One pot synthesis of Raspberry ketone over Pd loaded Zn-La bifunctional catalyst

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Abstract: Raspberry ketone also called as rheosmin is an important flavor compound from perfumery, cosmetics and food industry. It is synthesized by one pot aldol condensation of *p*-hydroxybenzaldehyde to α,β-unsaturated ketone and then further hydrogenated to obtain raspberry ketone over novel Pd loaded Zn-La(3:1) bifunctional catalyst. The catalyst was found to give the best conversion and selectivity at 160^{o}C. The catalyst was characterized by SEM, TEM, TGA-DSC, FTIR, CO_2-TPD and BET method before and after reaction. Pd-Zn-La was found to be stable, active and reusable up to 3 cycles. Reaction mechanism and kinetics were studied to note that the reaction is kinetically controlled.
Keywords: Raspberry ketone, bifunctional catalyst, aldol condensation

1. Introduction

Raspberry ketone is an important primary aromatic compound from the family of red raspberries. It also occurs in cranberries and blackberries. Natural extraction of pure raspberry ketone gives ~1-4 mg/kg of raspberries. Therefore, it is one of the most expensive chemicals from flavor industry. It ranks 2nd behind natural vanillin, with a total potential market value between 6 and 10 million Euros; however, currently the commercial demand cannot be met. Because of its intensive fragrance, raspberry ketone has found wide applications in food additives, perfumes and cosmetics. Enzymatic synthesis starts from coumaroyl-Co-A using benzalacetone synthase and reductase[1]. But the procedure is time consuming. Therefore one pot synthesis of raspberry ketone from *p*-hydroxybenzaldehyde (PHB) (Figure 1) is very useful on industrial scale. Here we have developed a novel Pd/Zn-La (3:1) bifunctional catalyst for synthesis of raspberry ketone selectively. In the first step aldol condensation of PHB occurs on basic sites to form α,β-unsaturated ketone i.e p-hydroxybenzalacetone (PHBA) which will be then get reduced on metal sites. Detailed kinetic study was carried out further. Mixed oxide with different combinations of Zn, La and Mg was tested for selective synthesis of PHBA. Combustion synthesized Zn:La with mole ratio 3:1 was found to offer the best results for this reaction.

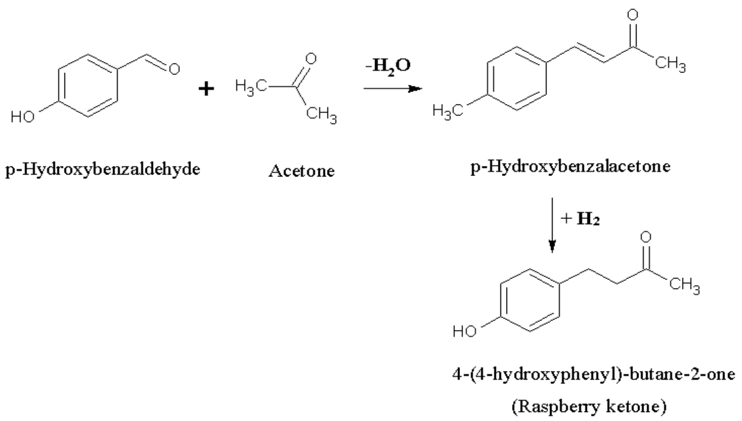

Figure 1. One pot synthesis of raspberry ketone

2. Experimental All the reactions were carried out in 100 ml autoclave. 1:20 mole ratio of 4HB to acetone was taken into the reactor. The reaction mixture was heated to optimum temperature, periodic sampling done and analyzed. Analysis was carried out using GC with TG-5 capillary column and FID detector.

3. Results and discussion

Catalyst Preparation: All the mixed oxide catalyst of different combinations of Mg, La and Zn were prepared by reported hydrothermal and combustion synthesis method.[2,3]

Catalyst characterization: SEM analysis was carried out to study surface characteristics of catalyst. CO_2 TPD was studied and it was found that Zn:La (3:1) synthesized by combustion method using glycine (fuel) led to higher basicity with 0.25 mmol/g total basic sites. TGA analysis showed that the catalyst is thermally stable up to 700°C.

Optimization of parameters: Different combinations of Zn, Mg and La were prepared by hydrothermal method and among which Zn:La (3:1) gave good selectivity for PHBA. Therefore further we have synthesized it with combustion method using different fuels for combustion. And among all Zn:La synthesized using glycine as a fuel offered the highest conversion of PHB and selectivity for PHBA (Table 1). It was selected as the best catalyst. 99% conversion of PHB was obtained at 160°C, 1:20 mole ratio of PHB:acetone and at 0.004 g/cm^3 of catalyst loading (Figures 2, 3). Further PHBA was reduced to form raspberry ketone by loading Pd on Zn:La. A kinetic model was developed to observe that the reaction is kinetically controlled.

Table 1. Comparison of catalyst synthesized by hydrothermal and combustion method

Catalyst	Conversion of 4 HB	Selectivity for PHBA	Selectivity for Diacetone alcohol	Selectivity for Mesityl oxide
Zn: La (3:1) Hydrothermal	31	47.4	28.2	24.4
Zn: La (3:1) Combustion with glycine	**87.6**	**61.9**	**8.3**	**29.8**
Zn: La (3:1) Combustion with glycerol	35.6	53.6	21.5	24.9
Zn: La (3:1) Combustion with urea	13	15	37.6	46.7

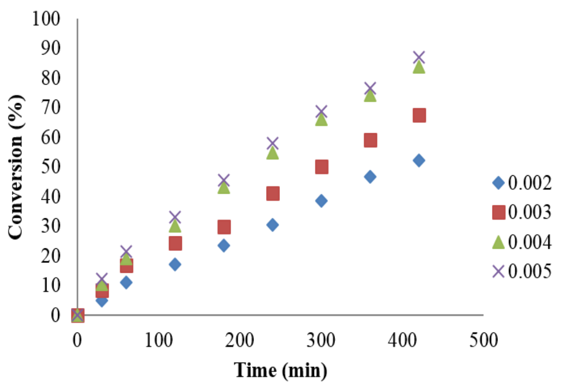

Figure 2. Effect of catalyst loading

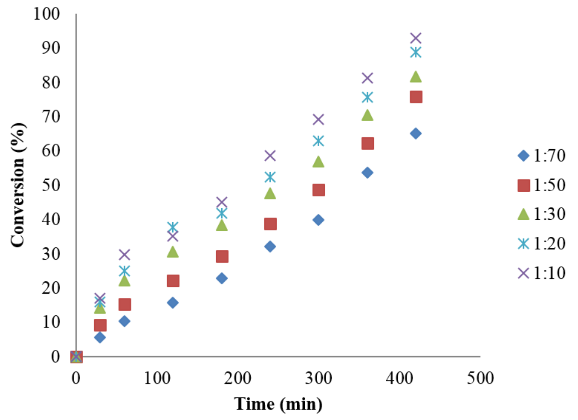

Figure 3. Effect of mole ratio

4. Conclusions

Novel catalyst Pd-Zn-La (3:1) prepared by combustion method shows the best activity in synthesis of raspberry ketone. Catalyst is robust, thermally stable and reusable. Reaction is kinetically controlled. ransfer.

References

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