

One-step synthesis of 2-pentanone from ethanol over K-Pd/MnO_x-ZrO₂-ZnO catalyst

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Abstract

A highly active and selective K-Pd/MnO_x-ZrO₂-ZnO catalyst for the one-step synthesis of 2-pentanone from ethanol is described. The possible reaction pathways for ethanol reaction over K-Pd/MnO_x-ZrO₂-ZnO catalyst were investigated by means of TPSR, CO₂- and NH₃-TPD techniques. The reactions were performed in a fixed bed continuous flow reactor. Complete conversion with high selectivity for 2-pentanone was observed under 370 ~ 390 °C, 2 ~ 4 MPa, GHSV = 8000 ~ 10,000 h⁻¹ and LHSV < 1.25 h⁻¹ conditions. Ethanol reactions over K-Pd/MnO_x-ZrO₂-ZnO catalyst showed that the catalyst could catalyze dehydrogenation, aldol, dehydration and hydrogenation reactions. Both acidic and basic properties are found on the surface of K-Pd/MnO_x-ZrO₂-ZnO catalyst, whose multifunctionality with the combination of basic, acid and metal sites may be responsible for the efficiency of the K-Pd/MnO_x-ZrO₂-ZnO catalyst.

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Keywords: K-Pd/MnO_x-ZrO₂-ZnO catalyst; Ethanol; 2-Pentanone

1. Introduction

2-Pentanone has increasingly used as industrial solvent and intermediate for preparation of pharmaceuticals and pesticides, especially as a dewaxing solvent for high-boiling petroleum fractions such as those boiling in the lubricating-oil range [1]. Currently available process for the synthesis of 2-pentanone is the liquid phase oxidation of 2-pentanol [2–5]. Stoichiometric amounts of hazardous and/or toxic reagents that generate copious amounts of wastes are used in this process. A contribution to the implementation of greener and sustainable chemistry could be the promotion of catalytic one-step process. A good example is the one-step condensation of carbonyls to higher molecular weight carbonyl compounds. At present this is performed by a homogeneous conventional three-step process. The latter involves, first a base-catalyzed condensation to aldol-type intermediate, followed by dehydration of this intermediate

on acid sites, and finally the selective hydrogenation of the resulting α,β -unsaturated carbonyl [6–8]. This process generates huge amounts of wastes. A purely heterogeneous one-step process could avoid these shortcomings. Since the one-step process is greener and more economical, there is a great interest in finding new catalyst systems. Various supported metal catalysts have recently been described which can be utilized in the one-step synthesis of methyl isobutyl ketone (MIBK) from acetone. These include Ni supported on MgO [9], ALPON [10], or Al₂O₃ [11], Pd-on-MgO promoted by Na [12], Pt-HMFI [13] and Pd or Ni supported on Mg/Al hydrotalcite [14]. Herein, we disclose a first report on the heterogeneous one-step synthesis of 2-pentanone from readily available ethanol over K-Pd/MnO_x-ZrO₂-ZnO catalyst. This route is a green and economical process.

2. Experimental

MnO_x-ZrO₂-ZnO (atomic ratios Mn:Zr:Zn = 2:2:1) catalyst was prepared by co-precipitation of the metal nitrates

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with potassium hydroxide at 75 °C, keeping the pH constant at 11.0. The precipitate was washed thoroughly with deionized water until the pH of the filtrate was brought to about 7.0, and then was dried at 120 °C for 10 h. The dry precipitate was pressed and sieved to sizes desired, then calcined at 450 °C for 3 h. K (K₂CO₃ as precursor) and Pd (Pd(NO₃)₂ as precursor) were doped by conventional impregnation method. The loadings of K and Pd were 1.0 and 0.5 wt.%, respectively.

The catalyst tests were performed in a fixed bed continuous flow reactor (i.d. = 9 mm). The catalyst (2 ml) with the size of 20 ~ 40 mesh particles was reduced in situ in pure H₂ at 420 °C and 2.0 MPa for 2 h before an evaluation. Catalyst evaluations were carried out at 350 ~ 400 °C, 1.0 ~ 4.0 MPa. N₂ was used as carrier gas and was monitored at 4000 ~ 12000 h⁻¹ (volume) and ethanol was pumped into the reactor and was set at 0.5 ~ 1.25 h⁻¹ (volume). The captured liquid products were analyzed by off-line Varian CP-3800 gas chromatography (GC) with a HP-FFAP capillary column and FI as detector using 1-pentanol as an internal standard. The tail gas was analyzed by on-line Agilent HP4890 GC with a Porapak QS column and TC as detector.

Temperature-programmed surface reaction (TPSR) experiments were performed on an America Micromeritics Autochem 2910. About 0.2 g of catalyst was placed in a quartz reactor and reduced by H₂ in a flow rate of 50 ml/min at 420 °C for 1 h, then purged by helium at the same temperature for 0.5 h. After cooling to 50 °C, the sample was saturated with ethanol. After purging treatment, the temperature was ramped at 15 °C/min to the desired temperature in a helium flow of 20 cm³/min. The signals of H₂ (*m/z* = 2), HCHO (*m/z* = 29, 30), CH₃CHO (*m/z* = 29, 44), CH₃COCH₃ (*m/z* = 15, 26) and CH₄ (*m/z* = 16, 15) were simultaneously recorded with a Balsers OmniStar 300.

In temperature-programmed CO₂ desorption (TPD) measurements, sample (0.2 g) was first reduced by H₂ in a flow rate of 50 ml/min at 420 °C for 1 h, then purged by helium at the same temperature for 0.5 h. After cooling to 50 °C, the sample was saturated with CO₂, then flushed with He to remove gas phase and weekly adsorbed CO₂. The temperature was then increased upto 700 °C at 10 °C/min and the desorption profile of CO₂ was monitored by mass spectrometry. NH₃-TPD was carried out in the same way.

3. Results and discussion

The products obtained by passing methanol, ethanol, and 1-propanol over the reduced K-Pd/MnO_x-ZrO₂-ZnO catalyst at 390 °C, 2.0 MPa, GHSV 10,000 h⁻¹ and LHSV 1 h⁻¹ are listed in Table 1. It was found that the principal products were CO₂ and methane, and the oxygenates in the products were dimethyl ether, 2-methyl-1-propanal, 2,4-dimethyl-3-pentanone and 2-methyl-1-propanol for the methanol feed. While the main product, 2-pentanone (41.9% based on carbon atom) was obtained in the case of ethanol as feed instead of methanol. The other oxygenates were acetone, 3-ethyl-

2-pentanone, 4-heptanone and 2-heptanone. D.J. Elliott et al. reported that 2-pentanone could be detected in the liquid products by passing ethanol over CuO/ZnO/Al₂O₃ catalyst under N₂ at 285 °C and 6.5 MPa, but the selectivity of 2-pentanone was very poor [15]. When 1-propanol was used as feed over the same catalyst, 3-pentanone (41.3% based on carbon atom) as the principal product was detected in the liquid products. The main oxygenated byproducts were 2-methyl-pentanal, 4-methyl-3-heptanone, and 2-methyl-1-pentanol.

As shown in Table 1, K-Pd/MnO_x-ZrO₂-ZnO catalyst showed high activity and selectivity for the formation of 2-pentanone from ethanol. In order to improve the activity and selectivity of K-Pd/MnO_x-ZrO₂-ZnO catalyst, the optimum conditional experiments, such as reaction temperature, pressure and space velocity, were carried out under 350 ~ 400 °C, 1.0 ~ 4.0 MPa, GHSV = 4000 ~ 12,000 h⁻¹ (volume) and

Table 1
The product distribution for different feed over K-Pd/MnO_x-ZrO₂-ZnO catalyst

Feed	Methanol	Ethanol	1-Propanol
Conversion (%)	100	100	81
Product distribution (C%)			
Dimethyl ether	12.1	0	0
2-Methyl-1-propanal	2.5	0	1.1
2,4-Dimethyl-3-pentanone	2.0	0	0
2-Methyl-1-propanol	2.7	0	0
Acetone	0	9.6	0
2-Pentanone	0	41.9	0
3-Ethyl-2-pentanone	0	7.3	0
4-Heptanone	0	8.7	0
2-Heptanone	0	7.7	0
3-Pentanone	0	0	41.3
2-Methyl-pentanal	0	0	17.0
4-Methyl-3-heptanone	0	0	14.9
2-Methyl-1-pentanol	0	0	3.3
Others	0	5.3	7.9
CH ₄	14.5	0.8	0
CO ₂	66.2	18.7	14.5

Reaction conditions: *T* = 390 °C, *P* = 2.0 MPa, LHSV = 1 h⁻¹, GHSV = 10,000 h⁻¹, Carrier gas: N₂.

Table 2
Effect of GHSV on the performance of K-Pd/MnO_x-ZrO₂-ZnO catalyst

GHSV/h ⁻¹	4000	8000	10,000	12,000
Conversion (%)	100	100	100	100
Product distribution (C%)				
Acetone	8.0	4.5	9.7	10.8
2-Pentanone	25.0	44.6	41.1	36.4
3-Ethyl-2-pentanone	5.9	7.3	6.5	4.3
4-Heptanone	8.8	8.8	7.6	6.0
2-Heptanone	4.2	6.9	6.6	5.7
Others	19.9	5.7	5.1	11.4
CH ₄	2.1	0.8	0.7	0.6
CO ₂	26.1	21.4	22.7	24.8

Reaction conditions: *T* = 370 °C, *P* = 2.0 MPa, LHSV = 0.5 h⁻¹, Carrier gas: N₂.

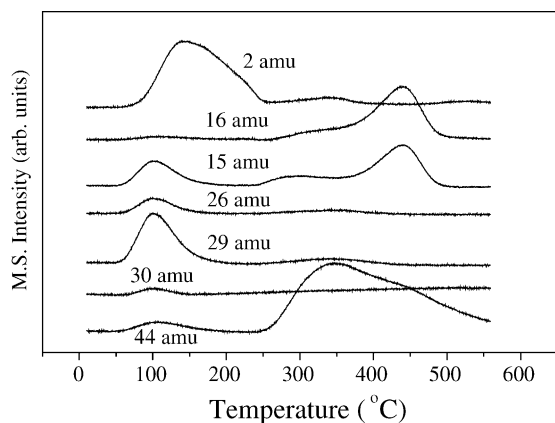


Fig. 1. Desorption spectra of 2, 15, 16, 26, 29, 30, 44 amu masses during TPSR.

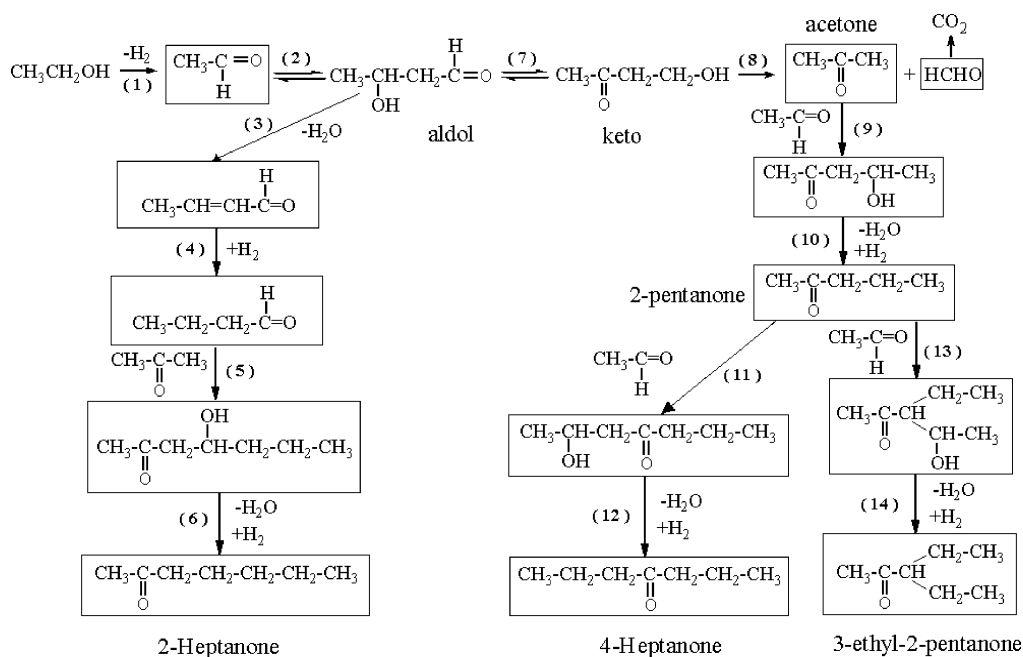
LHSV = 0.5 ~ 1.25 h⁻¹(volume) conditions. It was found that only GHSV had distinct effect (Table 2), The other process conditions on the product distribution were minor. The preferable GHSV, LHSV, temperature and pressure range between 8000 ~ 10,000 h⁻¹, 0.75 ~ 1.0 h⁻¹, 370 ~ 390 °C, and 2.0 ~ 4.0 MPa, respectively.

In order to understand ethanol reaction on K-Pd/MnO_x-ZrO₂-ZnO catalyst, temperature-programmed surface reaction of adsorbed ethanol on K-Pd/MnO_x-ZrO₂-ZnO catalyst was carried out. Desorption peaks of both mass 29 and mass 44 amu are simultaneously observed at the same temperature of about 100 °C, and the signal of mass 29 amu is stronger than that of mass 44 amu (see Fig. 1), which imply the formation of CH₃CHO. The H₂ (2 amu), HCHO (29 and 30 amu),

CH₃COCH₃ (15 and 26 amu) and CH₄ (16 and 15 amu) are also detected during TPSR. The results of TPSR suggest that the CH₃CHO can be formed at low temperature via dehydrogenation of CH₃CH₂OH on catalyst, and then be easily converted to CH₃COCH₃ and HCHO at almost same temperature. The CH₄ is formed at high temperature of about 440 °C, consistent with the fact of poor selectivity to CH₄ in the range of reaction temperature.

On the basis of the results of reactions and TPSR experiments, the possible reaction pathways involved in the formation of detected main products are shown in Scheme 1. Acetaldehyde is formed via ethanol dehydrogenation (step (1)). Aldol species formed from self-condensation of acetaldehyde produce 1-butylaldehyde (steps (2)–(4)). The condensation of 1-butylaldehyde-acetone leads to 2-heptanone (steps (5) and (6)). The aldol species (butanl-al-3-ol) converts to the keto form via H transfer (step (7)) [16]. Acetone is formed by reverse aldol condensation of the keto form of reaction intermediates (step (8)) [16]. The acetone-acetaldehyde condensation reaction (steps (9) and (10)) gives 2-pentanone [16]. 4-Heptanone is formed by condensation of aldol-type intermediates formed in 2-pentanone-acetaldehyde condensation reactions (steps (11) and (12)). 3-Ethyl-2-pentanone is also formed by condensation of aldol-type intermediates formed in 2-pentanone-acetaldehyde condensation reactions (steps (13) and (14)).

The results presented in Table 1 show that the reaction pathways by passing methanol and 1-propanol over K-Pd/MnO_x-ZrO₂-ZnO catalyst are similar to those in the case of ethanol as feed. In contrast, the selectivities to ketones are poor using methanol as feed, because the formaldehyde



Scheme 1. Reaction pathways for ethanol reactions over K-Pd/MnO_x-ZrO₂-ZnO catalyst.

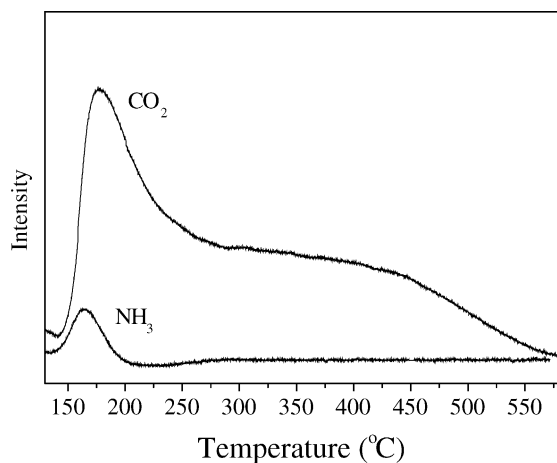


Fig. 2. CO_2 - and NH_3 -TPD-MS spectra of Pd-K/ MnO_x - ZrO_2 -ZnO catalyst.

formed via methanol dehydrogenation lacks the α -hydrogen required for aldol reaction.

It is emphasized that the K-Pd/ MnO_x - ZrO_2 -ZnO is an efficient catalyst not only for aldol reaction, but also for dehydration and hydrogenation reaction of aldol products. Therefore, the process of higher ketones production, generally including three units of aldol reaction, dehydration and hydrogenation, for example, methyl isopropyl ketone (MIPK) production [6,17,18], will be simplified into one unit using K-Pd/ MnO_x - ZrO_2 -ZnO catalyst.

TPD spectra of adsorbed CO_2 and NH_3 on the K-Pd/ MnO_x - ZrO_2 -ZnO catalyst are shown in Fig. 2. It is evident that the K-Pd/ MnO_x - ZrO_2 -ZnO catalyst adsorbs CO_2 and NH_3 , thus possesses both acidic and basic properties. The basic, acid and metal sites are required for aldol, dehydration and hydrogenation reaction, respectively [12].

4. Conclusions

K-Pd/ MnO_x - ZrO_2 -ZnO catalyst showed high activity and selectivity for the one-step synthesis of 2-pentanone from

readily available ethanol. Complete conversion with high selectivity for 2-pentanone was obtained under at $370 \sim 390^\circ\text{C}$, $2.0 \sim 4.0\text{MPa}$, $\text{GHSV} = 8000 \sim 10,000\text{h}^{-1}$ and $\text{LHSV} < 1.25\text{h}^{-1}$ conditions. The catalyst is multifunctional: the dehydrogenation, aldol, dehydration and hydrogenation reactions can be simultaneously accomplished on Pd-K/ MnO_x - ZrO_2 -ZnO catalyst. The efficiency of the K-Pd/ MnO_x - ZrO_2 -ZnO catalyst is probably attributed to the combination of basic, acid and metal sites on it.

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