

Effect of tin on Nb₂O₅/α-Al₂O₃ catalyst for ethylene oxide hydration

Yingcheng Li^{a,b}, Shirun Yan^{a,*}, Linping Qian^a, Weimin Yang^b, Zaiku Xie^b, Qingling Chen^b,
Bin Yue^a, Heyong He^{a,*}

^a Department of Chemistry and Shanghai, Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China

^b Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China

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Abstract

The effect of tin on the structure, acidity, and water adsorption property of Nb₂O₅/α-Al₂O₃ catalyst and on this catalyst's performance for ethylene oxide (EO) hydration were studied by XRD, Raman spectroscopy, NH₃-TPD, IR of pyridine and of H₂O adsorption, and catalytic tests. Characterization results revealed that the density of acidic sites decreased with the addition of tin and with increasing Sn/Nb ratio in the cases studied, whereas the acidity exhibited minimum strength at Sn/Nb = 0.08. The IR of water adsorption indicated that addition of tin significantly enhanced the water adsorption property of the catalyst. The catalytic tests revealed that monoethylene glycol (MEG) selectivity increased from 89.8% of the Nb₂O₅/α-Al₂O₃ catalyst to 94.0% of the tin-promoted catalyst maintaining the EO conversion at 99.7%, and the catalyst exhibited excellent stability. The enhanced water adsorption property of the tin-promoted catalyst is proposed to be responsible for the significant improvement in MEG selectivity.

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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 at 140–230 °C and 1.5–2.5 MPa using a large excess of water (20–25 mol of water per mol of EO) to achieve a glycol selectivity of 88–90%. The raw product of hydration is then dehydrated by rectification, which involves excessive energy consumption, making the process economically unattractive. Considerable efforts have been made to explore efficient hydration catalysts. A number of materials, including anion-exchange resin [1–3], quaternary phosphonium halides [4], polymeric organosilane ammonium salt [5], and macrocyclic chelating compounds [6], have been tested as hydration catalysts. Although these catalysts improved MEG selectivity to certain extent, some problems remained, including elution of the active species in water and poor thermal stability,

making long-run testing impossible. Consequently, the development of efficient catalysts for EO hydration that are also insoluble in water, thermally stable, and readily recoverable is highly desirable.

Niobic acid (Nb₂O₅ · nH₂O) has received much attention as a new solid acid catalyst [7–9] because of its strong acidity and structural stability in water. In previous work [10,11], we studied Nb₂O₅/α-Al₂O₃ prepared by chemical vapor deposition and by impregnation for EO hydration, and found that the yield of MEG over the supported niobium oxide calcined at 400 °C was comparable with that over Amberlite IR and Nafion XR (6%)/SiO₂, but much higher than that over AlPO₄-Cu(NO₃)₂ and HZSM-5. Comparing the catalytic performance of niobic acid with the niobium oxide supported on α-Al₂O₃ calcined at 400 °C revealed that the latter gave a MEG selectivity of 89%, compared with 83% over niobic acid at a similar EO conversion, 150 °C, and a H₂O/EO ratio of 22. The supported niobium oxide also demonstrated excellent stability over 1000 h on stream compared with the niobic acid catalyst, which deactivated gradually after 600 h on stream. Modification of the α-Al₂O₃ support before Nb₂O₅ loading with an

* Corresponding authors. Fax: +86 21 65642978.

E-mail addresses: sryan@fudan.edu.cn (S.R. Yan),
heyonghe@fudan.edu.cn (H.Y. He).

optimal amount of water-resistant basic material MgAl_2O_4 led to a 0.8% incremental MEG yield from the $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst [12]. Although the $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalysts and the MgAl_2O_4 -modified $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst exhibited higher MEG yield and better stability than niobic acid, the $\text{H}_2\text{O}/\text{EO}$ ratio was still high from an industrial standpoint. Therefore, further improvement of MEG selectivity at lower $\text{H}_2\text{O}/\text{EO}$ feeding ratios via modification of the catalyst is of significant industrial importance.

As a basic n-type semiconductor, tin oxide has often been used as a sensor under moisture conditions and as a catalytic material for the oxidation of organic molecules. Adsorption of water on the SnO_2 surface has been studied extensively [13–18]. Both molecular and dissociative (surface hydroxyls) water adsorbates have been observed on the SnO_2 surface, with hydroxyls the major species, and considerably less molecular water attached to O^{2-} ions through the hydrogen bond [16]. The strong hydrophilic property of SnO_2 inspired our curiosity as to whether it is feasible to improve water adsorption affinity to the $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst by introducing tin oxide species, which in turn increases the ratio of adsorbed H_2O to EO species on the catalyst surface so as to improve MEG selectivity without increasing the feeding ratio of $\text{H}_2\text{O}/\text{EO}$. In this paper, we investigate the effect of adding tin on the structure, acid property, and water adsorption property of the $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst, as well as on the catalyst's performance in EO hydration.

2. Experimental

2.1. Catalyst preparation

The procedure for preparing α -alumina support has been described elsewhere [10,11]. Tin-promoted catalysts were prepared by stepwise impregnation, as described below. The α -alumina support was first impregnated in vacuo with niobic acid (Companhia Brasileira de Metalurgia Mineracao, batch AD-2352) dissolved in an aqueous solution of oxalic acid, followed by drying at 150°C for 2 h. Then it was impregnated with the required amount of stannic chloride dissolved in an aqueous solution of hydrochloric acid in vacuo, followed by drying at 120°C for 2 h. The sample thus obtained was calcined in a quartz tube at 400°C under a flow of N_2/H_2 (5 v/v% of H_2) for 2 h and then under a nitrogen flow for another 2 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max-1400 diffractometer with a Cu target of a voltage of 40 kV and a current of 40 mA. The BET surface areas were determined by N_2 adsorption–desorption measurements at 77 K with a Micromeritics Tristar 3000 analyzer. Infrared (IR) spectra of pyridine adsorption and of water adsorption were recorded on 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 at a 1:1 weight ratio was heated at 300°C and evacuated in vacuo

for 4 h, then cooled to room temperature and exposed to 500 Pa of pyridine vapor for 15 min. The excess pyridine was removed by evacuation until vacuum achieved ~ 1 Pa. The spectra of the adsorbed pyridine were recorded at room temperature. For the water adsorption experiment, the catalyst was immersed in water for 24 h, then centrifuged and pressed into a thin disc. The sample disc was evacuated under ~ 3 Pa at room temperature for 4 h. The temperature was then raised to the required values (100 , 150 , 200 , and 250°C), and the spectra were recorded at each temperature after 15 min of equilibration.

Temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out on a flow system. Before ammonia adsorption, the sample was pretreated in a helium flow (30 mL/min) at 400°C for 1 h. Ammonia (10 v/v% in helium) adsorption was performed at 100°C for 1 h, after which the gas was switched to helium again. After a steady gas chromatography baseline was established, the temperature was ramped at a rate of $10^\circ\text{C}/\text{min}$ to 400°C under a helium stream. The desorption of ammonia was monitored by a thermal conductivity detector, and the desorbed ammonia was collected by absorption with a sulfuric acid solution and subsequently quantified by NaOH titration.

2.3. Reaction procedure

The catalytic test of EO hydration was performed on a fixed-bed reactor (10 mm i.d., 300 mm long). In a typical experiment, 10 mL of catalyst was loaded, and the reaction was performed at 150°C and 1.0 MPa with a liquid hourly space velocity of 10 h^{-1} unless specified otherwise. The products were collected in a cold trap and analyzed on an HP 6890 gas chromatograph with an HP-INNOWAX column and a flame ionization detector. Except for the stability test, the conversion and selectivity data presented in this paper are the steady-state values obtained after an induction period of 24 h on stream.

3. Results and discussion

3.1. Effect of tin on the structure of the supported niobium oxide

Fig. 1 shows XRD patterns of Sn-10wt% $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalysts with different Sn/Nb atomic ratios. No crystal phase of niobium pentoxide was detected for any sample, indicating that niobium oxide was well dispersed on the support. Besides the diffraction peaks of the support, the peaks with 2θ degree at 26.5, 33.9, and 51.8 corresponding to tetragonal stannic oxide (JCPDS no. 21-1250) were observed for all of the tin-promoted catalysts.

The diffraction peaks with 2θ degree at 28.9, 33.9, 49.2, and 54.5 corresponding to stannous niobate (SnNb_2O_6 , JCPDS no. 23-0592) appeared at a Sn/Nb ratio of 0.80. The intensities of the SnNb_2O_6 peaks increased with further increases in Sn/Nb ratio. Peaks with 2θ degree at 30.6 and 32.0 belonging to tetragonal β -Sn (JCPDS no. 4-0673) were also observed at a Sn/Nb ratio of 2.67. The XRD results thus indicate that tin was present predominantly as stannic oxide at Sn/Nb atomic

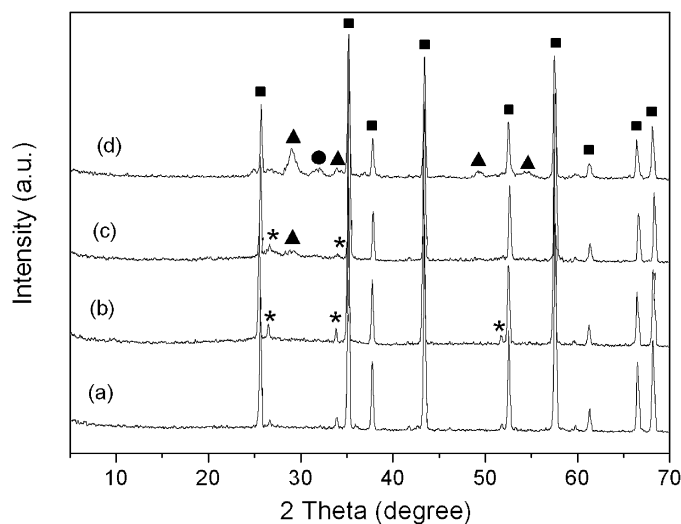


Fig. 1. XRD patterns of Sn-10wt%Nb₂O₅/α-Al₂O₃ with Sn/Nb ratios of (a) 0.016, (b) 0.08, (c) 0.80, and (d) 2.67. ■, α-Al₂O₃ (JCPDS No. 10-0173); ●, β-Sn (JCPDS No. 4-0673); ▲, SnNb₂O₆ (JCPDS No. 23-0592); *, SnO₂ (JCPDS No. 21-1250).

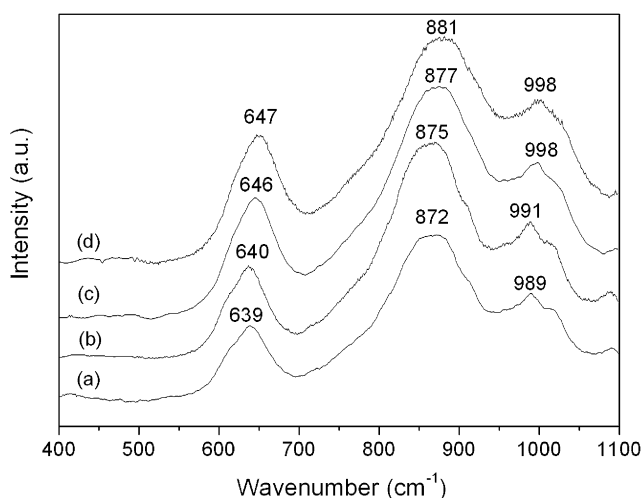


Fig. 2. Raman spectra of Sn-10wt%Nb₂O₅/α-Al₂O₃ with Sn/Nb ratios of (a) 0.016, (b) 0.08, (c) 0.80, and (d) 2.67.

ratios of 0.016 and 0.08, and that stannous niobate was formed at Sn/Nb ratios of 0.80 and above. On further increasing the Sn/Nb ratio to 2.67, metallic tin was formed while the sample was calcined under a hydrogen-containing atmosphere.

The BET surface areas of the α-Al₂O₃ support and 10wt%Nb₂O₅/α-Al₂O₃ catalyst were 0.5 and 5.6 m²/g, respectively. After the addition of tin, the BET surface areas of the Sn-10wt%Nb₂O₅/α-Al₂O₃ catalysts with Sn/Nb ratios of 0.016, 0.08, 0.80, and 2.67 were 13.3, 9.2, 8.3, and 7.6 m²/g, respectively.

The Raman spectra of the catalysts with different Sn/Nb ratios are shown in Fig. 2. The spectrum of sample with a Sn/Nb ratio of 0.016 showed bands at 639, 872, and 989 cm⁻¹. With increasing Sn/Nb ratio, the band at 639 cm⁻¹ shifted to 647 cm⁻¹, and the bands at 872 and 989 cm⁻¹ shifted to 881 and 998 cm⁻¹, respectively. In the meantime, the former

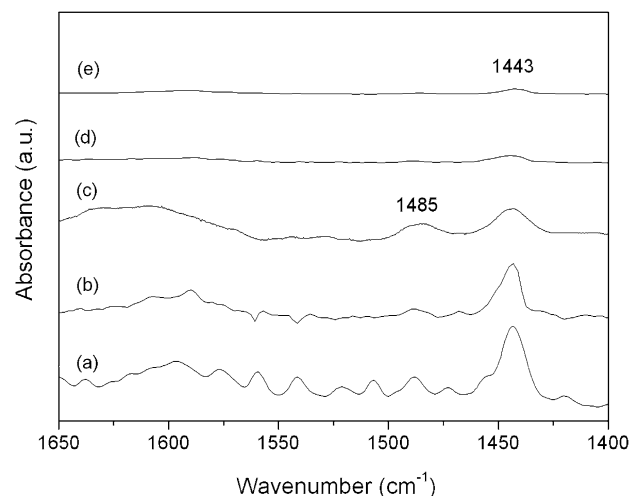


Fig. 3. IR spectra of pyridine adsorption at room temperature on the Sn-10wt%Nb₂O₅/α-Al₂O₃ catalysts with Sn/Nb ratios of (a) 0, (b) 0.016, (c) 0.08, (d) 0.80, and (e) 2.67.

two bands became more pronounced relative to the band at 998 cm⁻¹. Wachs et al. [19–22] studied the molecular structure of niobium oxide supported on alumina as a function of loading and dehydration in detail using Raman spectroscopy. They determined that the Raman band at ~639 cm⁻¹ should be assigned to slightly distorted octahedral NbO₆ connected with sharing corners [20]; the band at 872 cm⁻¹ could be ascribed to dehydrated surface niobium oxide species with moderately distorted NbO₆ structures with somewhat longer terminal Nb=O bonds [20–22]; and the band at 989 cm⁻¹ corresponds to a highly distorted octahedral NbO₆ having mono-oxo moiety of the terminal Nb=O bond. The blue-shift and intensity changes of the Raman bands at 639, 872, and 989 cm⁻¹ suggest that the structures of the surface niobium oxide species changed with changing Sn/Nb ratios, which may lead to changes in the acidity of the catalyst [19], as discussed below.

3.2. Effect of tin on catalyst acidity

Fig. 3 shows IR spectra of pyridine adsorption in the range of 1650–1400 cm⁻¹ on the Sn-10wt%Nb₂O₅/α-Al₂O₃ catalysts with different Sn/Nb atomic ratios. The absorptions at ~1610 and ~1450 cm⁻¹ were assigned to pyridine adsorbed on Lewis acid sites (LASs), and the absorption at 1550 cm⁻¹ accompanied by other peaks near 1640–1620 cm⁻¹ was assigned to pyridine adsorbed on Brønsted acid sites (BASs). The wavenumber of the band at around 1610 cm⁻¹ gives information about the strength of the LASs, and the intensity of the band at ~1450 cm⁻¹ is related to the number of LASs [23–25]. For both the unpromoted Nb₂O₅/α-Al₂O₃ and tin-promoted catalysts, absorption bands at ca. 1443 and 1485 cm⁻¹ with intensities decreasing with Sn/Nb ratio were observed and no absorption around 1550 cm⁻¹ was registered, indicating that only LASs exist on the surface of the catalysts and that the number of LASs decreases with increasing Sn/Nb ratio. FTIR of pyridine adsorption provided little quantitative information

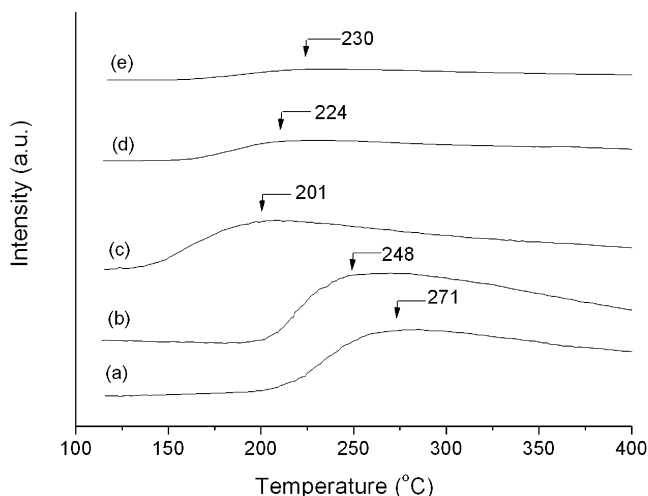


Fig. 4. NH_3 -TPD profiles of the $\text{Sn-10wt\%Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalysts with Sn/Nb ratios of (a) 0, (b) 0.016, (c) 0.08, (d) 0.80, and (e) 2.67.

on changes in Lewis acidity after the addition of tin, because no absorption band was registered at ca. 1610 cm^{-1} [25] for both the $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ and the tin-doped catalysts.

NH_3 -TPD experiments were carried out to investigate the effect of adding tin on the density and strength of acidity of the $10\text{wt\%Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst (shown in Fig. 4). Only a single broad ammonia desorption peak was observed for all of the catalysts studied. For the unpromoted catalyst, NH_3 desorption peaked at 271°C .

With increasing Sn/Nb ratio, the desorption peak initially shifted downward and achieved 201°C at a Sn/Nb ratio of 0.08, then shifted to higher temperatures with increasing Sn/Nb ratio above 0.08, achieving 230°C at a Sn/Nb ratio of 2.67. The densities of acidic sites quantified by NaOH titration of the desorbed ammonia of the catalysts with Sn/Nb atomic ratios of 0, 0.016, 0.08, 0.80, and 2.67 were 160.3, 120.5, 67.4, 28.3, and $19.1\text{ }\mu\text{mol/g}$, respectively. The NH_3 -TPD experiments clearly show that the density of acidic sites decreased monotonously with increasing Sn/Nb ratio, which is consistent with the IR of pyridine adsorption, whereas acid strength was lowest at a Sn/Nb ratio of 0.08.

3.3. Effect of tin on water adsorption property of the catalyst

IR spectra of the unpromoted $10\text{wt\%Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst after immersion in water and evacuation at room temperature and 3 Pa for 4 h were recorded under 3 Pa at different temperatures, as shown in Fig. 5. For comparison, the IR spectra of the $\text{Sn-10wt\%Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalysts with different Sn/Nb ratios and of the MgAl_2O_4 -modified catalyst after the same treatment were also recorded at 250°C and 3 Pa, as shown in Figs. 6 and 7. Only one broad band at around 3400 cm^{-1} , corresponding to H-bonded surface OH stretching modes (or strongly held water-related species) [26], was observed for the unpromoted $10\text{wt\%Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ at 100°C . The intensity of the band decreased with increasing temperature, and it was very weak and hardly observed at 250°C , indicating that most

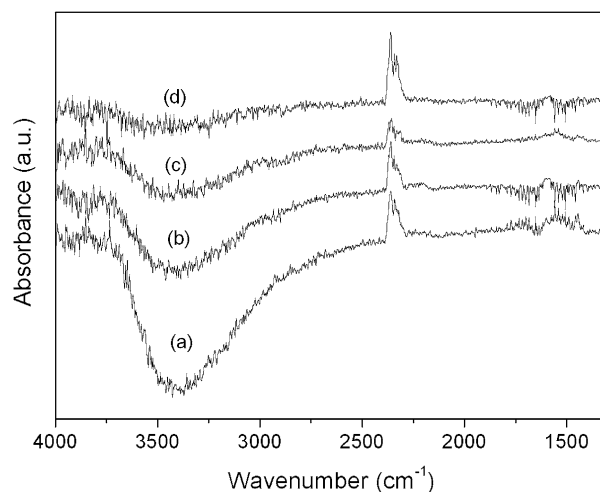


Fig. 5. IR spectra of $10\text{wt\%Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst after immersion in water and evacuation at room temperature recorded under 3 Pa at (a) 100, (b) 150, (c) 200, and (d) 250°C .

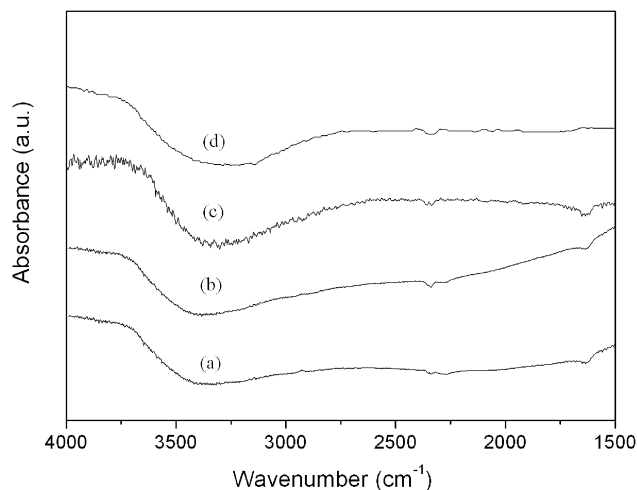


Fig. 6. IR spectra of $\text{Sn-10wt\%Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalysts with Sn/Nb ratios of (a) 0.016, (b) 0.08, (c) 0.80, and (d) 2.67 after immersion in water and evacuation at room temperature recorded at 3 Pa and 250°C .

adsorbed H_2O species were removed from the surface by evacuation at 3 Pa and 250°C .

For IR spectra of the tin-promoted catalysts (Fig. 6), the absorption band at around 3400 cm^{-1} was still obvious even at 250°C , especially for the sample with a Sn/Nb ratio of 0.80, indicating that water-related species was still strongly adsorbed on the surface of the tin-promoted catalysts even under evacuation at 3 Pa and 250°C . Comparing the IR spectra of the tin-promoted catalyst (Sn/Nb = 0.80) at 250°C with those for the unpromoted $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ and MgAl_2O_4 -modified catalysts (Fig. 7) revealed that the absorption band at around 3400 cm^{-1} of the former was much stronger than that for the latter, indicating that the addition of tin significantly improved the strength of water adsorption on the $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$, whereas the modification with MgAl_2O_4 had little improvement on water adsorption of the $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst, although it influenced the acidity of the catalyst, as reported previously [12].

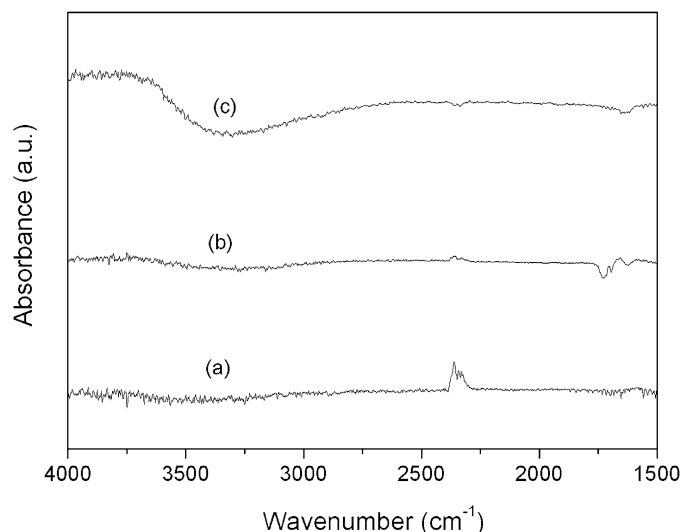


Fig. 7. IR spectra of (a) unpromoted 10wt%Nb₂O₅/α-Al₂O₃, (b) 10wt%Nb₂O₅/1.1wt%MgAl₂O₄/α-Al₂O₃, and (c) Sn-10wt%Nb₂O₅/α-Al₂O₃ with Sn/Nb ratio of 0.80 after immersion in water and evacuation at room temperature recorded under 3 Pa and 250 °C.

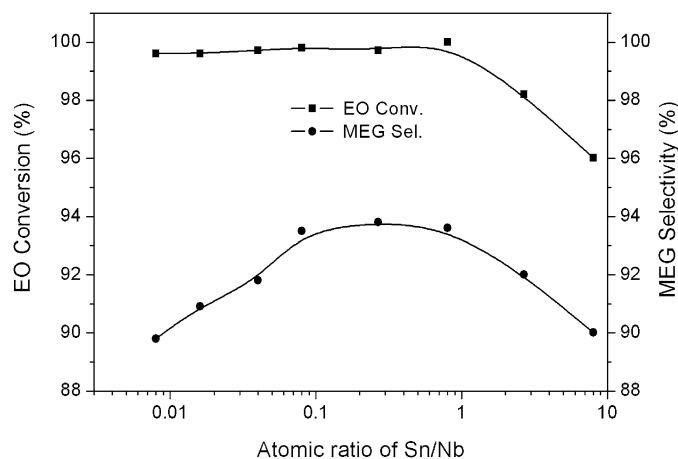


Fig. 8. Effect of Sn/Nb atomic ratio on EO conversion and MEG selectivity over Sn-10wt%Nb₂O₅/α-Al₂O₃ catalysts.

3.4. Effect of tin on the catalytic performance of the catalyst

Fig. 8 shows the reaction results over the Sn-10wt%Nb₂O₅/α-Al₂O₃ catalysts with different Sn/Nb atomic ratios. The EO conversion was nearly constant at 99.7% when the Sn/Nb ratio was below 0.80 and decreased monotonously with increasing Sn/Nb ratio above 0.80. However, MEG selectivity exhibited a different response to changes in Sn/Nb ratio. MEG selectivity increased initially with increasing Sn/Nb ratio below 0.08, and it remained nearly constant (~94%) at a Sn/Nb ratio of 0.08–0.80. At Sn/Nb ratios above 0.80, MEG selectivity decreased sharply. Further analysis of the products reveals that the decrease in MEG selectivity was associated with the increase in selectivity to diethylene glycol (DEG) and triethylene glycol (TEG). Fig. 8 implies that adding a suitable amount of tin to the Nb₂O₅/α-Al₂O₃ catalyst could inhibit the polymerization reactions in EO hydration and hence improve MEG selectivity.

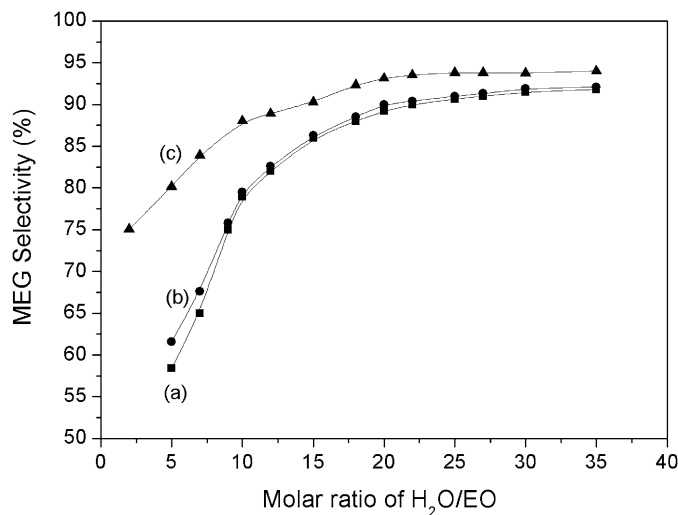
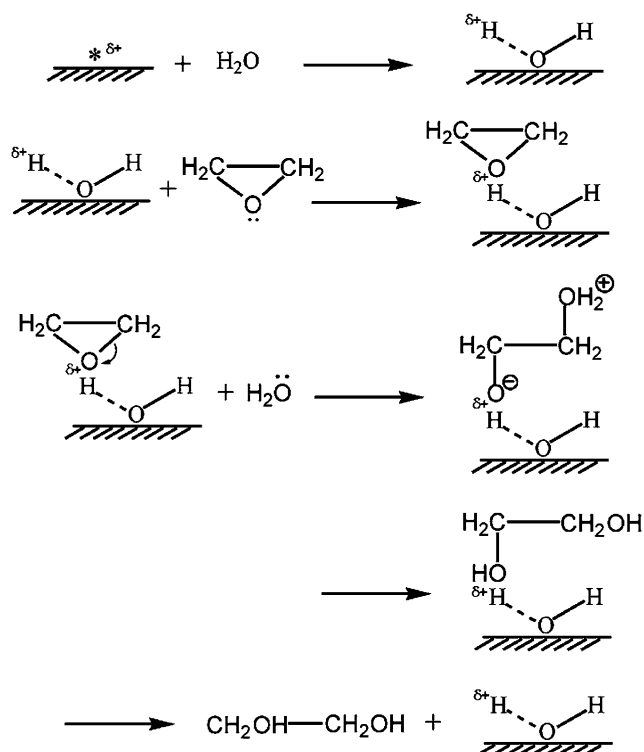


Fig. 9. Dependence of MEG selectivity on H₂O/EO molar ratio for catalytic hydration using (a) 10wt%Nb₂O₅/α-Al₂O₃ catalyst, (b) 10wt%Nb₂O₅/1.1wt%MgAl₂O₄/α-Al₂O₃ catalyst, and (c) Sn-10wt%Nb₂O₅/α-Al₂O₃ catalyst with Sn/Nb ratio of 0.80.

Fig. 9 illustrates the dependence of MEG selectivity on the H₂O/EO molar ratio over the unpromoted Nb₂O₅/α-Al₂O₃ catalyst, tin-promoted catalyst, and MgAl₂O₄-modified catalyst. The EO conversion was nearly the same (99.7%) for hydration over these three catalysts. Fig. 9 that shows the tin-promoted catalyst gave much higher MEG selectivity than the unpromoted Nb₂O₅/α-Al₂O₃ and MgAl₂O₄-modified catalysts under the same H₂O/EO feeding ratio. The MEG selectivity increased with H₂O/EO ratio for all three catalysts at H₂O/EO ratios <20. At H₂O/EO ratios >20, MEG selectivity increased slightly with H₂O/EO ratio over the unpromoted Nb₂O₅/α-Al₂O₃ catalyst and the MgAl₂O₄-modified catalyst. However, MEG selectivity remained almost unchanged with H₂O/EO ratios >20 for the tin-promoted catalyst. Comparing MEG selectivity obtained at a H₂O/EO ratio of 22 over these three catalysts reveals that it was 89.8% for the unpromoted 10wt%Nb₂O₅/α-Al₂O₃ catalyst, 90.7% for the MgAl₂O₄-modified catalyst, and 94.0% for the tin-promoted catalyst (Sn/Nb = 0.80). On the other hand, to achieve the same MEG selectivity as that obtained using the unpromoted 10wt%Nb₂O₅/α-Al₂O₃ and MgAl₂O₄-modified catalysts, the H₂O/EO feeding ratio can be reduced significantly when using the tin promoted catalyst.

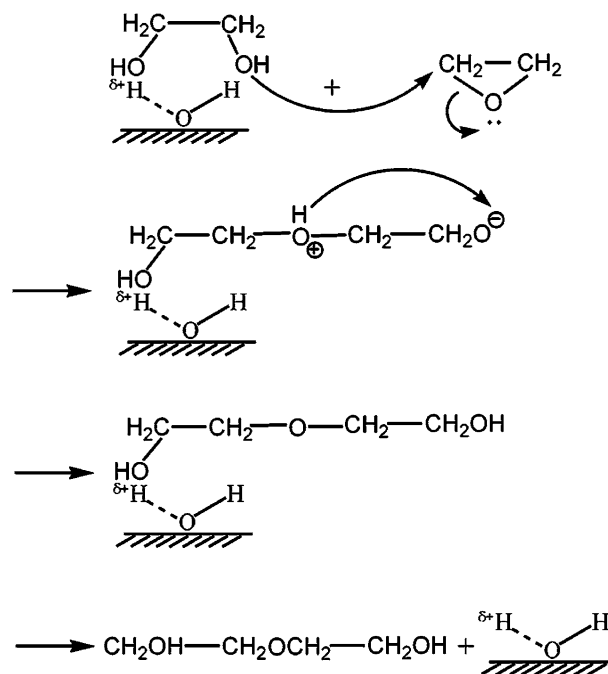
The improved selectivity to MEG of the tin-promoted catalyst may be related to its acidity and strong affinity to water, as shown in Figs. 4 and 5. It is generally accepted that mineral-acid-catalyzed homogeneous EO hydration proceeds as follows: EO first reacts with acid to form protonated EO, and then the protonated EO further reacts with nucleophile H₂O to form a protonated glycol, which transfers a proton to a molecule of H₂O to form the glycol and hydronium ion [27]. Although the catalysts studied in the present work are heterogeneous, they are acid catalysts in nature; thus, the reaction mechanisms should be similar. In view of the composition of the feeding reactant, we propose that the reaction first involves the adsorption of H₂O onto acidic sites to form positively charged water



Scheme 1.

species (or Bronsted acidity), which may act as the actual active site for reaction with EO, leading to the formation of positively charged EO species. Subsequently, the positively charged EO is attacked by nucleophile H_2O , followed by proton transfer to form positively charged MEG. After desorption of the product MEG, the positively charged water species on the catalyst surface recovers (see Scheme 1). As side reactions, the positively charged adsorbed MEG may react with another EO to form diethylene glycol and other polyglycols (see Scheme 2).

The acidity of catalyst, the surface $\text{H}_2\text{O}/\text{EO}$ ratio, and the reaction conditions may affect the behavior of the adsorbed MEG and the product selectivity. If MEG were strongly adsorbed on the acidic site or if the surface $\text{H}_2\text{O}/\text{EO}$ ratio were low, then the probability of polymerization would be high. In contrast, if MEG desorbed easily from the catalyst surface or if the surface $\text{H}_2\text{O}/\text{EO}$ ratio were high, then polymerization would be inhibited and MEG selectivity would be improved. A large excess of water is often used to suppress the polymerization reactions and increase selectivity to MEG. For the unpromoted catalyst, the strength and density of acidity were relatively high, which may have led to the strong adsorption of MEG on the surface and thus an increased probability of polymerization reaction. For the tin-promoted catalysts, the strength of acidity was reduced compared with the unpromoted $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$ catalyst (see Fig. 4), which may have facilitated desorption of MEG from the surface compared with that over $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$. On the other hand, water adsorption was also improved for the tin-promoted catalysts (see Figs. 5–7), which may have increased the number of surface-adsorbed hydroxyl groups (OH^-) and $\text{H}_2\text{O}/\text{EO}$ ratio, that is, the number of activated H_2O species



Scheme 2.

in the vicinity of EO. The increased surface $\text{H}_2\text{O}/\text{EO}$ ratio together with the reduced acid strength resulted in significantly improved MEG selectivity for the tin-promoted catalyst. For the MgAl_2O_4 -modified catalyst, the strength of acidity was lower and MEG selectivity greater compared with $\text{Nb}_2\text{O}_5/\alpha\text{-Al}_2\text{O}_3$, as reported previously [12]. However, the increment of MEG selectivity was not as remarkable as that over the tin-promoted catalyst. This might be ascribed to the different water adsorption properties of these catalysts, as shown in Fig. 7. Fig. 9 seems to indicate that in terms of MEG selectivity, water adsorption property is a very important factor influencing surface $\text{H}_2\text{O}/\text{EO}$ ratio, and the introduction of hydrophilic species, like stannic oxide, into the catalyst could significantly improve MEG selectivity without increasing the feeding $\text{H}_2\text{O}/\text{EO}$ ratio.

To investigate the possibility of long-run testing of the tin-promoted catalyst, the catalytic test was carried out for 1000 h on stream (Fig. 10). The tin-promoted catalyst demonstrated excellent stability at 1000 h on stream, with no obvious decline in EO conversion and MEG selectivity. The tin-promoted catalyst's remarkable stability may be ascribed to its insolubility in water, and its high selectivity to MEG due to its strong affinity to water, as discussed earlier. Its insolubility in water allows the catalyst to work without elution by water, and its high selectivity to MEG inhibits the formation of polymerized products that are readily retained and accumulated on the catalyst surface and may partially block the active catalyst sites, as discussed previously [10]. The results shown in Figs. 9 and 10 seem to demonstrate that when designing and preparing efficient catalysts for EO hydration, in addition to appropriately modifying acidity, one can effectively modify the water adsorption properties by introducing water-insoluble hydrophilic species, such as tin.

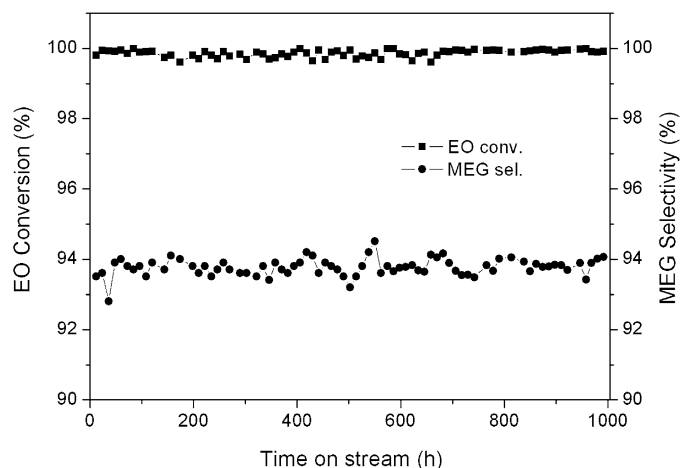


Fig. 10. Dependence of EO conversion and MEG selectivity on time-on-stream for Sn-10wt%Nb₂O₅/α-Al₂O₃ catalyst with Sn/Nb ratio of 0.80 at reaction conditions of 150 °C, 1.0 MPa, LHSV of 10 h⁻¹ and H₂O/EO (mol) of 22.

4. Conclusion

The addition of tin to 10 wt% Nb₂O₅/α-Al₂O₃ catalyst influenced both the acidity and water adsorption property of the catalyst. The state of tin in the catalyst varied from stannic oxide, to partially stannous niobate, and to partially metallic tin with Sn/Nb ratios of 0.016–2.67, leading to varying decreases in acidity and density. Meanwhile, the introduction of tin significantly improved the water adsorption affinity compared with that of the unpromoted Nb₂O₅/α-Al₂O₃ catalyst and the MgAl₂O₄-modified catalyst, which consequently resulted in significantly increased MEG selectivity in EO hydration. The tin-promoted catalysts exhibited good stability at 1000 h on stream. The results obtained in this work indicate that modifying the water adsorption property of the catalyst by introducing water-insoluble hydrophilic species such as tin oxide so as to influence the surface H₂O/EO ratio may be a very effective way to improve MEG selectivity in EO hydration.

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