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Preparation of ethylene glycol via catalytic hydration with highly efficient supported niobia catalyst

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Ethylene glycol was prepared by hydration of ethylene oxide over highly efficient supported niobia catalyst prepared by chemical vapor deposition. The catalyst showed much better hydration performance in activity and selectivity than other solid acid catalysts. An ethylene glycol yield of 91% was achieved at optimal conditions.

KEY WORDS: ethylene glycol; hydration; supported niobia catalyst; chemical vapor deposition.

1. Introduction

Monoethylene glycol (MEG) is widely used in chemical industry. The production of MEG from ethylene oxide (EO) by thermal and non-catalytic hydration is a well-known process. However, low MEG selectivity and use of large excess amount of water which causes high energy expenditure are economically unattractive [1], and extensive efforts have been paid to explore the suitable catalysts for catalytic hydration of EO. Although a number of acids, including acidic ion-exchange resins, have been used to improve the selectivity, some problems still remain [2–7].

Niobic acid ($Nb_2O_5A \cdot nH_2O$) has been paid much attention as a new solid acid catalyst for years [8–9] because of its high acidity and structural stability in water. Therefore, niobic acid has been used in acid-catalyzed reactions in which water molecules participate or are liberated, such as olefin hydration and esterification [8,9]. Furthermore, its affinity for both water and organic substrate [10] makes it used for the ring-opening reaction of 1,2-aromatic epoxide, such as isomerization and solvolysis of phenyloxirane [10–12].

Here we report a very effective niobium oxide catalyst for hydration of EO to synthesize ethylene glycol. The use of supported niobium oxide catalyst appears favorable, because of easy separation of the product from the catalyst and high EO conversion and MEG selectivity.

2. Experimental

2.1. Catalyst preparation

The supported niobia catalyst was prepared *via* the following steps. Pseudo-boehmite (Condea Chemie, Pural-SB) was extruded, dried at 120 °C and calcined at 1400 °C under static air for 4 h to form α-alumina support. The support was ground and sieved to pellets with diameter of 0.8–1.0 mm. Then the alumina-supported niobium oxides were prepared by chemical vapor deposition of niobium pentachloride at 150 °C as described in the literature [13], followed by hydrolysis under a flow of hydrogen saturated with water vapor at 150 °C. Finally, the catalyst was calcinated at certain temperature under a flow of nitrogen for 2–4 h.

2.2. Reaction Procedure

The reaction of EO hydration was tested over a fixed-bed reactor with an inner diameter of 10 mm and length of 300 mm. The reaction was carried out at temperature of 150 °C and pressure of 1.5 MPa with H_2O/EO mole ratio of 22 and LHSV of 10 h^{-1}. In a typical experiment, 10 mL of catalyst was loaded. For comparison, in non-catalytic reaction the same volume of quartz sand with the same particle size was loaded. The products were analyzed on a HP 6890 gas chromatograph with HP-INNOWAX column and flame ionization detector.

2.3. Characterization

2.3.1. Infrared spectra of adsorbed pyridine

A Nicolet Nexus 470 FT-IR spectrometer was used. The sample disc containing catalyst and KBr with 1 : 1 in weight ratio was heated to 180 °C and

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evacuated under vacuum for 4 h, then cooled down to room temperature and exposed to 500 Pa of pyridine vapor for 15 min. The excess amount of pyridine was removed by evacuation until vacuum returned to the level of 1 Pa. The spectra of adsorbed pyridine were recorded at room temperature, 100, 150, 200 and 250 °C.

2.3.2. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on a Perkin-Elmer PHI 5000C ESCA System using the $\text{MgK}_{\acute{a}}$ radiation from a dual anode operating at a voltage of 10 kV and a current of 40 mA under vacuum of 4.0×10^{-8} Pa. The XPS spectra were calibrated against the carbonaceous C_{1s} photoelectron line.

2.3.3. X-ray diffraction (XRD)

XRD patterns were recorded using a Rigaku D/MAX-1400 diffractometer with a Cu target, a voltage of 40 kV and a current of 40 mA.

3. Results and discussion

3.1. Catalytic performance

The results of non-catalytic hydration and catalytic hydration of EO are summarized in table 1. Compared with non-catalytic reaction, EO conversion increased from 34% to 100% on keeping MEG selectivity almost unchanged when the hydration was carried out over the $Nb_2O_5/\alpha\text{-}Al_2O_3$ catalyst. By comparing with the results of other catalysts and with those reported in the literature, it is found that the yield of MEG over the supported niobium oxide is close to that of Nafion XR (6%)/SiO_2 [14], but much higher than that of $AlPO_4$–$Cu(NO_3)_2$ [14] and HZSM-5. In view of insolubility in water of niobium oxide, the catalyst studied in the present work shows very promising perspective.

3.2. Effect of calcination temperature

The dependence of catalytic performance on calcination temperature is shown in figure 1. When the calcination temperature was under 450 °C, catalytic activity was almost unchanged. However, the activity decreased when the calcination temperature was over 500 °C, and declined remarkably over 600 °C. XRD also showed that a crystalline phase, TT-Nb_2O_5, started to form above 600 °C. At 700 °C two diffraction peaks at 2θ?value of 22.86° and 28.59°, corresponding to TT-Nb_2O_5 characteristic peaks, were clearly observed with the strong diffraction peaks of the support α-Al_2O_3 (figure 2).

Table 1
Comparison of non-catalytic hydration and catalytic hydration of EO

Catalyst	EO conversion (%)	MEG selectivity (%)
–	< 34	92
$Nb_2O_5/\alpha\text{-}Al_2O_3$	100	91
$Nb_2O_5 \cdot nH_2O$,	100	83
HZSM-5 (Si/Al = 61.2)	98	76
$AlPO_4$–$Cu(NO_3)_2$ [14]	90	57
Nafion XR (6%)/SiO_2 [14]	94	94

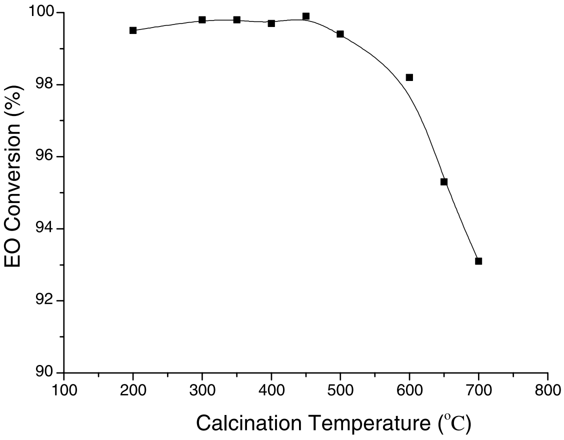

Figure 1. Relationship between calcination temperature and activity of $Nb_2O_5/\alpha\text{-}Al_2O_3$.

Thus, calcination temperature is an important parameter to control the activation of supported niobium oxide catalysts. The decrease of the catalytic activity occurred along with the appearance of TT-Nb_2O_5. Therefore, TT-Nb_2O_5 seems to be ineffective in the hydration of EO.

3.3. IR studies

The acidity of the supported niobium oxide and bulk niobic acid was determined by infrared spectra of pyridine adsorption, as shown in figures 3–5. Characteristic absorption at 1437–1448 cm^{-1} was assigned to pyridine adsorbed on Lewis acid sites, and the absorption at 1540 cm^{-1} was assigned to pyridine adsorbed on Brønsted acid sites.

IR experiment shows that the surface of α-Al_2O_3 prepared in this work is nearly neutral. The $Nb_2O_5/\alpha\text{-}Al_2O_3$ catalyst calcined at 400 °C, which exhibited the best catalytic performance, is found to have Lewis acids and a very little Brønsted acid sites at room temperature (Figure 3). However, all pyridine molecules adsorbed entirely desorbed below 100 °C. In contrast, bulk niobic acid demonstrated strong Brønsted and Lewis acidities (figure 4) even at desorption temperature of 150 °C. The IR study, thus, shows that the acidity of the $Nb_2O_5/\alpha\text{-}Al_2O_3$ catalyst calcined at 400 °C is much weaker than that of bulk Nb_2O_5. Figure 5 reveals the relationship between calcination temperature and the acidity of the catalyst. The amount of acidic sites decreased monotonously with increasing the calcination temperature. The higher calcination temperature used, the lower amount of acidic sites of the catalyst showed. Detailed studies indicated that the acidic strength did not show

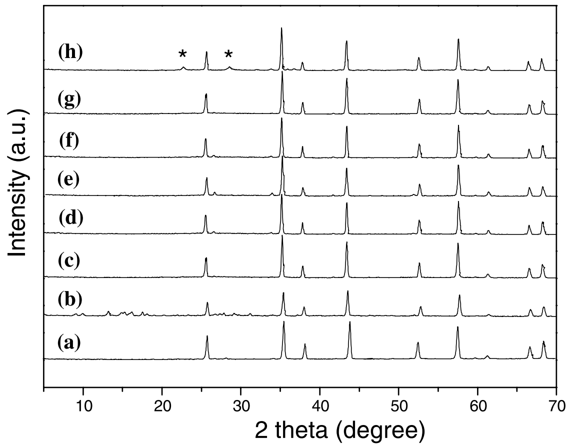

Figure 2. XRD patterns of (a) α-Al_2O_3 and Nb_2O_5/α-Al_2O_3 calcinated at (b) 120 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C, (g) 600 °C, and (h) 700 °C. Asterisks denote the peaks of TT-Nb_2O_5 phase. The peaks from α-Al_2O_3 are indicated by arrows.

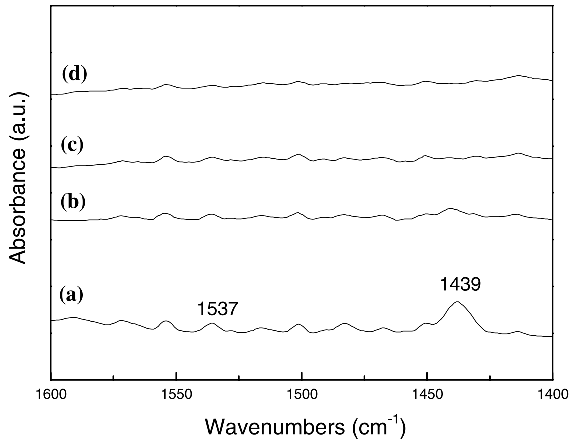

Figure 3. IR spectra of pyridine adsorption on Nb_2O_5/α-Al_2O_3 calcined at 400 °C at different temperatures: (a) room temperature, (b) 100 °C, (c) 150 °C, and (d) 200 °C.

large change under 400 °C, but decreased with higher calcination temperatures. By correlating reaction performance with the acidity of the catalysts it is found that EO conversion over the supported niobium oxide calcined at 200 and 400 °C and over bulk niobic acid was almost the same while the selectivity to MEG over supported niobia was higher than that over niobic acid. The acidity of these three samples was quite different. This seems to imply that in a certain range of acidity, the conversion of EO was independent of the acidity, but the selectivity to MEG decreased with increasing the strength of Lewis acidity.

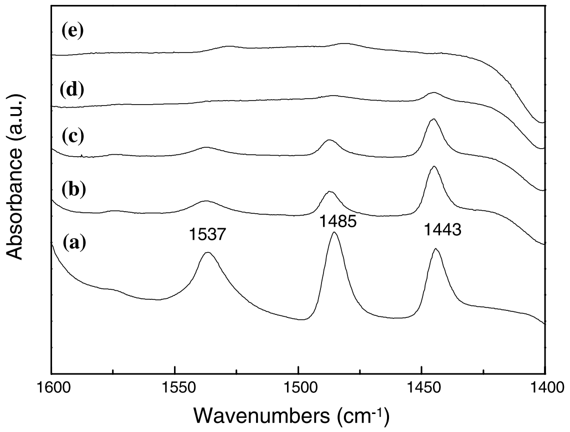

Figure 4. IR spectra of pyridine adsorption on Nb2O5 · nH2O, at (a) room temperature, (b) 100 °C, (c) 150 ° C, (d) 200 ° C, and (e) 250 °C.

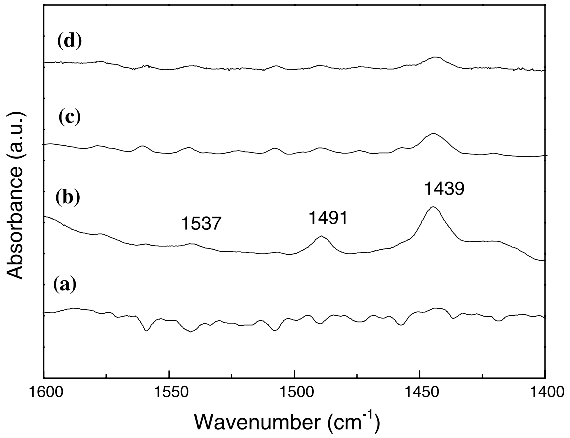

Figure 5. IR spectra of pyridine adsorption at room temperature on (a) α-Al_2O_3, and Nb_2O_5/α-Al_2O_3 calcined at (b) 200 °C, (c) 400 °C, and (d) 700 °C.

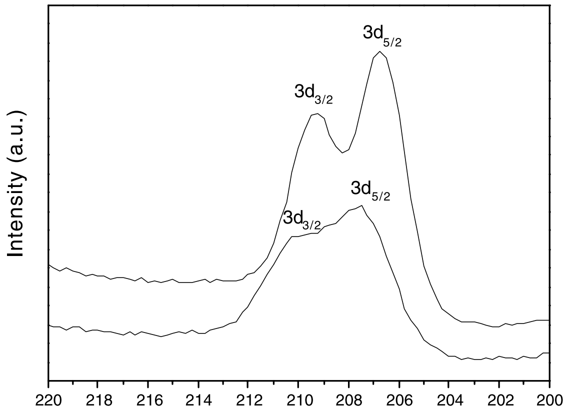

Figure 6. XPS in the Nb $3d_{5/2}$ and Nb $3d_{3/2}$ region of (a) $Nb_2O_5 \cdot nH_2O$, and (b) Nb_2O_5/α-Al_2O_3 calcined at 400 °C for 4 h.

3.4. XPS studies

Figure 6 shows the XPS spectra of niobic acid and supported niobium oxide catalyst in Nb 3d region and details of their XPS results are shown in table 2. The reference value of Nb^{5+} of Nb_2O_5 is between 207.3 and 207.8 eV [15]. The catalyst calcined at 400 °C produced

Table 2
XPS results for niobic acid and supported niobium oxide

Samples	Binding energy (eV)		$\bar{\Delta}BE^a$(eV)
	Nb $3d_{5/2}$	Nb $3d_{3/2}$	
Nb2O5 · nH2O,	206.65	209.38	2.73
Nb_2O_5/α-Al_2O_3 (400 °C)	207.27	210.04	2.77

a single symmetric $3d_{5/2}$ component which, on the basis of its binding energy, could be assigned to oxidation state of Nb^{5+} [16,17]. The XPS results indicate that the catalyst calcined at 400 °C under hydrogen atmosphere in this work keeps its original oxidation state similar to that of niobic acid.

4. Conclusions

The niobium oxide supported on α-alumina was found to be an effective catalyst for selective catalytic hydration of EO under mild conditions. The catalyst showed a high activity and selectivity for hydration of EO and the yield of MEG reached 91% at the LHSV of 10 h^{-1}. The acidity of the niobium oxide catalyst was much weaker than that of bulk Nb_2O_5 phases and apparently influenced the properties of the catalysts. Calcination temperature was an important parameter that controls the activation of supported niobium oxide catalysts. TT-Nb_2O_5 formed over 600 °C was ineffective to the hydration of EO. Calcination temperature for preparation of the catalysts was, therefore, preferred in the range of 300–450 °C.

Acknowledgment

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