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Highly selective Pd/KX catalysts for low-pressure one-step synthesis of 2-ethylhexanal from n-butyraldehyde and hydrogen

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2-ethylhexanal (2EH) was directly synthesized from n-butyraldehyde and hydrogen at 1 atm and 150 °C using the catalysts prepared by supporting tetraamine palladium(II) chloride on the potassium ion-exchanged zeolite X (Pd/KXW) and on the potassium ion-added zeolite X (Pd/KXU). The latter catalyst contains a larger amount of potassium ion and exhibits higher activity and very high selectivity to 2EH (>93%) due to its greater basicity. The main reaction path possibly starts from self-condensation of n-butyraldehyde on the catalyst basic sites to form 2-ethyl-3-hydroxyhexanal followed by dehydration to 2-ethyl-2-hexenal which was then hydrogenated on the metallic Pd sites to 2EH.

Keywords: n-butyraldehyde, 2-ethylhexanal, hydrogenation, palladium, zeolite X supported palladium

1. Introduction

2-ethylhexanal (2EH) is a raw material for the manufacture of octanic acid and perfumes; it is traditionally made by the hydrogenation of 2-ethyl-2-hexenal (2E2H) in the liquid phase [1–4]. With a Pd/Al_2O_3 catalyst, a high reaction rate for the formation of 2EH was found both in the presence and absence of $FeCl_2$ and a very low rate for further hydrogenation of the C=O double bond to the alcohol [1]. The kinetics of the hydrogenation of 2E2H was studied on the Pd/SiO_2 catalyst in a continuously stirred tank reactor; the catalyst was completely selective with no 2-ethylhexanol or 2-ethylhexenol being produced [2]. With nickel and nickel boride in a batch slurry reactor, 2E2H was hydrogenated to both 2EH and 2-ethylhexanol [4]. In the gas phase hydrogenation of 2E2H over a Pt/Al_2O_3 catalyst, the addition of oxygen decreased the deactivation rate and the products included 2EH, 2-ethylhexanol and deoxygenated aldehyde [5]. In order to obtain 2EH from 2E2H at high selectivity, selective hydrogenation on the C=C double bond of 2E2H is necessary. With a palladium catalyst, saturated aldehydes can be produced from the corresponding unsaturated aldehydes at high yields [6].

Self-condensation of n-butyraldehyde to produce 2E2H has been studied over a variety of catalysts, viz. metal carboxylate [7], titanium dioxides [8], alkaline earth oxides [9], γ-alumina [9], mixed metal oxides ($MgO–Al_2O_3$, $CaO–Al_2O_3$) [10], and zeolite X [9]. For alkaline earth oxide catalyst and alkali ion-modified γ-alumina catalyst, the dimer was formed by self-condensation of n-butyraldehyde and the trimeric glycol ester was produced via cross condensation between n-butyraldehyde and the dimer. The selectivity of the dimer and trimer were correlated with acid–base properties of the catalyst [9]. Two types of alkali ion-modified zeolites X, i.e., the alkali ion-exchanged zeolites and alkali ion-added zeolites, were utilized for the isomerization of 1-butene at 273 K; the ion-added zeolites containing alkali ions in excess of ion exchange capacity exhibited high catalyic activity due to the generation of strongly basic sites in the zeolite cavities [11]. For self-condensation of n-butyraldehyde, the alkali ion-added zeolites also exhibited higher activity than the ion-exchanged zeolite [9].

In this study, we report low-pressure one-step synthesis of 2EH from n-butyraldehyde and hydrogen. Bifunctional catalysts capable of producing aldol condensation, dehydration and selective hydrogenation are prepared by supporting palladium on potassium ion-exchanged zeolite X and on potassium ion-added zeolite X. The latter catalyst exhibits very high selectivity of 2EH (>93%) and shows significantly better results in both the catalyst activity and the yield of 2EH. The catalytic results are correlated with the basicities and the metallic sites of catalysts. In addition, the reaction path is proposed.

2. Experimental

The potassium ion-exchanged and ion-added zeolite X were prepared in a similar way as described in the literature [11]. NaX (Strem 14-8790) was ion-exchanged with a 0.4 N solution of potassium acetate at 60 °C for 12 h and the solution was filtered. After completing the fourth exchange, the catalysts were divided into two parts. The first part was washed with de-ionized water, whereas the second part was kept unwashed. Both catalysts were dried at room temperature in the desiccator, heated in air at 110 °C for 12 h and finally calcined in air at 400 °C for 4 h. The resulted catalysts were denoted as KXW and KXU, respectively. Each

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KX was then impregnated with a solution of tetraamine palladium(II) chloride monohydrate (98%, Aldrich), dried at 110 °C for 12 h and calcined at 400 °C for 4 h in air to contain 0.5 wt% palladium supported on KX, viz. Pd/KXW and Pd/KXU. The percentages of ion exchange of NaX zeolite were determined with an atomic absorption spectrometer (Hitachi Z-6100).

The powder X-ray patterns of both Pd/KX and NaX were measured with a XRD spectrometer (Shimadzu XD-5). Pd/KX catalysts exhibit similar but less intense peaks as compared with those of NaX zeolite, indicating only slight change of crystal structure during the preparation process. The BET surface areas of Pd/KX catalysts were determined with a sorption analyzer (Micromeritics ASAP 2000). The catalyst basicity was determined by temperature-programmed desorption of carbon dioxide. Before adsorption, 0.1 g of the catalyst sample was heated under helium flow (40 ml/min) with a rate of 10–500 °C to remove water from the sample and then cooled to room temperature. Measured pulses of carbon dioxide (pulse volume 0.5 ml) were injected into helium gas and carried through the sample until saturated adsorption. Then the temperature was increased to 110 °C and remained there for 2 h to remove the physisorbed carbon dioxide. Finally, the system was heated from 110 to 400 °C at 10 °C per min and kept at 400 °C for 0.5 h. The TPD diagrams were obtained by monitoring the desorbed gas with a thermal conductivity detector.

The catalytic reaction was performed at 150 °C and 1 atm in a fixed-bed, integral-flow reactor (1.7 cm I.D. × 50 cm). Prior to the reaction, the Pd/KX catalyst was treated with hydrogen gas (50 ml/min) of high purity (99.99%) at 400 °C for 2 h and then cooled to the reaction temperature with flowing dry nitrogen gas. Reagent grade n-butyraldehyde and hydrogen gas with a molar ratio of 1 : 1 were fed into the flow reactor at a total flow rate of 0.027 $\mathrm{mol\,h^{-1}}$ via a microfeeder (Raze A-99) and a gas flow controller (SCOT 52–36E), respectively. The reaction products were condensed into liquids at -10 °C, identified with a GC-MS (Hitachi M-52) and periodically analyzed by a gas chromatograph (HP 5890 series II) equipped with a PONA column (Supelco 0.2 mm × 50 m) and a flame-ionization detector.

3. Results and discussion

Figure 1 shows the temperature-programmed desorption of carbon dioxide profile from Pd/KXW and Pd/KXU samples. Table 1 compares the catalyst properties of Pd/KXW and Pd/KXU. The Pd/KXU catalyst exhibits higher content of potassium ion and larger amount of basic sites, while its surface area is slightly smaller. In the reaction of n-butyraldehyde and molecular hydrogen, the conversion of n-butyraldehyde (X_B), the selectivity (S_i) and the yield (Y_i) of ith product are defined on the basis of converted n-butyraldehyde:

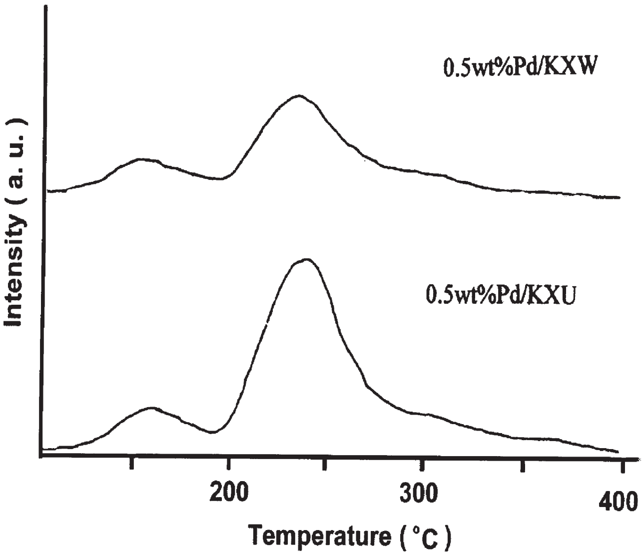

Figure 1. TPD of CO_2 profile for Pd/KXW and Pd/KXU.

Table 1
The catalyst properties.

Catalyst	Pd/KXW	Pd/KXU
K^+/Al^{3+} (mol%)	80	89
$(K^+ + Na^+)/Al^{3+}$ (mol%)	90	103
Pd content (wt%)	0.5	0.5
BET surface area (m^2/g)	394	361
Base amount (mmol CO_2/g)	0.106	0.161

$$X_\mathrm{B}(\mathrm{mol\%}) = \left(1 - \frac{\text{mol of } n\text{-butyraldehyde in the product}}{\text{mol of } n\text{-butyraldehyde in the feed}}\right) \times 100\%,$$

$$S_i(\mathrm{mol\%}) = \frac{\text{mol of } n\text{-butyraldehyde converted to } i\text{th product}}{\text{mol of } n\text{-butyraldehyde reacted}} \times 100\%,$$

$$Y_i(\mathrm{mol\%}) = \frac{\text{mol of } n\text{-butyraldehyde converted to } i\text{th product}}{\text{mol of } n\text{-butyraldehyde in the feed}} \times 100\%.$$

Under our reaction conditions, viz. 150 °C, 1 atm, n-butyraldehyde/hydrogen molar ratio 1 : 1 and $W/F_\mathrm{B} = 22.2$ $\mathrm{g_{cat}}$ h/mol n-butyraldehyde, the major product is 2EH with selectivity more than 91% for Pd/KXW and 93% for Pd/KXU. The minor products include 1-butanol, 2E2H, and a trimer of n-butyraldehyde. The exact structure of this trimer is not clear and its selectivity is less than 3%. In the reaction of n-butyraldehyde and hydrogen over KXW and KXU zeolites, no hydrogenated product is observed. This demonstrates the role of palladium as metallic sites for hydrogenation.

Figure 2 shows the catalyst activity as a function of time-on-stream for the conversion of n-butyraldehyde over Pd/KXW and Pd/KXU catalysts. Both catalysts exhibit faster decay rates during the initial 2 h process time and

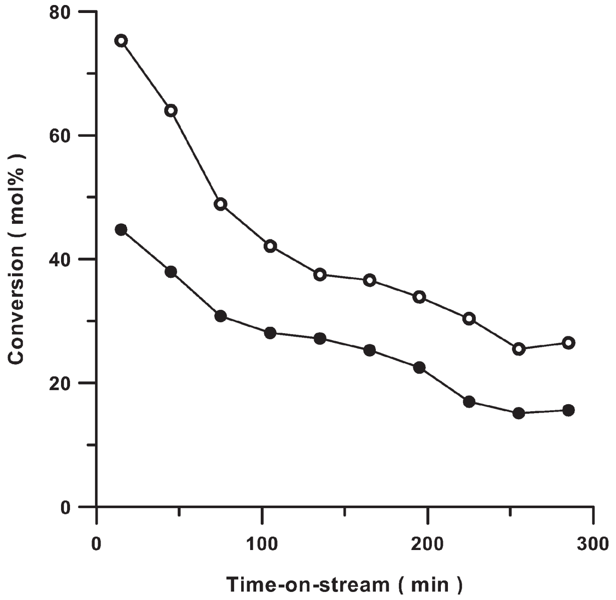

Figure 2. n-butyraldehyde conversion as a function of time-on-stream. (●) Pd/KXW; (○) Pd/KXU.

thereafter show much less variation in the catalyst activities. The Pd/KXU catalyst exhibits apparently higher activity. Such result is attributed to its larger amount of basic sites (figure 1). Figure 3 shows the effect of time-on-stream on the selectivities to 2EH, 2E2H, and 1-butanol. With both catalysts, the selectivities to 2EH are very high and slightly increase with increasing the process time, i.e., 91–94% for Pd/KXW and 93–96% for Pd/KXU.

Figure 4 illustrates the possible reaction network. The main path (I) starts from self-condensation of n-butyraldehyde on the catalyst basic sites to form 2-ethyl-3-hydroxyhexanal (2E3HH) followed by dehydration to 2E2H. Then selective hydrogenation of 2E2H on metallic Pd sites leads to the formation of 2EH. The minor path corresponds to direct hydrogenation of n-butyraldehyde on the C=O double bond to yield 1-butanol (path II). The formation of 2E3HH from n-butyraldehyde is supposed to be the rate-limiting step due to the extremely high selectivity of the hydrogenated product 2E2H. Only little yield of 1-butanol and negligible quantity of 2-ethylhexenol or 2-ethylhexanol are produced; these results imply that highly selective hydrogenation occurs on the C=C double bond of the unsaturated aldehyde of 2E2H in accordance with the catalytic behavior of a palladium supported catalyst [6].

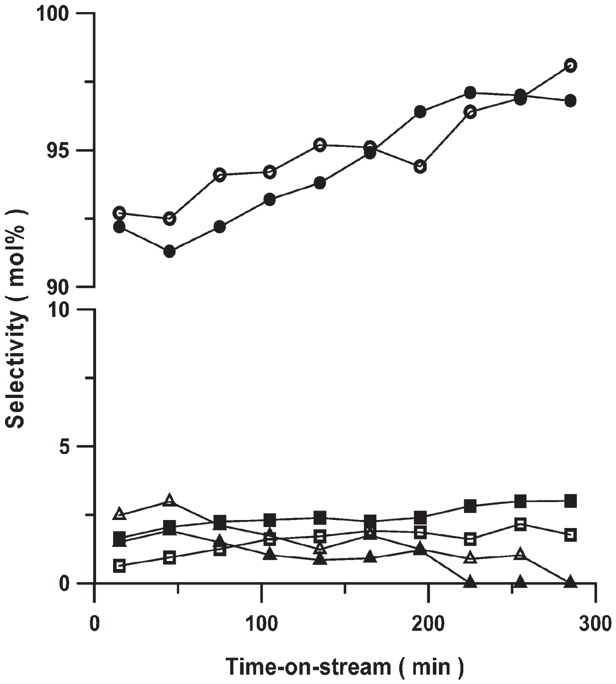

Figure 3. Product selectivities as a function of time-on-stream. Over Pd/KXW: (●) 2EH, (▲) 2E2H, (■) 1-butanol; over Pd/KXU: (○) 2EH, (△) 2E2H, (☐) 1-butanol.

4. Conclusion

In this study, highly selective one-step formation of 2EH from n-butyraldehyde and hydrogen is attained with the potassium ion-added zeolite X supported palladium catalyst (Pd/KXU). Such catalyst contains notably larger amount of basic sites and exhibits higher catalytic activity and 2EH selectivity. Therefore, Pd/KXU is a potential catalyst for direct synthesis of 2EH from n-butyraldehyde and hydrogen.

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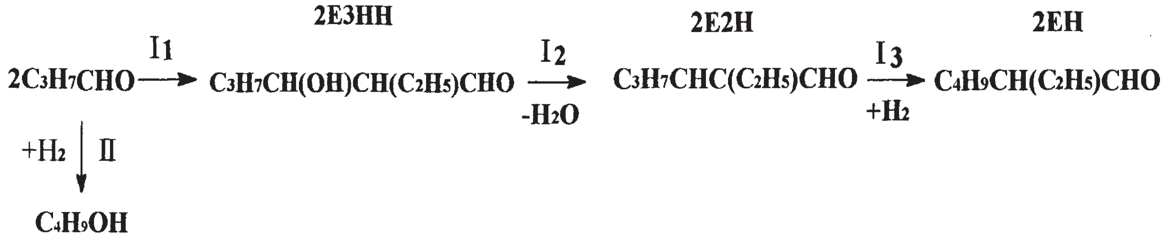

Figure 4. The proposed reaction paths in the synthesis of 2EH.

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