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One-step Synthesis of *n*-Butanol from Ethanol Condensation over Alumina-supported Metal Catalysts

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Abstract: One-step synthesis of *n*-butanol from bimolecular condensation of ethanol was firstly achieved over nickel supported gamma alumina catalyst. A mechanism of dehydration path for the growth of carbon chain by eliminating a hydroxy group from one ethanol molecule with a α-H of other ethanol molecule rather than aldol condensation was verified.

Keywords: Ethanol condensation, *n*-butanol, nickel supported on gamma alumina, dehydration.

An important commercial chemical, *n*-butanol, was widely used as an organic solvent and an additive to gasoline as well. The traditional synthetic method of *n*-butanol was aldol condensation of acetaldehyde, followed by catalytic hydrogenation of the condensed intermediates over basic zeolites[1]. It was reported[2-4] that *n*-butanol was produced with the selectivity of 43 % at optimum reaction temperature of 420°C *via* bimolecular condensation of ethanol on alkali cation zeolites such as Rb-LiX zeolite. An alternative mechanism was proposed [2], in which one molecule of ethanol its C-H bond in β-position was activated on the basic zeolite and condensed with another ethanol molecule by dehydration.

In the present study the gamma alumina-supported nickel catalyst was the first time to be utilized as a catalyst to achieve bimolecular condensation of ethanol to give *n*-butanol with the selectivity of 64% at relatively low reaction temperature of 200°C. The possible reaction mechanism examined in this study supported the mechanism reported in reference[2].

Experimental

Alumina-supported metal catalysts were prepared by adding 20 to 40 mesh γ-Al_2O_3 (purchased from Shanghai Chemical Reagent Company) to a solution containing the required amount of $Ni(NO_3)_2 \cdot 6H_2O$ (or other nitrates needed). The mixture was kept at room temperature for two days and then was dried at 150°C. Before catalytic testing 1.0 g catalyst was loaded in a ceramic tube reactor and pretreated under hydrogen flow at 500°C for 4 h.

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The ethanol condensation reactions were carried out at 200˚C and 1 atm in a fixed bed ceramic tube reactor with the inner diameter of 8 mm. Ethanol was introduced by a pump with LHSV of 0.67 h^{-1}. The products were analyzed by GC-FID(HP-1102G) equipped with OV-101 column and identified by GC/MS(HP5970).

The X-ray diffraction of the catalyst was performed with Ni-filtered Cu-*K*α radiation from a 12-kW Rigaku rotating anode X-ray source operated at 45 kV and 50 mA after the catalyst was reduced by hydrogen at 500˚C for 4 h and cooled to room temperature under hydrogen flow in a specially designed cell.

Temperature-programmed reduction (TPR) of the catalysts was performed in a micro-reactor (*ca.* 80 mg sample loading) at a heating rate of 10˚C min^{-1} using a mixture of 5 vol % H_2/N_2 as reducing gas after passing through a 4A molecular sieve trap to remove water. A gas chromatography with TCD was used for monitoring the hydrogen consumption and recorded the TPR profiles.

Results and Discussion

The catalytic performances over 8%Fe/γ-Al_2O_3, 8%Co/γ-Al_2O_3 and 8%Ni/γ-Al_2O_3 catalysts were given in **Table 1**. It can be seen from **Table 1** that among them the 8%Ni/γ-Al_2O_3 catalyst exhibited the highest catalytic activity with 19.1% conversion of ethanol and 64.3% selectivity of *n*-butanol, respectively. However no *n*-butanol was obtained over 8%Fe/γ-Al_2O, mainly producing acetaldehyde. Over 8%Co/γ-Al_2O_3 catalyst the considerable amounts of *n*-butanol was obtained with selectivity of 22%.

To optimize nickel loading for alumina–supported nickel catalysts, three different loading catalysts, 4%Ni/γ-Al_2O_3, 8%Ni/γ-Al_2O_3 and 15%Ni/γ-Al_2O_3 were prepared and their catalytic performances at the same reaction conditions were listed in **Table 2**.

Table 1 The catalytic performances of different catalysts over ethanol condensation reactions

Catalyst	Ethanol Conv.(%)	AD sel.(%)	BD sel.(%)	EA Sel(%)	BO Sel.(%)	others
8%Fe/γ-Al_2O_3	2.7	95.0	0	0	0	5.0
8%Co/γ-Al_2O_3	17.2	14.1	15.9	29.2	22.7	18.4
8%Ni/γ-Al_2O_3	19.1	5.8	3.8	3.1	64.3	23.0

a) Reaction conditions: temp: 200˚ C; LHSV: 0.67 h^{-1}

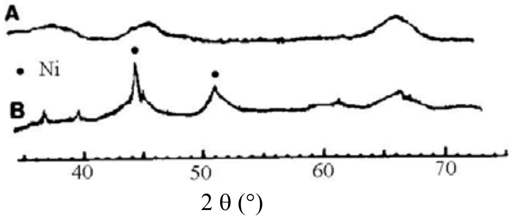
b) AD: Acetaldehyde; BD: Butaldehyde; EA: Ethanyl acetate; BO: *n*-butanol

c) Others: 2-Ethylbutanol, *n*-hexanol, ethyl ether, *n*-butyl ether *etc.*

Table 2 Catalytic performances over different nickel loading catalysts

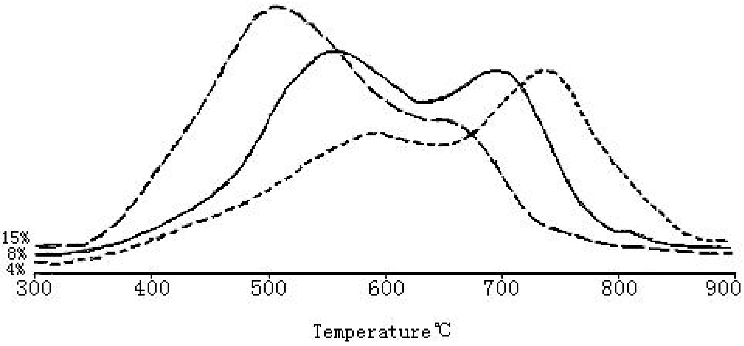
catalyst	Ethanol Conv. (%)	*n*-Butanol yield(%)
4%Ni/γ-Al_2O_3	15.6	8.6
8%Ni/γ-Al_2O_3	19.1	12.3
15%Ni/γ-Al_2O_3	12.0	5.6

Figure 1 XRD patterns of γ-Al_2O_3 and 8%Ni/γ-Al_2O_3



A: Blank γ-Al_2O_3 B: 8%Ni/γ-Al_2O_3 after H_2 reduction

Figure 2 Profiles of temperature-programmed reduction over 4%Ni/γ-Al_2O_3, 8%Ni/γ-Al_2O_3 and 15%Ni/γ-Al_2O_3



From therein one can see that 8%Ni/γ-Al_2O_3 catalyst demonstrated relatively high catalytic activity and selectivity of *n*-butanol. To explore the active site of the catalyst, semi-in-situ XRD was performed and the results was shown in **Figure 1**. From the XRD profiles Ni(0) was confirmed in the catalyst and it may act as the active sites.

This will be further confirmed by TPR profiles as shown in **Figure 2**. In the TPR profiles the first peak maximum (T_M) in the lower temperature region due to the reduction of $Ni(NO_3)_2$ to NiO were observed on three catalysts. The corresponding T_M values: 510°C(on 15%Ni/γ-Al_2O_3), 560°C(on 8%Ni/γ-Al_2O_3) and 590°C (on 4%Ni/γ-Al_2O_3) were shifted to higher temperatures as decreasing nickel loading. The second peak maximum(T_M) in the higher temperature region mainly ascribed to the reduction of NiO to Ni(0)[5] were observed on both 8%Ni/γ-Al_2O_3 and 4%Ni/γ-Al_2O_3 samples; while only tiny peak on 15%Ni/γ-Al_2O_3 sample indicating the formation of less Ni(0) species over high loading sample. Analogously the T_M values of second reduction peaks: 705°C (on 8%Ni/γ-Al_2O_3) and 745°C (on 4%Ni/γ-Al_2O_3) showed the same tendency. Reduction of NiO to Ni(0) required increasing temperature as nickel loading decreased. The reason probably was attributed to that low nickel loading catalyst had a relatively large proportion of unreduced nickel which was stabilized at the vacancies of γ-Al_2O_3 with defective spinel structure[6]. Therefore 8%Ni supported on γ-Al_2O_3 may be a suitable catalyst which exhibited relatively high catalytic activity as given in **Table 3**. It implied that metallic nickel was most likely to be the active sites for ethanol condensation to *n*-butanol.

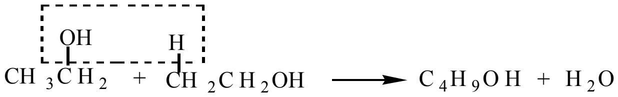
To explore the reaction mechanism of bimolecular condensation of ethanol to *n*-butanol by separately adding acetaldehyde and crotonaldehyde into the reactant feed, the variation in reactivities was observed as listed in **Table 3**.

2-Ethylbutanol and *n*-hexanol were detected in the products. They were considered as the products of the condensation of ethanol and *n*-butanol[2]. However the products of higher molecular weight alcohols such as 2-ethylbutanol and *n*-hexanol were remarkably decreased compared with the case of absence of so called intermediates. After the addition of crotonaldehyde to the reactant feed the yield of *n*-butanol obviously decreased as given in **Table 3**, it revealed that crotonaldehyde was not able to be a intermediate of this ethanol condensation reaction. This point was consistent with the reported mechanism in literature[2]. It indicated that the growth of carbon chain in this ethanol condensation reaction was not taken place *via* aldol condensation pathway. The following alternative dehydration path (**Scheme 1**) for extending the carbon chain by eliminating a hydroxyl group from one ethanol molecule with a α-H of other ethanol molecule was verified.

Table 3 The effect of addtion of different “intermediates” on reactivity of ethanol condensation reactions

“Intermediate ” added	*n*-butanol yield (%)	2-ethylbutanol yield(%)	*n*-hexanol yield(%)
10% Acetaldehyde	4.3	0.7	0.2
10 % crotonaldehyde	3.8	0.3	0.1
No intermediate	12.3	1.5	0.9

Scheme 1 Dehydration pathway



$$CH_3\overset{OH}{C}H_2 + \overset{H}{C}H_2CH_2OH \longrightarrow C_4H_9OH + H_2O$$

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