



Acetaldehyde Production from Ethanol over Ni-Based Catalysts

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ABSTRACT

The aim of this work was to study the catalytic ethanol dehydrogenation to acetaldehyde over nickel based catalysts. SnO_2 , Al_2O_3 and SiO_2 were used as supporting materials. The reactions were carried out in a catalytic flow system operated in the temperature range of 200 and 350°C under atmospheric pressure. Various parameters such as Ni loading, a kind of supporting materials, contact time on the ethanol conversion and selectivity to acetaldehyde were investigated. The main product in all cases is acetaldehyde, with secondary products such as ethyl acetate and diethyl ether. It has been found that Ni/ SnO_2 showed the highest ethanol conversion with high selectivity to acetaldehyde. The 10 wt% Ni/ SnO_2 exhibited the highest yield of acetaldehyde at 300°C with low contact time (0.05g min^{-1}). The deactivation of 10 wt% Ni/ SnO_2 was occurred after 200 minutes on stream due to the formation of Ni – Sn alloy phase.

Keywords: Acetaldehyde, Dehydrogenation, Ethanol.

1. INTRODUCTION

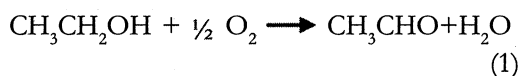
Acetaldehyde is an organic chemical compound, which is used as an intermediate for the synthesis of other chemicals. It can be used as a raw material for the production of acetic acid, acetic anhydride, ethyl acetate, butyl aldehyde, crotonaldehyde, pyridine, peracetic acid and vinyl acetate. Acetaldehyde is also used as a solvent in the production of rubber, in tanning of leather, in the paper industry, as a

fruit and fish preservative, as a flavoring agent, as a denaturant for alcohol and in composition of fuel.

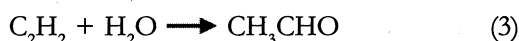
Acetaldehyde can be synthesized by various methods including partial oxidation of ethanol or ethylene (reaction (1) and (2)), hydration of acetylene (reaction (3)) and ethanol dehydrogenation (reaction (4)). The disadvantages of partial oxidation method are

using an expensive catalyst and high reaction temperature [1-2]. The hydration of acetylene involves the use of mercury as mercuric complex which is a toxic material [2]. Thus, the alternative ethanol dehydrogenation method has been very interesting for producing acetaldehyde. This method uses only one reactant, ethanol, which can be synthesized from more abundant resources such as fermentation of agricultural products. Additionally, the co-product of this reaction is hydrogen, which can be used as energy source for fuel cell.

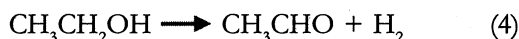
Partial oxidation of ethanol or ethylene



Hydration of acetylene



Ethanol dehydrogenation



Chang et al. [3] reported that dehydrogenation of ethanol using copper catalyst exhibited very high activity for dehydrogenation of ethanol into acetaldehyde. However, the application of copper catalyst is usually confined to rapid deactivation, which results predominantly from sintering due to the inherently low melting point of copper metal phase. Badlani and Wachs [4] studied methanol conversion over various types of metal oxides and found that NiO could promote the dehydrogenation of methanol into formaldehyde. Thus, nickel based catalysts were interested for the catalytic ethanol dehydrogenation into acetaldehyde. This research has been focus on the ethanol

dehydrogenation over supported Ni catalysts. The effects of various parameters such as Ni loading, a kind of supporting materials and contact time on ethanol conversion and selectivity to acetaldehyde were investigated and reported.

2. MATERIALS AND METHODS

2.1 Catalyst preparation

Ni based catalysts were prepared by impregnation method. SnO_2 , Al_2O_3 and SiO_2 were used as supporting materials. $\text{Ni}(\text{NO}_3)_2$ was used as a Ni precursor. The Ni loading was set up to 5, 10 or 15 wt% by varying the nickel nitrate concentrations. The supported was impregnated with an aqueous solution of nickel nitrate. The impregnated solid was dried in oven at 110°C over night. After drying, the dried samples were calcined in air at 400°C for 2 h.

2.2 Catalyst characterization

Identification of the fresh and spent catalyst phases was performed by X-ray diffraction analysis using a Bruker D 8 Advance diffractometer. The patterns were run with nickel-filtered copper radiation ($\lambda=1.5405$). The X-ray tube was operated at 40 kV and 25 mA.

2.3 Ethanol dehydrogenation reaction

Ethanol dehydrogenation was carried out in a conventional fixed-bed flow-type reaction system as shown in Figure 1. Ethanol was fed into the reactor using nitrogen as carrier gas with the concentration of 10% ethanol at standard gas condition (total flow rate of 20 or 40 ml min⁻¹). The reactions were carried out in the temperature range of 200 and 350°C. The reaction temperatures were measured at the center of the catalyst bed. The compositions of feed and products were analyzed by on-line gas chromatograph (Shimadzu GC 14B) equipped with thermal

conductivity and flame ionization detectors, and Porapak-Q separating column.

The ethanol conversion, acetaldehyde

selectivity and yield, and contact time were calculated according to the following formulae:

$$\text{EtOH con. (\%)} = \frac{\text{Moles of reacted EtOH}}{\text{Moles of EtOH in feed}} \times 100 \quad (5)$$

$$\text{AcH selc. (\%)} = \frac{\text{Moles of produced AcH}}{\text{Moles of reacted EtOH}} \times 100 \quad (6)$$

$$\text{AcH yield (\%)} = \frac{\text{Moles of produced AcH}}{\text{Moles of EtOH in feed}} \times 100 \quad (7)$$

$$\text{Contact time (W/F)} = \frac{\text{Catalyst weight (g)}}{\text{Total ethanol feed rate (ml/min.)}} \quad (8)$$

Where:

EtOH con. = Ethanol conversion

AcH selc. = Acetaldehyde selectivity

AcH yield = Acetaldehyde yield

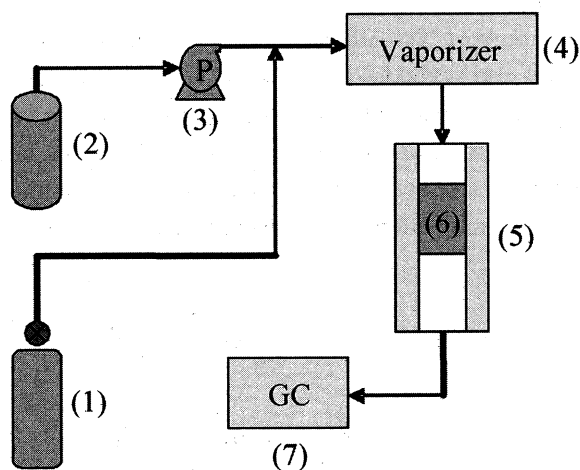


Figure 1. Equipment of the Ethanol dehydrogenation system.

- (1) N₂ gas (2) Ethanol tank (3) Pump (4) Vaporizer
(5) Reactor (6) Catalyst bed (7) Gas chromatograph

3. RESULTS AND DISCUSSION

3.1 Ethanol dehydrogenation over Ni-based catalysts

The ethanol conversion and acetaldehyde

selectivity over Ni based catalysts in the temperature range between 200 and 350°C were summarized in Table 1. The results given in Table 1 indicate that all of supported 5 wt%

Ni catalysts exhibit high selectivity to acetaldehyde more than 75% at the reaction temperatures of 200°C and 250°C. Further, in case of all the supported Ni catalysts gave low ethanol conversion excluding Ni/SnO₂. Ni/SnO₂ showed the highest ethanol conversion of 41.48% and acetaldehyde selectivity of 83.73% at 300°C. It can be seen that ethanol conversion over Ni/SnO₂

increased with an increasing of temperature, however, it has been shown the sharply deactivation by increasing of temperature reached up to 350°C due to the deactivation of catalyst. These results suggested that the Ni/SnO₂ was more active and stable for the production of acetaldehyde from ethanol at 300°C.

Table 1. Ethanol conversion and acetaldehyde selectivity at 200 – 350°C over Ni based catalysts. Conditions: total flow rate 40 ml/min (10% EtOH), catalyst weight: 1g, 5 wt% Ni loading

Temp (°C)	Conversion (%)			Acetaldehyde selectivity (%)		
	Ni/SnO ₂	Ni/Al ₂ O ₃	Ni/SiO ₂	Ni/SnO ₂	Ni/Al ₂ O ₃	Ni/SiO ₂
200	1.24	0.29	0.43	100	100	100
250	9.23	1.25	1.99	98.87	77.71	97.98
300	41.48	7.55	7.45	83.73	59.47	77.13
350	33.11	24.64	0	84.07	53.78	0

3.2 Effect of Ni loading

The effects of the amount of Ni loading on the ethanol conversion and acetaldehyde selectivity over Ni/SnO₂ were investigated and shown in Fig. 2. It has been found that the production of acetaldehyde correlated with Ni loading. The ethanol conversion increased

monotonically with the Ni loading up to 10 wt% after that the ethanol conversion and acetaldehyde yield were not changed significantly. It has been suggested that 10 wt% Ni/SnO₂ was suitable for the production of acetaldehyde from ethanol.

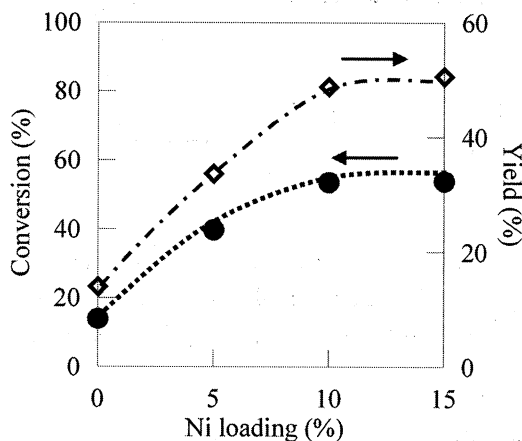


Figure 2. Ethanol conversion and acetaldehyde yield over Ni/SnO₂ as a function of Ni loading at 300°C. ♦ Acetaldehyde yield, ● Ethanol conversion

3.3 Effect of contact time

The effect of contact time on the ethanol dehydrogenation performance of 10%Ni/SnO₂ at 300°C has been shown in Figure 3. It was observed that the conversion of ethanol increased up to 62% when the W/F value increased up to 0.15 g min ml⁻¹. The products of this reaction consisted of two main categories. The major product was acetaldehyde (higher than 80%) and the minor product was ethyl acetate. The trace of diethyl ether (less than 1%) was also found, however,

it was not concerned to be the main category of the hydrogenation products. The selectivity to acetaldehyde decreased with the increase of the W/F ratio due to the formation of ethyl acetate. It should be noted that the selectivity of acetaldehyde was reached up to 100% at low contact time of 0.05 g min ml⁻¹ or lower. The extrapolation to zero space time indicated that the acetaldehyde was a primary product, and ethyl acetate was produced from the dehydrogenation of acetaldehyde [5].

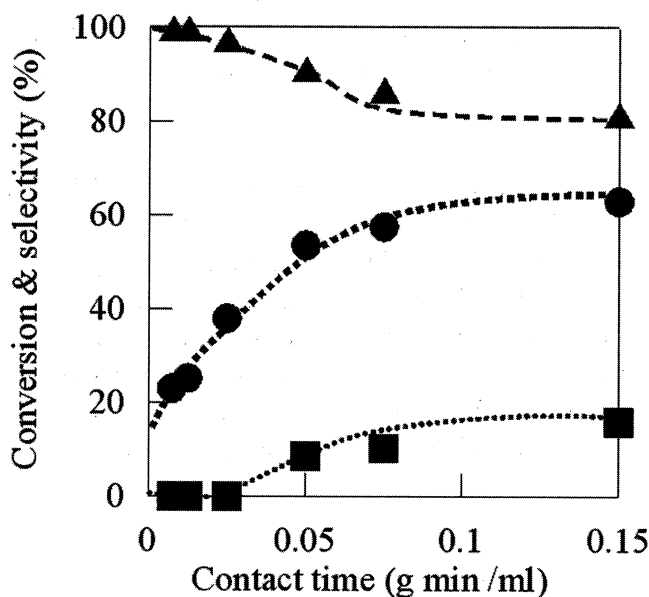


Figure 3. Ethanol conversion, acetaldehyde and ethyl acetate selectivity over 10 wt% Ni/SnO₂ as a function of contact time at 300°C. Conditions: total flow rate 20 ml/min (10% EtOH); Catalyst weight: 1 g.

▲ Acetaldehyde selectivity, ● Ethanol conversion, ■ Ethyl acetate selectivity

3.4 Catalyst stability

The ethanol dehydrogenation over 10 wt% Ni/SnO₂ at 300°C was studied for long period of time in order to confirm the catalyst stability which was very important for the commercial application. During the initial period of the reaction (200 min on stream), the conversion and selectivity of Ni/SnO₂

catalyst seem to be constant, however, it can be seen that the deactivation of catalysts was started when the catalyst was used over 200 minutes on stream (Fig. 4). Further, it must be pointed out that there was little or no change in acetaldehyde selectivity with reaction time.

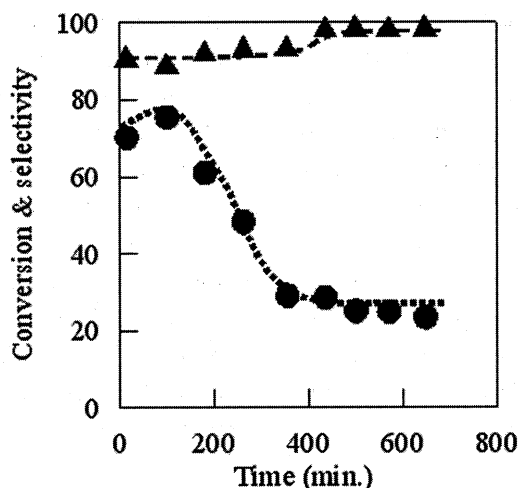


Figure 4. Conversion and selectivity as a function of time 10 wt% Ni/SnO₂ at 300°C.

● Acetaldehyde selectivity, ▲ Ethanol conversion, Conditions: total flow rate 20 ml/min (10% EtOH); catalyst weight: 1 g.

Considering the XRD patterns of fresh 10 wt% Ni/SnO₂ catalyst shown in Fig. 5 a) showed peaks corresponding to NiO (2θ: 37.28 and 43.25) and SnO₂ (2θ: 26.59, 33.88, 37.956, 38.98, 51.78 and 54.76) but the XRD patterns of catalyst after the reaction showed peaks of Ni – Sn (2θ : 30.59, 43.25, 44.60 and 57.56) and SnO₂ as shown in Fig. 5 b).

The formation of Ni – Sn alloy phase may cause the catalyst deactivation. It is interesting that the acetaldehyde selectivity has been almost constant during the reaction (Fig. 4). This strongly suggests that the formation of Ni – Sn phase corresponded to the decreasing of number of active sites but it did not promote any reactions.

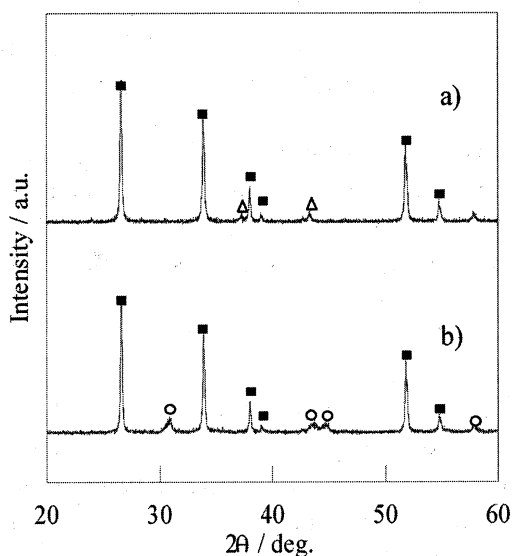


Figure 5. X-ray diffraction patterns of a) fresh 10 wt% Ni/SnO₂ and b) 10 wt% Ni/SnO₂ after the reaction at 300°C for 600 min. (■ SnO₂, △ NiO, ○ Ni-Sn)

4. CONCLUSION

Ni/SnO₂ catalysts exhibited better catalytic ethanol dehydrogenation and selectivity to acetaldehyde than Ni/Al₂O₃ and Ni/SiO₂. Acetaldehyde is a primary product of the reaction with ethyl acetate produced as a secondary product. Based on the experimental results, we recommended the Ni/SnO₂ with 10 wt% of Ni content and reaction temperature at 300°C for production of acetaldehyde in order to achieve high activity and good selectivity. Nevertheless, the catalyst deactivation was observed after 200 minutes on stream due to the formation of Ni – Sn phase.

5. ACKNOWLEDGEMENTS

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