

## ETHYLENE HYDRATION OVER NIOBIC ACID CATALYSTS

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Niobic acids preheated in vacuo at moderate temperatures (200-220 °C) were found to be highly active for ethylene hydration to form ethyl alcohol. The activity at steady state was higher than that of a well known solid phosphoric acid, the selectivity being more than 97% at a reaction temperature of 220 °C.

Recently, we reported that the surface of niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) showed a strong acidic character ( $\text{H}_0 \leq -5.6$ ) even when heated in air at moderate temperatures (100-300 °C) and catalyzed several reactions, such as 1-butene isomerization and 2-butanol dehydration, with high activity.<sup>1)</sup> In this communication, we wish to report the catalytic activity for ethylene hydration which is an industrially important reaction for the production of ethyl alcohol.

A niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , the purity; 99.8%) supplied by CBMM Co. Ltd. was used after washing with distilled water, drying at 100 °C and evacuating at different temperatures for 2 h. A  $\text{Nb}_2\text{O}_5\text{-F}$  was prepared by immersing the niobic acid in a 1.3% HF solution, followed by washing, drying, and evacuation. A  $\text{Nb}_2\text{O}_5\text{-SO}_4^{2-}$  was prepared by impregnating  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  with 0.1 M  $\text{H}_2\text{SO}_4$  solution followed by evaporating to dryness and evacuating. The content of  $\text{SO}_4^{2-}$  was 1.1%. For comparison, a solid phosphoric acid (SPA) supplied from Mitsui Toatsu Co. Ltd. which was evacuated only for 3 min to minimize the removal of phosphoric acid from the catalyst and a nickel sulfate ( $\text{NiSO}_4 \cdot x\text{H}_2\text{O}$ ) calcined in air at 300 °C for 3 h were examined.

The reaction was carried out in a closed recirculation system having a volume of 200 ml. The water vapor (ca. 7.3 kPa) supplied by an evaporator which was thermostated at 40 °C was mixed with ethylene (ca. 36 or 48 kPa) in the system

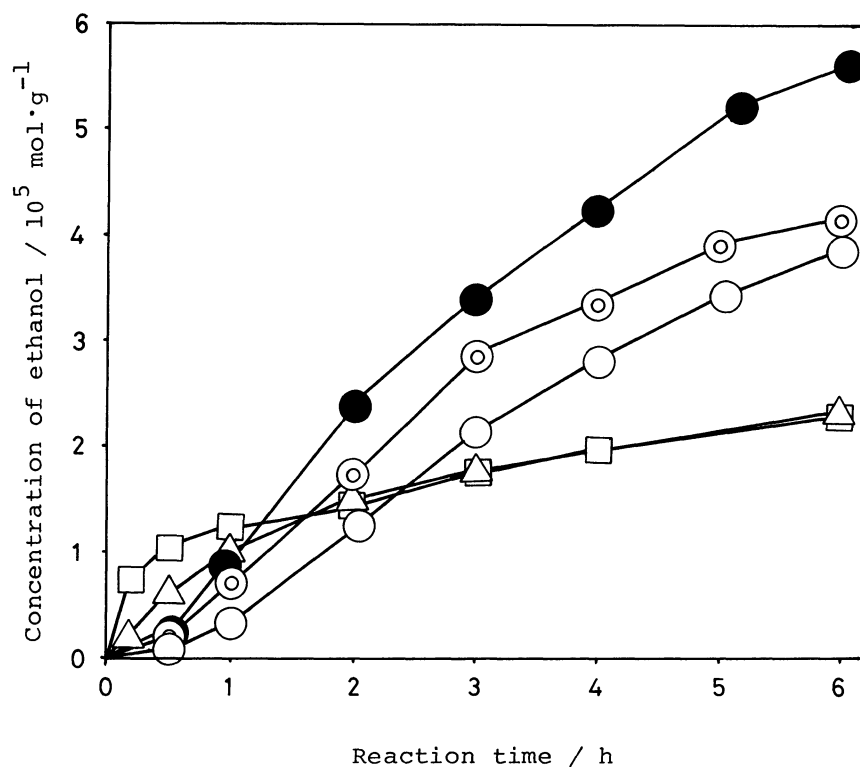


Fig. 1. Hydration of ethylene over various catalysts.

Reaction temperature : 220 °C,

C<sub>2</sub>H<sub>4</sub> : ca. 36 kPa, H<sub>2</sub>O (vapor) : ca. 7.3 kPa,

○ : Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O, ● : Nb<sub>2</sub>O<sub>5</sub>-SO<sub>4</sub><sup>2-</sup>, ⊙ : Nb<sub>2</sub>O<sub>5</sub>-F,  
 □ : NiSO<sub>4</sub>·xH<sub>2</sub>O, △ : solid phosphoric acid.

and allowed to react. The products were absorbed and collected in the water of the evaporator and analyzed by gas chromatography.

The changes in activity of the five catalysts for ethylene hydration at 220 °C with reaction time are shown in Fig. 1. The NiSO<sub>4</sub>·xH<sub>2</sub>O catalyst which was reported to be active for ethylene hydration<sup>2)</sup> and the solid phosphoric acid catalyst which is widely used in industry showed a high activity in an early stage of the reaction, but the activity decreased rapidly. On the other hand, the activity of Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O was considerably low in an early stage of the reaction, but increased gradually as the reaction proceeded and was kept high. This induction period was observed only at the 1st run. The Nb<sub>2</sub>O<sub>5</sub>-F and Nb<sub>2</sub>O<sub>5</sub>-SO<sub>4</sub><sup>2-</sup> catalysts also showed induction periods like Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O and their activities were much higher than those of NiSO<sub>4</sub>·xH<sub>2</sub>O and

Table 1. Catalytic Activities and Selectivities for Ethylene Hydration

Catalyst	Run	Evacuation	Reaction	Concn of ethanol <sup>a)</sup>	Selectivity
		temp / °C	temp/ °C	10 <sup>5</sup> mol·g <sup>-1</sup>	%
Nb <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O	1st <sup>b)</sup>	220	220	2.15	97.2
	1st	200	180	0.20	86.9
	4th	200	180	0.61	90.1
	8th	200	180	0.82	90.4
	1st	300	180	0.14	87.4
	1st	400	180	0.13	79.5
Nb <sub>2</sub> O <sub>5</sub> -SO <sub>4</sub> <sup>2-</sup>	1st <sup>b)</sup>	220	220	3.42	97.7
	1st	200	180	0.37	92.5
	4th	200	180	1.02	92.5
Nb <sub>2</sub> O <sub>5</sub> -F	1st <sup>b)</sup>	220	220	2.87	97.3
	1st	200	180	0.83	95.1
	4th	200	180	1.46	96.6
NiSO <sub>4</sub> ·xH <sub>2</sub> O SPA <sup>c)</sup>	1st <sup>b)</sup>	220	220	1.76	98.9
	1st <sup>b)</sup>	220 <sup>d)</sup>	220	1.80	99.5
	1st	180 <sup>d)</sup>	180	3.13	100
	2nd	180 <sup>d)</sup>	180	1.49	100
	3rd	180 <sup>d)</sup>	180	0.60	100

$\text{C}_2\text{H}_4$ : ca. 48 kPa,  $\text{H}_2\text{O}$  (vapor): ca. 7.3 kPa.

a) Concentration of ethanol solution in evaporator after 3 h.

b)  $\text{C}_2\text{H}_4$ : ca. 36 kPa.

c) Solid phosphoric acid.

d) Evacuated for 3 min.

solid phosphoric acid in a later stage of the reaction.

The activity and selectivity of each catalyst at a reaction temperature of 180 °C are shown in Table 1. A  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  evacuated at 200 °C showed a low activity at the 1st run. However, the activity increased gradually as the run was repeated under the same activation and reaction conditions and reached a steady state at the 8th run.

When  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  was evacuated at a high temperature of 300 or 400 °C, the activity remained low even after the run was repeated. It is noteworthy that the activity increase was observed only when the catalyst was evacuated at 200–220 °C. Over  $\text{Nb}_2\text{O}_5\text{-F}$  and  $\text{Nb}_2\text{O}_5\text{-SO}_4^{2-}$  evacuated at 200 °C, the activity increase was also observed. The steady state activities at 4th run were two and three times higher than those of the 1st runs, respectively. In contrast to these activity increase, the activity of the solid phosphoric acid catalyst decreased awfully as the run was repeated. The selectivities for the formation of ethyl alcohol at 220 °C over  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ,  $\text{Nb}_2\text{O}_5\text{-F}$ , and  $\text{Nb}_2\text{O}_5\text{-SO}_4^{2-}$  were more than 97%, a small amount of the other product being acetaldehyde.

In conclusion,  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ,  $\text{Nb}_2\text{O}_5\text{-F}$ , and  $\text{Nb}_2\text{O}_5\text{-SO}_4^{2-}$  evacuated at relatively low temperatures which showed higher activity than  $\text{NiSO}_4 \cdot x\text{H}_2\text{O}$  and solid phosphoric acid at steady states are promising as catalysts for ethylene hydration. In particular, a simple solid acid,  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  which does not contain F and  $\text{SO}_4^{2-}$  will be the best as a practical catalyst, since the catalysts containing F and  $\text{SO}_4^{2-}$  may lose F and  $\text{SO}_4^{2-}$  which are undesirable materials causing corrosion when used for very long periods.

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#### References

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