acidity of zinc-chromium catalyst has been measured by DFTIR study of pyridine adsorption as shown in Fig. 3. The bands at 1540 and 1450 cm⁻¹ are attributed to Brønsted and Lewis acid sites respectively^{19,24}. Moreover, the band at 1490 cm⁻¹ is attributed to the adsorption of pyridine on Brønsted and Lewis acid sites together as well as Hydrogen-bonded pyridine. All catalysts of Cr₂O₃, Zn-Cr (10:1) and ZnO with strong bands at 1450 cm⁻¹ have Lewis

acid sites. However, only pure chromium and Zn-Cr (10:1) mixed oxides have a small quantity of Brønsted acid sites in their spectra, while, ZnO has no Brønsted acid sites (Fig. 3). Both Lewis and Brønsted acid sites are responsible for the ketonisation of pentanoic acid to form 5-nonanone as IR patterns for pyridine adsorption show (Fig. 3) and this is in agreement with the literature²⁵. This catalytic property can affect the catalytic activity.

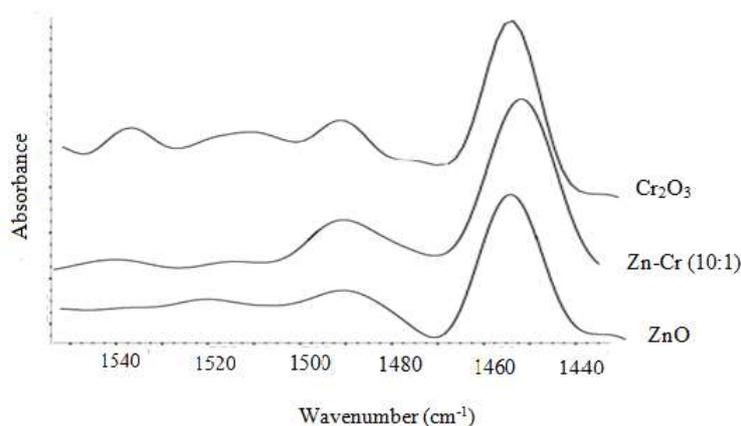


Figure 3 DRIFT spectra of pyridine adsorption for zinc-chromium catalysts.

Catalyst performance

Table 2 illustrates catalytic ketonisation of pentanoic acid over zinc-chromium catalysts. The reaction was carried out at 350 °C, with 20 mLmin⁻¹ flow of N₂, 0.2 of catalyst and 2 % vol of acid used. All catalysts were active, but zinc-chromium (10:1) catalyst was the most active one. The catalyst gave 82% of selectivity for 5-nonanone at 86% conversion (70.52% yield) with only 4% of hydrocarbons produced. These hydrocarbons might be C1-C4 or

higher alkanes and alkenes¹⁵ obtained by acid-catalysed cracking of 5-nonanoic acid¹⁹. CO and CO₂ were not monitored and the unknown remaining might be some deoxygenates products¹⁹. It can be noted that zinc and chrome ratio play a role in ketonisation of pentanoic acid. The acid conversion and ketone selectivity are slightly decreased by increasing the ration of Zn to Cr and this is in agreement with previous report¹⁹.

Table 2. Ketonisation of pentanoic acid over 0.2 g Zinc-Chromium mixed oxide catalysts at 350°C, 1 bar, 2 vol% 20 mLmin⁻¹ N₂, 4.0 h g mol⁻¹ space-time, and 4 h TOS.

Catalyst	Conversion (%)	Selectivity (%)		
		5-Nonanone	Hydrocarbons	Unknown
Cr ₂ O ₃	82	45	9	46
Zn-Cr(1:30)	76	60	11	29
Zn-Cr(1:20)	75	64	13	23
Zn-Cr(1:10)	71	58	9	38
Zn-Cr(1:6)	68	51	7	42
Zn-Cr(1:3)	82	42	11	47
Zn-Cr(1:1)	78	49	9	42
Zn-Cr(10:1)	86	82	4	14
Zn-Cr(20:1)	84	52	9	39
Zn-Cr(30:1)	79	61	7	32
ZnO	84	56	11	33

Table 3 Zinc-Chromium (10:1) oxide catalyst performance in pentanoic acid ketonisation, 1 bar, 20 mLmin⁻¹ N₂, 0.2 g of catalyst, 2 vol% of acid, 4.0 h g mol⁻¹, and 4 h TOS.

Temperature, °C	Conversion (%)	Selectivity (%)		
		5-nonanone	Hydrocarbons	Unknown
300	3	94	2	4
320	42	87	6	7
350	86	82	4	14
380	88	59	9	32
400	95	15	55	30

Effect of temperature

Table 3 shows the ketonisation of pentanoic acid in the range of temperature (300-400 °C). At 300 °C, only 3% of pentanoic acid was converted to 5-nonanone. However, the conversion of acid increased with increasing the temperature from 300

to 400 °C. At 350 °C the catalyst showed the best performance. Increasing the temperature to 400°C, acid conversion reached 95%, but 5-nonanone selectivity decreased to only 15% and the highest amount of hydrocarbons formed by cracking. Generally, ketonisation reaction was affected by

temperature. Increasing the temperature increased the activity, and it can be seen that the selectivity of ketone was reduced.

Activation Energy for ketonisation of pentanoic acid over Zinc-Chromium oxide (10:1)

Activation energy for the pentanoic acid over 0.2 g zinc-chromium catalyst (10:1) at 300-400 °C under 20 mL/min of N₂ flow and 2 vol % of acid was measured as shown in fig. 4. The activation energy is 100 kJ mol⁻¹

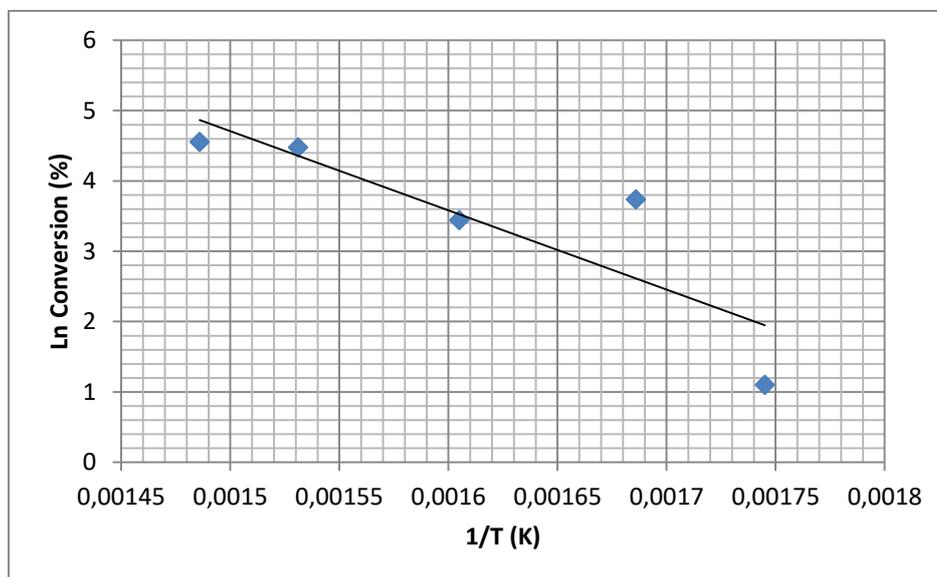


Figure 4. Arrhenius plots of ketonisation of pentanoic acid over Zinc-Chromium (10:1) oxide (300-400°C, 1 bar pressure, 0.2 g catalyst, 20 mL min⁻¹ N₂ flow rate and 2 vol % of pentanoic acid).

Stability of Zinc-Chromium catalyst for ketonisation of pentanoic acid

Zinc-Chromium (10:1) oxide showed the best performance at 350 °C, 20 mL of N₂ flow and 20 vol% of pentanoic acid in the ketonisation of pentanoic acid. In this case, the catalyst was tested for at least 20 hours' time on stream. The catalyst reached the steady state from first hour TOS. The

catalyst was stable with a small decrease in acid conversion. After 18 hours, pentanoic acid conversion decreased from 86 to 73% as shown in Fig. 5. The decrease in catalytic performance with time could be due to the deposition of coke. The catalyst was regenerated by heating under oxidizing conditions. The regenerated catalyst showed similar activity as the fresh catalyst.

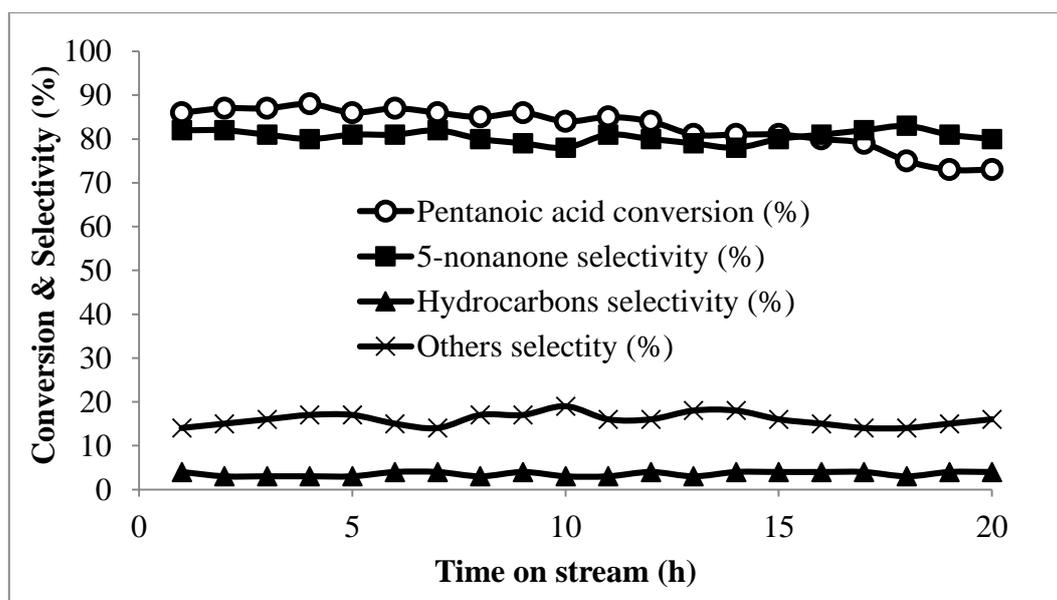


Figure 5. Ketonisation of pentanoic acid on Zinc-Chromium (10:1) oxide (350°C, 1 bar pressure, 0.2 g catalyst, 2 vol % of acid, 20 mL min⁻¹ N₂ flow rate and 4.0 h mol⁻¹ space-time).

This work has demonstrated that zinc-chromium oxide catalysts are active and durable for the

ketonisation of pentanoic acid in the gas phase at 300-400 °C in the flow of N₂ and at ambient

pressure. Zinc-chromium (10:1) oxide catalysts showed the best catalytic activity with around 71% of 5-nonanone yield. This catalyst was stable for 20 h TOS with small deactivation due to the coke deposition on the catalyst surface. BET, XRD, DRIFTS pyridine adsorption techniques were used for the characterization of the catalysts used in this work.

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