Catal Lett (2008) 124:85–90
DOI 10.1007/s10562-008-9428-2

Effect of Calcination Temperature on Structure and Properties of Sn–Nb_2O_5/α-Al_2O_3 Catalyst for Ethylene Oxide Hydration

Yingcheng Li · Shirun Yan · Weimin Yang · Zaiku Xie · Qingling Chen · Bin Yue · Heyong He

Received: 11 October 2007 / Accepted: 7 February 2008 / Published online: 26 February 2008

Abstract Sn–Nb_2O_5/α-Al_2O_3 catalysts were prepared by impregnation and tested for ethylene oxide (EO) hydration to form ethylene glycol. The effect of the calcination temperature on the structure, acidity, H_2O and EO adsorption properties and catalytic performance of the catalyst were investigated by using XRD, TG-DTA, IR, NH_3-TPD and EO-TPD. It was found that the phase compositions, acidity, the EO adsorption strength and water adsorption capacity of the Sn–Nb_2O_5/α-Al_2O_3 catalyst were markedly influenced by the calcination temperature. The catalyst calcined at a temperature between 350 and 400 °C showed the best catalytic performance. A correlation between catalytic performance and characterization was proposed.

Keywords Niobium oxide · Tin oxide · Ethylene oxide · Hydration · Calcination temperature

1 Introduction

The production of monoethylene glycol (MEG) by non-catalytic hydration of ethylene oxide (EO) is a well-known process. It is usually performed with large excess of water (20–25 moles of water per mole of EO) to achieve a glycol selectivity of 88–90%. The raw product of hydration is then dehydrated by rectification which involves large energy consumption and makes the process economically unattractive. Considerable efforts have been paid to explore efficient hydration catalysts. A number of materials such as anion exchange resin [1–3], quaternary phosphonium halides [4], polymeric organosilane ammonium [5], and macrocyclic chelating compounds [6] have been tested as the hydration catalysts. Although these catalysts improved MEG selectivity to certain extent, some problems still remained, such as elution of the active species in water and poor thermal stability. Therefore, development of efficient catalysts for EO hydration which are also insoluble in water, thermally stable and readily recoverable is highly desirable.

Niobic acid ($Nb_2O_5 \cdot nH_2O$) has been paid much attention as a new solid acid catalyst for years [7–9] because of its high acidity and structural stability in water. In our previous papers [10, 11], Nb_2O_5/α-Al_2O_3 catalyst prepared by chemical vapor deposition and/or by impregnation was studied for EO hydration. It was found that the yield of MEG over the supported niobium oxide reached ~89%, which was comparable with that over Amberlite IR, Nafion XR (6%)/SiO_2, but much higher than that over $AlPO_4$–$Cu(NO_3)_2$ and over HZSM-5. The supported niobium oxide also demonstrated excellent stability within 1,000 h on-stream. Modification of α-Al_2O_3 support with optimal amount of water-resistant base material $MgAl_2O_4$ led to a 0.8% increment of MEG yield from the Nb_2O_5/α-Al_2O_3 catalyst [12]. But the H_2O/EO feeding ratio was still high from an industrial standpoint. To further improve the catalytic performance of the supported niobia catalyst, hydrophilic species of SnO_2 was introduced to the Nb_2O_5/α-Al_2O_3 catalyst. It was found that introduction of Sn species significantly improved the water adsorption capacity and hence the H_2O/EO ratio on the catalyst

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Y. Li (✉) · W. Yang · Z. Xie · Q. Chen
SINOPEC Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, P.R. China
e-mail: lyc@sript.com.cn

S. Yan · B. Yue · H. He
Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P.R. China

surface, and thereby resulted in a significant increase in MEG selectivity. A MEG selectivity of 94.0% at EO conversion of 99.7% was obtained at Sn/Nb atomic ratio of (0.80 [13].

The effect of calcination temperature in the development of catalytic active and selective phases is an interesting topic already studied in other mixed metal oxide systems [14]. In this paper, the effect of calcination temperature on the structure, acidity, EO and water adsorption properties as well as the catalytic performance of Sn–Nb_2O_5/α-Al_2O_3 catalysts was investigated.

2 Experimental

2.1 Catalyst Preparation

The procedure for preparation of α-alumina support has been described elsewhere [10, 11]. The Sn–Nb_2O_5/α-Al_2O_3 catalysts were prepared by stepwise impregnation, as described below. The α-alumina support was impregnated under vacuum with niobic acid (Companhia Brasileira de Metalurgiae Mineracao, batch AD-2352) dissolved in an aqueous solution of oxalic acid, followed by drying at 150 °C for 2 h. The resulting solid was impregnated with stannic chloride dissolved in an aqueous solution of hydrochloric acid under vacuum, followed by drying again at 120 °C for 2 h and subsequently calcined in a quartz tube at different temperatures for 2 h under a flow of N_2/H_2 (5 v/v% of H_2), and then for other 2 h under nitrogen atmosphere to obtain tin-promoted 10 wt% Nb_2O_5/α-Al_2O_3 (Sn/Nb = 0.8) (abbreviated as Sn–Nb_2O_5/α-Al_2O_3) catalyst. SnO_2/α-Al_2O_3 was prepared by impregnation of α-alumina support with stannic chloride, dried at 120 °C for 2 h, then calcined at 400 °C under a nitrogen flow for 4 h.

2.2 Catalyst Characterization

The powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max-1400 diffractometer using a Cu Kα radiation at a tube voltage of 40 kV and a current of 40 mA.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with a Rigaku TG-DTA apparatus in the temperature range between room temperature and 800 °C under air atmosphere.

The infrared (IR) spectra of pyridine adsorption and water adsorption were recorded with a Nicolet Nexus 470 FTIR spectrometer with 4 cm^{-1} resolution using an in situ cell. For the pyridine adsorption experiment, the sample disc containing catalyst and KBr with 1:1 in weight ratio was heated to 300 °C and 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 achieved ~1 Pa. The spectra of adsorbed pyridine were recorded at room temperature. For the water adsorption experiment, the catalyst was immersed in water for 24 h, and then centrifuged and dried at 100 °C for 2 h and pressed into a thin disc. The sample disc was evacuated under 3 Pa at room temperature for 4 h. Then the temperature was raised to 250 °C, and the spectra were recorded at 250 °C after 15 min equilibration.

The temperature programmed desorption of ammonia (NH_3-TPD) was carried out in a flow system. Before ammonia adsorption, the sample was pretreated in a helium flow (30 mL/min) at the calcination temperature for 1 h. Ammonia (10 v/v% in helium) adsorption was performed at 100 °C for 1 h, then the gas was switched to helium again. When a steady gas chromatography baseline was established, the temperature was ramped at a rate of 10 °C/min to 400 °C under a helium stream. The desorption of ammonia was monitored by a thermal conductivity detector, and the desorbed ammonia was absorbed with a sulfuric acid solution and quantified by NaOH titration. For temperature programmed desorption of ethylene oxide (EO-TPD), the samples were pretreated as mentioned above. EO was introduced to the catalyst bed by nitrogen bubbling and adsorbed at 50 °C for 1 h and then the temperature was raised to 400 °C at a rate of 10 °C/min under a helium stream and the amount of desorbed EO was detected by TCD.

2.3 Reaction Procedure

The catalytic test for EO hydration was performed in a fixed-bed reactor with an inner diameter of 10 mm and length of 300 mm. In a typical experiment 10 mL of catalyst was loaded. The reaction was performed at temperature of 150 °C and pressure of 1.0 MPa. The liquid hourly space velocity (LHSV) used was 10 h^{-1}. The products were collected in a cold trap and analyzed on a HP 6890 gas chromatograph equipped with a HP-INNOWAX column and a flame ionization detector.

3 Results and Discussion

3.1 Effect of Calcination Temperature on the Structure of Catalyst

The XRD patterns of the Sn–Nb_2O_5/α-Al_2O_3 catalysts calcined at different temperatures are shown in Fig. 1. For the samples calcined at 300 °C and below, the diffraction peaks with $2\theta°$ at 26.5 and 33.9 corresponding to tetragonal stannic oxide (JCPDS No. 21-1250) were observed, and the maximal intensities were found at calcination temperatures

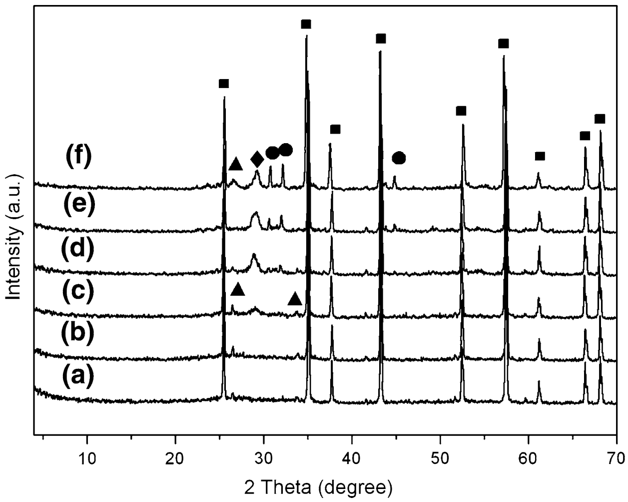

Fig. 1 XRD patterns of Sn–Nb_2O_5/α-Al_2O_3 catalyst calcined at (**a**) 200, (**b**) 300, (**c**) 400, (**d**) 500, (**e**) 600 and (**f**) 700 °C. ■ α-Al_2O_3 (JCPDS No. 10-0173) ● β-Sn (JCPDS No. 4-0673) ◆ $SnNb_2O_6$ (JCPDS No. 23-0592) ▲ SnO_2 (JCPDS No. 21-1250)

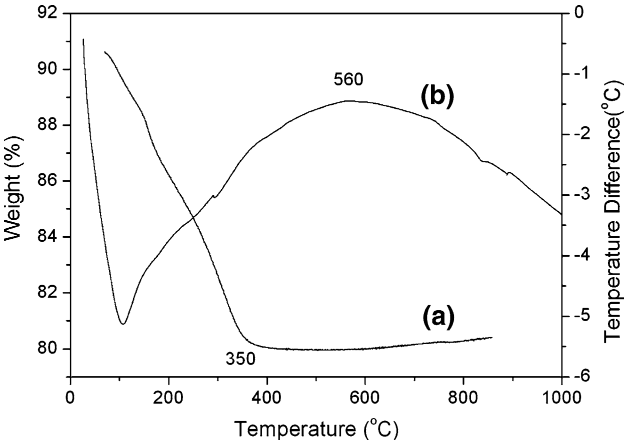

Fig. 2 TG and DTA profiles of Sn–Nb_2O_5/α-Al_2O_3 catalyst (**a**) TGA and (**b**) DTA

between 300 and 400 °C. With increasing the calcination temperature up to 400 °C, the diffraction peak with $2\theta°$ at 28.9 corresponding to stannous niobate ($SnNb_2O_6$) (JCPDS No. 23-0592) appeared [15]. The diffraction peak of $SnNb_2O_6$ became sharper and the intensity increased with increasing calcination temperature. When the calcination temperature was up to 500 °C, the peaks with $2\theta°$ at 30.6 and 32.0 belonging to tetragonal β-Sn (JCPDS No. 4-0673) were observed. The intensity of β-Sn increased with increasing calcination temperature. It is interesting to note that TT-Nb_2O_5 phase which was observed in unpromoted Nb_2O_5/Al_2O_3 catalyst at calcination temperature of 700 °C [11, 16], was not detected in the tin promoted catalyst. The XRD results indicate that the composition of the catalyst was markedly influenced by the calcination temperature. Surface species of the catalyst can react with each other during calcination and the addition of tin retarded the agglomeration of niobia and the formation of TT-Nb_2O_5 phase at higher calcination temperature.

The TGA curve of the uncalcined Sn–Nb_2O_5/α-Al_2O_3 catalyst, as shown in Fig. 2, revealed that the weight-loss of the catalyst occurred in the temperature range between 100 and 350 °C, and no further weight-loss was observed above 350 °C, indicating that the dehydration and decomposition of the catalyst precursor were completed at 350 °C. The DTA curve of the catalyst showed an endothermic peak around 100 °C and a broad exothermic band peaked at 560 °C. The endothermic peak should be ascribed to the dehydration of the catalyst precursor, and the exothermic band may be assignable to the reactions among surface species of the catalyst, such as tetragonal stannic oxide reacted with niobic oxide to form stannous niobate, and the tin-containing compounds were reduced to β-Sn under hydrogen atmosphere, as observed in XRD patterns. The TGA and DTA profiles indicated that dehydration and decomposition process of the catalyst precursor can be completed at 350 °C and calcinations above 350 °C may lead to the further inter-reactions among each component.

3.2 Effect of Calcination Temperature on the Acidity of the Catalyst

As an acid catalyzed reaction, the conversion and selectivity of hydration reaction are dependent upon the surface acidic properties of the catalyst. In order to get an understanding of the dependence of acidic properties of Sn–Nb_2O_5/α-Al_2O_3 catalyst on calcination temperature, The IR spectra of pyridine adsorption in the range of 1,400–1,600 cm^{-1} were recorded as shown in Fig. 3. According to the literature [17, 18], the absorption band at

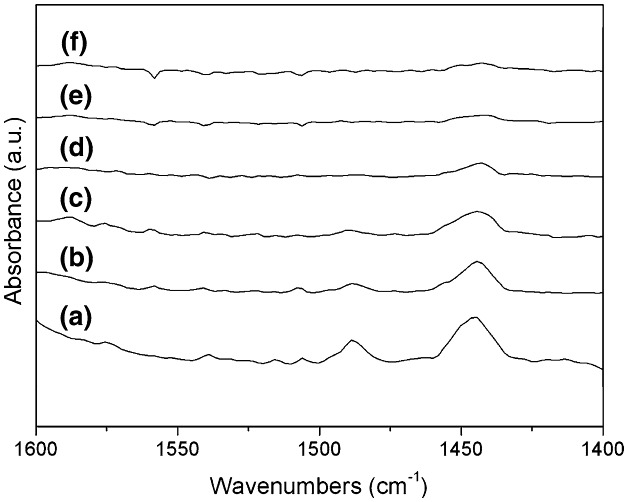

Fig. 3 IR spectra of pyridine adsorption at room temperature on Sn–Nb_2O_5/α-Al_2O_3 catalyst calcined at (**a**) 200, (**b**) 300, (**c**) 400, (**d**) 500 (**e**) 600 and (**f**) 700 °C, respectively

~1,450 cm^{-1} were assigned to pyridine adsorbed on Lewis acid sites (LAS), and the absorption band at ~1,550 cm^{-1} was assigned to pyridine adsorbed on Brønsted acid sites (BAS). Figure 3 shows that for the Sn–Nb_2O_5/α-Al_2O_3 catalysts calcined at 200 °C and above, there were no Brönsted acid sites on the surface of the catalyst as no absorption band at ca. 1,550 cm^{-1} was observed. The intensity of the absorption band at 1,450 cm^{-1} decreased with increasing calcination temperature, indicating that the density of LAS decreased with increasing calcination temperature.

Figure 4 reveals the relationship among calcination temperature, ammonia desorption temperature and density of acidic sites. It shows that the ammonia desorption temperature increased from 183 to 224 °C when calcination temperature increased from 200 to 400 °C. When further increasing calcination temperature up to 700 °C, the ammonia desorption temperature decreased to 180 °C. The density of acidic sites at different calcination temperatures was quantified by NaOH titration. The acidic densities of catalysts with calcination temperature of 200, 300, 350, 400, 450, 500, 600 and 700 °C were 139.3, 120.4, 72.9, 26.6, 33.1, 34.8, 35.9 and 44.1 μmol/g separately. The results thus indicated that the maximum acidic strength and minimum density of acidic sites were observed for the tin-promoted catalyst calcined at 400 °C. The increase of the acid sites density in catalysts heat-treated above 400 °C may be related with the stannous niobate ($SnNb_2O_6$) as shown in XRD.

3.3 Effect of Calcination Temperature on H_2O and EO Adsorption Properties of the Sn–Nb_2O_5/α-Al_2O_3 Catalyst

In order to further investigate the relationship between structure and function of the catalyst, the H_2O and EO adsorption properties of the catalyst were investigated by using the Infrared spectra of water adsorption and temperature programmed desorption of EO.

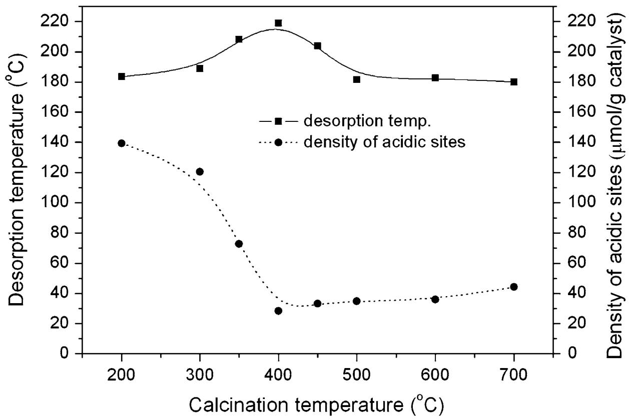

Fig. 4 Relationship among NH_3-TPD desorption temperature, density of acidic sites and calcination temperature over Sn–Nb_2O_5/α-Al_2O_3 catalyst

The IR spectra of the Sn–Nb_2O_5/α-Al_2O_3 catalyst calcined at different temperatures are shown in Fig. 5. Only one broad band around 3,500 cm^{-1}, corresponding to H-bonded surface OH stretching modes (or strongly held water-related species) [19] was observed for the catalyst calcined at 200 °C. The intensity of the band decreased with increasing calcination temperature, and it was very weak and hardly observed when calcination temperature was above 500 °C, indicating that strength of water adsorption on the surface of Sn–Nb_2O_5/α-Al_2O_3 catalyst was weakened with increasing calcination temperature. The relative amount of chemisorbed water on the surface of Sn–Nb_2O_5/α-Al_2O_3 catalyst calcined at different temperatures was measured by TGA as shown in Fig. 6 [19]. Because the decomposition of catalyst precursor could not be completed

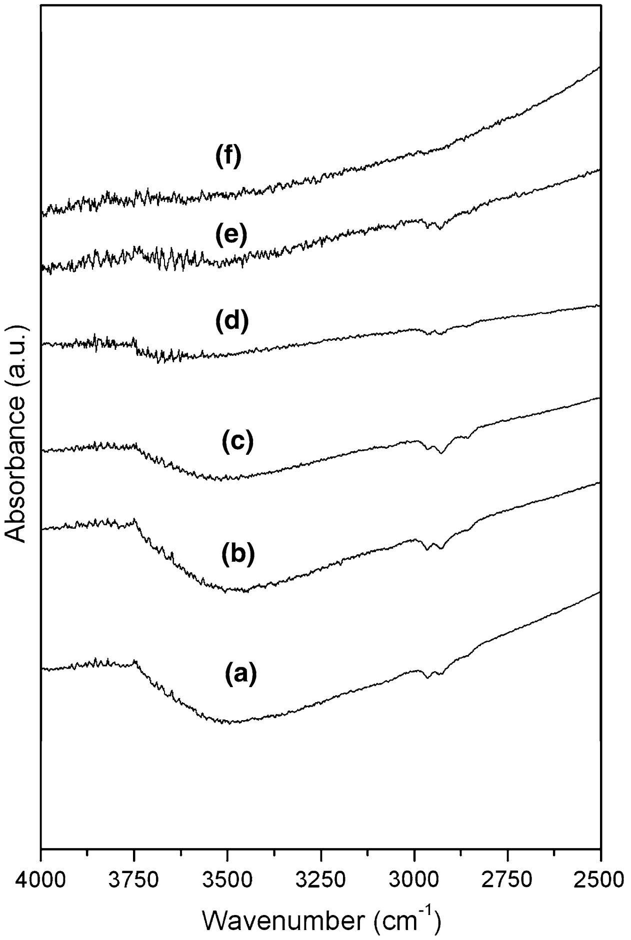

Fig. 5 IR spectra of Sn–Nb_2O_5/α-Al_2O_3 catalyst calcined at different temperatures. Catalyst pretreatment condition: the calcined catalyst was immersed in water for 24 h, then centrifuged and dried at 100 °C for 2 h, finally evacuated under 3 Pa at room temperature for 4 h and recorded at 250 °C. (**a**) 200, (**b**) 300, (**c**) 400, (**d**) 500, (**e**) 600 and (**f**) 700 °C

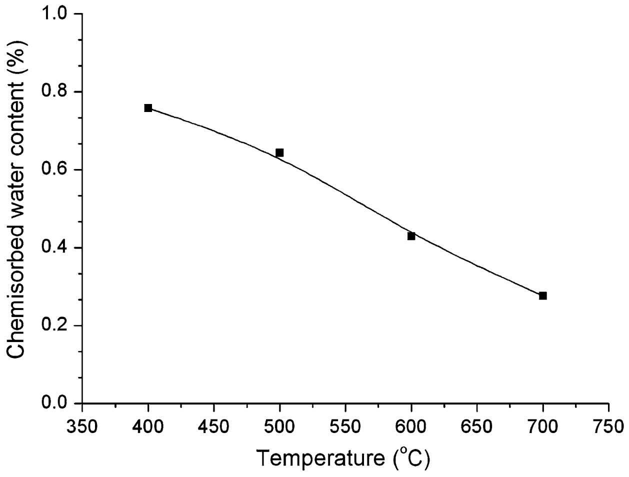

Fig. 6 Capacity of water chemisorption at Sn–Nb_2O_5/α-Al_2O_3 catalyst calcined at different temperatures

when calcination temperature was below 350 °C, only the amount of water adsorbed on the catalyst calcined at 400 °C and above was studied by TG. The amount of chemisorbed water decreased from 0.76 wt% (based on the weight of the catalyst) at calcination temperature of 400 °C to 0.28 wt% at calcination temperature of 700 °C.

The EO-TPD profiles of catalyst are shown in Fig. 7. The EO-TPD indicated that no EO desorption signal was observed on α-Al_2O_3 support and metallic tin, indicating that EO molecule was non-chemisorbed on the surface on both substances. Only one desorption peak at 133 °C was observed for SnO_2/α-Al_2O_3. For the unpromoted Nb_2O_5/α-Al_2O_3 catalyst calcined at 400 °C, two kinds of desorption peaks, which could be ascribed to weak adsorption species (WS) and strong adsorption species (SS) were observed at 138 and 327 °C, respectively. When the calcination temperature was raised to 700 °C, only SS at desorption temperature of 350 °C was observed. It seems reasonable to deduce that EO was strongly chemisorbed on the surface of TT-Nb_2O_5 (formed at 700 °C [11]).

For the tin promoted catalyst calcined at 400 °C, the desorption temperatures of WS and SS on the surface of catalyst, were 103 and 343 °C, respectively. With increasing calcination temperature up to 700 °C, only SS was observed at 369 °C. The XRD results showed that SnO_2, $SnNb_2O_6$ and β-Sn were observed at calcination temperatures of 300, 400, 700 °C. The higher calcination temperatures used, the more $SnNb_2O_6$ formed. As no TT-Nb_2O_5 was detected, from SS peak variation tendency, we deduce that EO was strongly absorbed on $SnNb_2O_6$ phase.

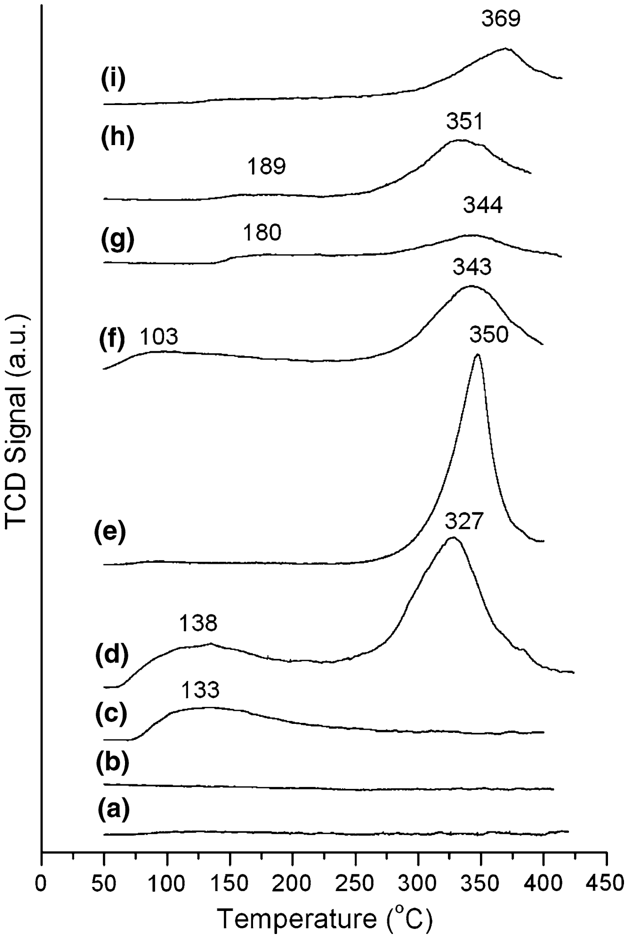

Fig. 7 EO-TPD profiles of (**a**) α-Al_2O_3, (**b**) Sn, (**c**) SnO_2/α-Al_2O_3, (**d**) Nb_2O_5/α-Al_2O_3/400 °C/4 h, (**e**) Nb_2O_5/α-Al_2O_3/700 °C/4 h, (**f**) Sn–Nb_2O_5/α-Al_2O_3/400 °C/4 h, (**g**) Sn–Nb_2O_5/α-Al_2O_3/500 °C/4 h, (**h**) Sn–Nb_2O_5/α-Al_2O_3/600 °C/4 h and (**i**) Sn–Nb_2O_5/α-Al_2O_3/700 °C/4 h

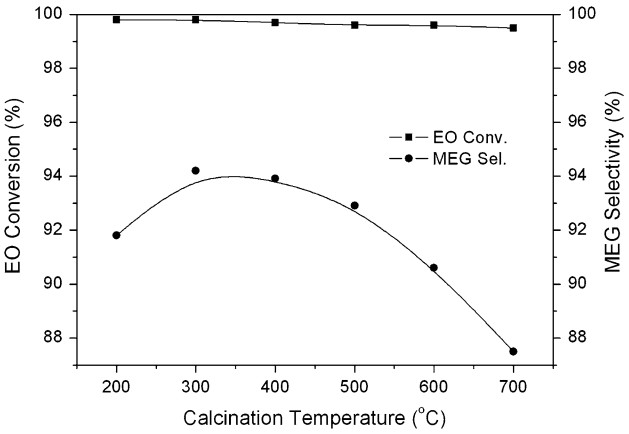

Fig. 8 Dependence of EO hydration over Sn–Nb_2O_5/α-Al_2O_3 catalyst on calcination temperature. Reaction conditions: temp. = 150 °C, press. = 1.0 MPa, H_2O/EO = 22, LHSV = 10 h^{-1}

3.4 Effect of Calcination Temperature on the Catalytic Performance

The dependence of catalytic performance of EO hydration on calcination temperature is shown in Fig. 8. EO conversion did not change obviously with calcination temperature. However, the MEG selectivity responded differently. It was found that MEG selectivity increased with calcination temperature below 300 °C and reached the maximum of ca. 94.0% at calcination temperatures between 300 and 400 °C. The MEG selectivity decreased sharply with further increasing calcination temperature above 400 °C. The MEG selectivity was only 86% at calcination temperature of 700 °C.

In EO hydration, depending on the surface H_2O/EO ratio and the acidity of the catalyst, the primary product may preferentially desorb from the active sites to give MEG or react with EO to generate polymerized products. If EO is strongly adsorbed on the surface of the catalyst or the surface H_2O/EO ratio was low, the polymerization may easily occur. On the contrary, if MEG (or EO) was easily desorbed from the surface of the catalyst, or if the surface H_2O/EO ratio was high, the polymerization may be inhibited and the MEG selectivity was high. From IR of H_2O adsoprtion results, one finds that the capacity of chemisorbed water of the catalyst decreased with increasing calcination temperature. The XRD results also indicated that the intensities of the hydrophilic species of SnO_2, which was helpful to improve the MEG selectivity [13], reached the maximum at calcination temperatures between 300 and 400 °C. Furthermore, the NH_3-TPD results showed that acidic strength reached maximum and the density of acidic sites reached the minimum at calcination temperature about 400 °C, which afforded the suitable acid properties. In view of the above reasons, the best catalytic performance observed for the catalyst at calcination temperature of 400 °C was easily understood.

4 Conclusions

Calcination temperature is an important parameter that controls the composition, acidity, H_2O and EO adsorption properties of the Sn–Nb_2O_5/α-Al_2O_3 catalyst. SnO_2, $SnNb_2O_6$ and β-Sn were formed at calcination temperatures of 300, 400 and 500 °C, respectively. The existence of different tin containing species exhibited the different effect on the acidity and catalytic performance of the catalyst.

The existence of strong hydrophilic property of SnO_2 as well as weak adsorption species on the surface of the Sn–Nb_2O_5/α-Al_2O_3 is beneficial to the formation of MEG.

It is of great importance to control the calcination temperature in order to generate suitable EO and water adsorption properties. In terms of MEG yield, suitable calcination temperature is in a range between 350 and 400 °C.

Acknowledgments Supplying of niobic acid by CBMM Int. Ltd. is gratefully acknowledged. This work was supported by the National Basic Research Program of China (2003CB615807), the NSF of China (20005310) and the NSF of Shanghai Science and Technology Committee (03DJ14004).

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