# Effects of support modification on $Nb_2O_5/\alpha$-$Al_2O_3$ catalyst for ethylene oxide hydration

Yingcheng Li[a,b], Shirun Yan[a,*], Weimin Yang[b], Zaiku Xie[b],
Qingling Chen[b], Bin Yue[a], Heyong He[a,*]

[a] *Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China*
[b] *Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China*

## Abstract

Effect of $MgAl_2O_4$ on the structure, acidity as well as the catalytic performance of $Nb_2O_5/\alpha$-$Al_2O_3$ catalyst for ethylene oxide hydration was studied using IR, XRD, $NH_3$-TPD, $CO_2$-TPD and catalytic reaction. Modification of $\alpha$-$Al_2O_3$ support with $MgAl_2O_4$ led to an increase in both basicity and mechanical strength of the support. As a result, the density and strength of the acidity of the niobium oxide catalyst supported on the $MgAl_2O_4$ modified $\alpha$-$Al_2O_3$ reduced in comparison with that supported on the pure $\alpha$-$Al_2O_3$. The acidity of 10% $Nb_2O_5/MgAl_2O_4/\alpha$-$Al_2O_3$ decreased with increasing loading of $MgAl_2O_4$. Catalytic test showed that EO conversion decreased monotonously with increasing $MgAl_2O_4$ loading, whereas the selectivity to MEG exhibited a maximum of 90.6% at $MgAl_2O_4$ loading of 2.23%. In terms of MEG yield, optimal $MgAl_2O_4$ loading should be around 2%. Durability test demonstrated that 10% $Nb_2O_5/MgAl_2O_4/\alpha$-$Al_2O_3$ catalyst exhibited excellent stability within 1000 h time-on-stream.
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## 1. Introduction

Niobium compounds are interesting and important catalytic materials for various reactions. Hydrated niobium pentoxide ($Nb_2O_5 \cdot nH_2O$), which is called niobic acid, has an acid strength corresponding to that of 70% $H_2SO_4$ when calcined at relatively low temperature (100–300 °C). The acidity of niobic acid decreases with increasing calcination temperatures and becomes almost neutral after calcination at 500 °C [1]. The strong acidity and high structural stability in water make niobic acid as a water-tolerant solid acid catalyst for reactions with water participation or liberation, such as dehydration, esterification and hydration of small olefins [2–6].

Also, niobic acid has been used for the ring-opening reaction of 1,2-aromatic epoxide, such as isomerization and solvolysis of phenyloxirane [7–9].

In our previous studies [10,11], the niobium oxide supported on $\alpha$-$Al_2O_3$ prepared by chemical vapor deposition and impregnation was studied for hydration of ethylene oxide (EO) to produce monoethylene glycol (MEG). It was found that the yield of MEG over the supported niobium oxide calcined at 400 °C was close to that of Amberlite IR, Nafion XR (6%)/$SiO_2$ and sulfuric acid, but much higher than that of $AlPO_4$–$Cu(NO_3)_2$ and HZSM-5. A comparison of niobic acid with the niobium oxide supported on $\alpha$-$Al_2O_3$ calcined at 400 °C showed that both catalysts have near 100% of EO conversion at reaction temperature of 150 °C and $H_2O$/EO ratio of 22. However, the latter gave a MEG selectivity of 89% compared with 83% that over niobic acid. The supported niobium oxide also exhibited excellent stability within 1000 h time-on-stream in comparison with the niobic acid catalyst

* Corresponding authors. Tel.: +86 21 65643916/3792x4;
fax: +86 21 65642978/1740.
*E-mail addresses:* sryan@fudan.edu.cn (S. Yan),
heyonghe@fudan.edu.cn (H. He).

over which deactivation started after 600 h. The characterizations demonstrated that the acidity of the $\alpha$-$Al_2O_3$ supported niobium oxide calcined at 400 °C was weaker than that of the niobic acid. A correlation of catalytic behavior with acidity indicated that the conversion of EO was proportional to the acid density, while the selectivity to MEG and durability of the catalyst decreased with increasing of the acidic strength of the catalyst. The strong acidity of the catalyst leads to the re-adsorption and secondary reaction of the primary product of MEG, resulting in a decrease of the MEG selectivity and in the formation of polymerized glycols. The accumulation of the polymerized glycols on the surface may block the acidic sites, leading to the deactivation of the catalyst. Therefore, there should be a compromise of the strength with the density of acid sites of the catalyst to achieve an optimal yield of MEG.

Magnesia-alumina spinel, $MgAl_2O_4$, has remarkable chemical stability and thermal stability and thus has been used as an important catalytic material [12,13]. In this paper, $MgAl_2O_4$ was used to modify $\alpha$-$Al_2O_3$ as well as the $Nb_2O_5$/$\alpha$-$Al_2O_3$ catalyst. Effects of $MgAl_2O_4$ on the acid–base properties of $Al_2O_3$ and $Nb_2O_5$/$\alpha$-$Al_2O_3$ catalyst and on the catalytic performance for ethylene oxide hydration were investigated.

## 2. Experimental

### 2.1. Catalysts preparation

The supported niobia catalysts were prepared via the following steps. Pseudo-boehmite (Condea Chemie, Pural-SB) and extruded, dried at 120 °C and calcined at 1400 °C under static air for 4 h to form $\alpha$-$Al_2O_3$ support. The $\alpha$-$Al_2O_3$ was ground and sieved to pellets with 0.8–1.0 mm diameter and then impregnated with an aqueous solution containing required amount of $Mg(NO_3)_2$ and $Al(NO_3)_3$, dried at 120 °C and calcined at 1400 °C for another 4 h to form the modified $MgAl_2O_4$/$\alpha$-$Al_2O_3$ support. The catalysts were prepared under vacuum by impregnating the modified $MgAl_2O_4$/$\alpha$-$Al_2O_3$ support with an aqueous solution of niobic acid (Companhia Brasileira de Metalurgiae Mineracao, batch AD-2352) containing 1.8 mol L$^{-1}$ oxalic acid. The sample was then dried at 120 °C for 2 h and subsequently calcined at 400 °C in a quartz tube for 2 h under a flow of nitrogen containing 5 vol.% $H_2$ for 2 h, and finally activated at 400 °C under nitrogen for another 2 h.

The $Nb_2O_5$/$\alpha$-$Al_2O_3$ catalyst was prepared by impregnating $\alpha$-$Al_2O_3$ with an aqueous solution of niobic acid as described in our previous publication [10].

### 2.2. Catalyst characterization

Infrared (IR) spectra of pyridine adsorption were recorded on a Nicolet Nexus 470 FT-IR spectrometer with 4 cm$^{-1}$ resolution. The sample disc containing catalyst and KBr with 1:1 in weight ratio was heated to 180 °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 returned to the level of 1 Pa. The spectra of adsorbed pyridine were recorded at room temperature and 150 °C in vacuum.

X-ray diffraction (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.

Temperature-programmed desorption of ammonia ($NH_3$-TPD) was carried out in a flow system. The samples were pretreated under a helium flow (30 mL/min) at 400 °C for 1 h. Ammonia (10% in helium) was adsorbed at 100 °C for 1 h and then the temperature was raised to 400 °C at a rate of 20 °C/min under a helium stream. Desorption of ammonia was monitored by thermal conductivity detector (TCD). The amount of adsorbed ammonia was absorbed with sulfuric acid solution and quantified by NaOH titration.

Temperature-programmed desorption of carbon dioxide ($CO_2$-TPD) was carried out in a flow system. The samples were pretreated under helium flow (30 mL/min) at 400 °C for 1 h. Carbon dioxide (10% in helium) was adsorbed at room temperature for 1 h and then the temperature was raised to 500 °C at a rate of 20 °C/min under a helium stream. The amount of desorbed carbon dioxide was detected by TCD.

The analysis of niobium and iron contents in the effluent was performed on BAIRD PS-6 ICP spectrometer.

Pore volume, pore diameter and surface area were measured with mercury filling method on CORETEST SYSTEMS MIS-621 apparatus.

The mechanical strength (grain crushing strength) was measured with a DL-II mechanical tester manufactured by Dalian Research Institute of Chemical Engineering. The measurement was carried out on a sufficient number of grains in order to obtain reliable results.

### 2.3. Catalytic reaction

The reaction of ethylene oxide hydration was carried out over a fixed-bed reactor with an inner diameter of 10 mm and length of 300 mm at temperature of 150 °C, pressure of 1.5 MPa, molar ratio of $H_2O$/EO of 22 and LHSV of 30 h$^{-1}$. In a typical experiment, 10 mL of catalyst was loaded. The products were analyzed on an HP 6890 gas chromatograph with an HP-INNOWAX column and a flame ionization detector. The quantification was made by an internal standard method using ethylene glycol monobutyl ether (EGME) as the internal standard.

## 3. Results and discussion

### 3.1. Structure and textural properties of $\alpha$-$Al_2O_3$ support modified with $MgAl_2O_4$

XRD patterns of the $\alpha$-$Al_2O_3$ support modified with different loadings of $MgAl_2O_4$ are shown in Fig. 1. Only
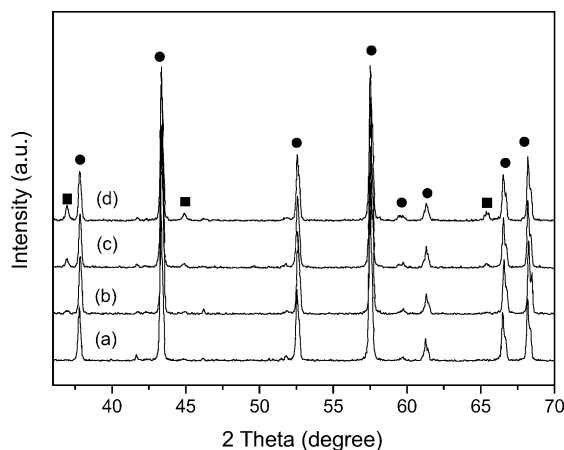
Fig. 1. XRD patterns of $\alpha$-$Al_2O_3$ modified with different $MgAl_2O_3$ loadings: (■) $MgAl_2O_4$; (●) $\alpha$-$Al_2O_3$.



Fig. 2. $CO_2$-TPD profiles of $\alpha$-$Al_2O_3$ modified with different $MgAl_2O_4$ loadings.

diffraction peaks of $\alpha$-$Al_2O_3$ were observed at $MgAl_2O_4$ loading of 0.23%. The diffraction peaks with $2\theta$ at 36.85°, 44.83° and 65.24° which are assignable to (3 1 1), (4 0 0) and (4 4 0) crystal planes of of $MgAl_2O_4$ (JCPDS No. 21-1152), respectively, were observed in the sample with the $MgAl_2O_4$ loading of 1.13%. The intensity of the $MgAl_2O_4$ peaks increased with further increasing $MgAl_2O_4$ loadings, indicating that the spinel phase $MgAl_2O_4$ was formed on the surface of $\alpha$-$Al_2O_3$.

Table 1 shows the effect of $MgAl_2O_4$ modification on the mechanical strength and porous properties of the $\alpha$-$Al_2O_3$ support. Mechanical strength increased significantly with increasing $MgAl_2O_4$ loadings, while the pore volume, surface areas and pore diameters decreased with increasing $MgAl_2O_4$ loadings. This is easily understood because the deposition of $MgAl_2O_4$ on the inner wall of $\alpha$-$Al_2O_3$ reduces the pore volume and surface area of the support. Meanwhile, the increase of wall thickness may lead to an increase of the mechanical strength of the support.

### 3.2. Effect of $MgAl_2O_4$ modification on the acid–base properties of $\alpha$-$Al_2O_3$

Fig. 2 shows the $CO_2$-TPD profiles of $\alpha$-$Al_2O_3$ support modified with different amount of $MgAl_2O_4$, in which the signal was normalized based on unit mass. No desorption was detected when $MgAl_2O_4$ loading was below 2.23%. One broad desorption peak between 90 and 200 °C was observed
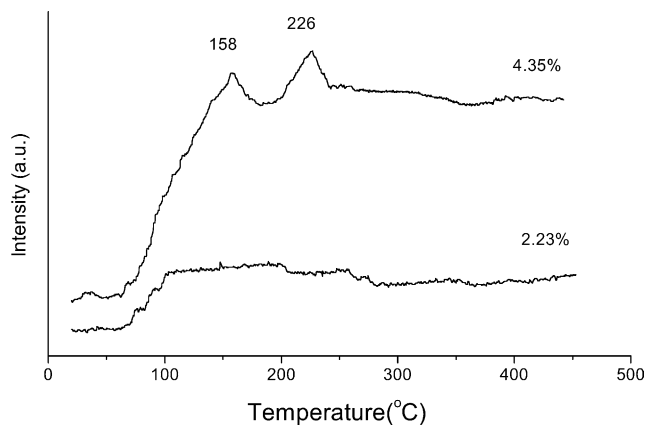
at the $MgAl_2O_4$ loading of 2.23%. On increasing $MgAl_2O_4$ loading up to 4.35%, two desorption peaks at 158 and 226 °C appeared, indicating that two types of basic site with different strengths were formed on the modified $\alpha$-$Al_2O_3$ surface. In comparison with the pure $\alpha$-$Al_2O_3$ support that has no $CO_2$-TPD peaks, it is found that the modification of $\alpha$-$Al_2O_3$ with $MgAl_2O_4$ increased the basicity of the support. $NH_3$-TPD experiment showed that no desorption of $NH_3$ over both $\alpha$-$Al_2O_3$ and $MgAl_2O_4$ modified $\alpha$-$Al_2O_3$ in the temperature range studied, indicating no acidic sites on the supports.

### 3.3. Effect of $MgAl_2O_4$ modification on the acidity of the $Nb_2O_5/\alpha$-$Al_2O_3$ catalysts

IR spectra after pyridine adsorption and desorption at room temperature and 150 °C and the $NH_3$-TPD experiments were carried out to investigate the effect of the support modification with $MgAl_2O_4$ on the acidity of the $Nb_2O_5/\alpha$-$Al_2O_3$ catalyst. The IR results are shown in Figs. 3 and 4. The absorptions at ~1610 and ~1450 $cm^{-1}$ were assigned to pyridine adsorbed on Lewis acid sites (LAS), 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 (BAS). The wavenumber of the band around 1610 $cm^{-1}$ gives information about the strength of LAS, and the intensity of the band at ~1450 $cm^{-1}$ is related to the number of LAS [14,15]. Fig. 3 shows the spectra after pyridine desorption at room temperature. No IR absorption band was observed for $\alpha$-$Al_2O_3$ support. For the

Table 1
Effect of $MgAl_2O_4$ modification on the characters of $\alpha$-$Al_2O_3$

| Samples | Mechanical strength (N cm$^{-1}$) | Pore volume (cm$^3$ g$^{-1}$) | Surface area (m$^2$ g$^{-1}$) | Pore diameter (μm) |
|---|---|---|---|---|
| $\alpha$-$Al_2O_3$ | 11.43 | 0.702 | 0.45 | 8.830 |
| 0.23% $MgAl_2O_4/\alpha$-$Al_2O_3$ | 12.17 | 0.601 | 0.44 | 7.918 |
| 1.13% $MgAl_2O_4/\alpha$-$Al_2O_3$ | 14.01 | 0.595 | 0.40 | 6.646 |
| 2.23% $MgAl_2O_4/\alpha$-$Al_2O_3$ | 16.73 | 0.515 | 0.36 | 5.432 |
| 4.35% $MgAl_2O_4/\alpha$-$Al_2O_3$ | 19.75 | 0.418 | 0.32 | 2.298 |
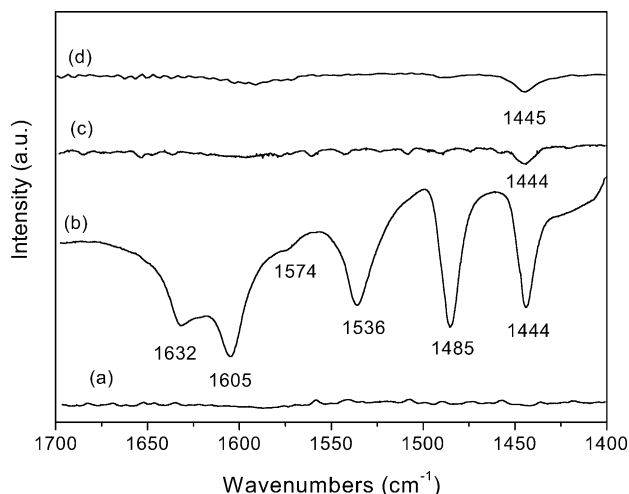
Fig. 3. IR spectra after pyridine desorption at room temperature on (a) α-Al$_2$O$_3$, (b) niobic acid, (c) 10% Nb$_2$O$_5$/α-Al$_2$O$_3$, and (d) 10% Nb$_2$O$_5$/2.23% MgAl$_2$O$_4$/α-Al$_2$O$_3$.

Nb$_2$O$_5$/α-Al$_2$O$_3$ and Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalysts, only the band around 1445 cm$^{-1}$ was observed. For niobic acid, however, absorption bands at 1632 and 1536 cm$^{-1}$ corresponding to pyridine species bound to BAS and bands at 1605, 1574, 1485 and 1444 cm$^{-1}$ corresponding to pyridine species bound to LAS were clearly observed. After evacuation at 150 °C the absorption at ca. 1444 cm$^{-1}$ disappeared for both Nb$_2$O$_5$/α-Al$_2$O$_3$ and Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalysts as shown in Fig. 4. However, for niobic acid the bands at 1636, 1608, 1574, 1537, 1487 and 1444 cm$^{-1}$ still appeared. The IR experiments indicate that the surface of α-Al$_2$O$_3$ was nearly neutral, in accordance with the CO$_2$-TPD experiment. Niobic acid demonstrated both Brønsted and Lewis acidities. In contrast, Nb$_2$O$_5$ supported on α-Al$_2$O$_3$ and on MgAl$_2$O$_4$ modified α-Al$_2$O$_3$ were found to have only Lewis acidic sites.

FT-IR could not give any valuable information on the strength of acidity effected by MgAl$_2$O$_4$, as no absorption



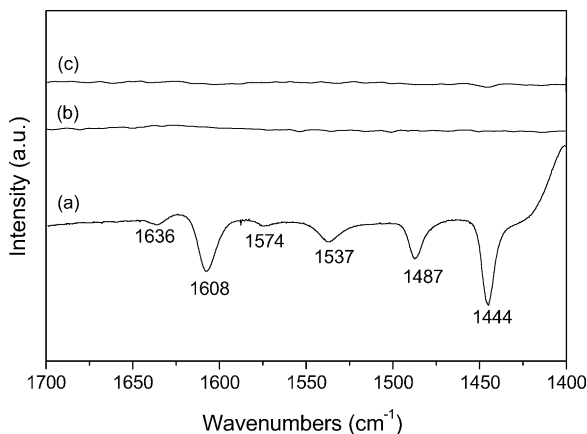Fig. 4. IR spectra after pyridine desorption at 150 °C on (a) niobic acid, (b) 10% Nb$_2$O$_5$/α-Al$_2$O$_3$, and (c) 10% Nb$_2$O$_5$/2.23% MgAl$_2$O$_4$/α-Al$_2$O$_3$.
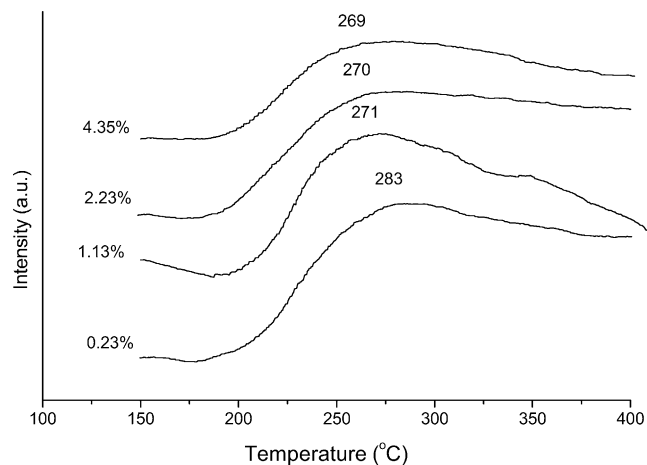


Fig. 5. NH$_3$-TPD profiles of 10% Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalysts with different MgAl$_2$O$_3$ contents.

bands were registered at ca. 1610 cm$^{-1}$ region [14] for both Nb$_2$O$_5$/α-Al$_2$O$_3$ and Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalysts. However, it is clear that the acidity of Nb$_2$O$_5$ supported either on α-Al$_2$O$_3$ or on the MgAl$_2$O$_4$ modified α-Al$_2$O$_3$ was much weaker than that of the niobic acid.

Fig. 5 shows the NH$_3$-TPD profiles of Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalysts with different MgAl$_2$O$_4$ loadings. Only one broad desorption peak was observed in all the catalysts. The temperature of the desorption peak shifted from 285 °C of unpromoted Nb$_2$O$_5$/α-Al$_2$O$_3$ (not shown) to 283 and 269 °C with increasing MgAl$_2$O$_4$ loadings from 0.23% to 4.35%, respectively. This indicates that mainly weak acidic sites existed on the surface of Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ and the strength of acidity of the catalysts decreased with increasing MgAl$_2$O$_4$ loadings.

The concentration of acidic centers of the catalysts with MgAl$_2$O$_4$ loadings of 0, 0.23, 1.13, 2.23, and 4.35 wt.% determined by NaOH titration of desorbed NH$_3$ were 161,157, 147, 129 and 109 μmol/g, respectively. The decrement of the acid density with increasing the loading of MgAl$_2$O$_4$ may be caused by the basic nature of MgAl$_2$O$_4$ as observed by CO$_2$-TPD, as MgAl$_2$O$_4$ may partially neutralize the acidic sites of niobium oxide adhered to it.

### 3.4. Effect of MgAl$_2$O$_4$ loadings on the catalytic performance

Fig. 6 shows the effect of MgAl$_2$O$_4$ loadings on the catalytic performance of Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ for EO hydration. EO conversion decreased with the addition of MgAl$_2$O$_4$ and with increasing the loading of MgAl$_2$O$_4$ in the range studied, e.g. it decreased from 99.8% of unpromoted Nb$_2$O$_5$/α-Al$_2$O$_3$ to 99.5% at MgAl$_2$O$_4$ loading of 2.23%. The selectivity to MEG was slightly increased with MgAl$_2$O$_4$ loadings below 2.23%, and achieved a maximum of 90.6% at MgAl$_2$O$_4$ loading of 2.23% in comparison with that of 89.8% for the pure α-Al$_2$O$_3$ supported catalyst. On further increas-

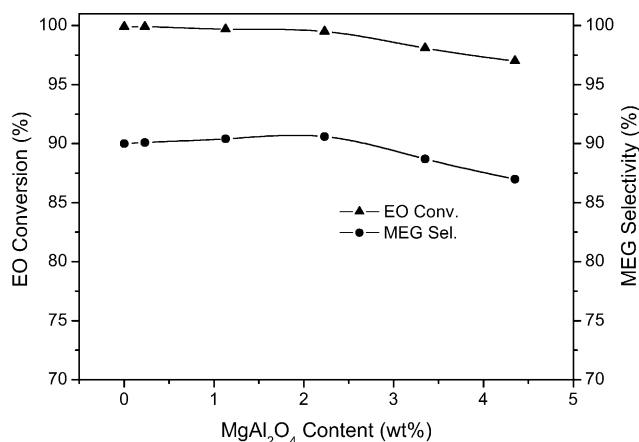Fig. 6. Effect of MgAl$_2$O$_4$ loadings on the catalytic properties of Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalyst.



Fig. 7. Stability test of 10% Nb$_2$O$_5$/2.23% MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalyst.

ing the MgAl$_2$O$_4$ loadings above 2.23%, MEG selectivity decreased noticeably. In order to better understand the influence of support modification on MEG selectivity, additional experiment was carried out, in which the reaction temperature was raised by 5 °C for 10% Nb$_2$O$_5$/2.23% MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalyst to keep the EO conversion same as that over 10% Nb$_2$O$_5$/α-Al$_2$O$_3$ catalyst. The results showed that at the same EO conversion of 99.8% the MEG selectivity over 10% Nb$_2$O$_5$/2.23% MgAl$_2$O$_4$/α-Al$_2$O$_3$ and 10% Nb$_2$O$_5$/α-Al$_2$O$_3$ catalysts were 90.7% and 89.8%, respectively. The decrement of EO conversion with increasing MgAl$_2$O$_4$ loading may be interpreted by the decreasing of acid density as observed by NH$_3$-TPD, because the catalytic activity of acid catalyzed hydration is proportional to the density of the active acidic sites. The reason for the maximum MEG selectivity appearing at MgAl$_2$O$_4$ loading of 2.23% may be explained as follows. Depending on the reaction conditions and the catalyst used, the primary product of hydration may preferentially desorbs from the active sites or remains on the active sites. If the primary product desorbs from the catalyst surface, the MEG would be produced; if the MEG remains on active sites, the polymerization or other secondary reactions possibly occur, and thus the selectivity to MEG would decrease. It is generally accepted that under the same reaction conditions the higher strength of acidity may favor the adsorption of MEG. As the acidity strength of the catalyst decreases with increasing the loading of MgAl$_2$O$_4$ up to 2.23%, the adsorption of the primary product of MEG becomes weaker. Hence, the selectivity to MEG increases. When the acidity strength of the catalyst decreases further by further increasing the loading of MgAl$_2$O$_4$ from 2.23%, the contribution of non-catalytic hydration to the overall reaction and to total products would increase. Therefore, the selectivity to MEG decreases, as the selectivity of non-catalytic hydration is known to be significantly lower than that of the acid catalyzed hydration. The above results indicated that modification of α-Al$_2$O$_3$ with certain amount of MgAl$_2$O$_4$ led to a compromise between the
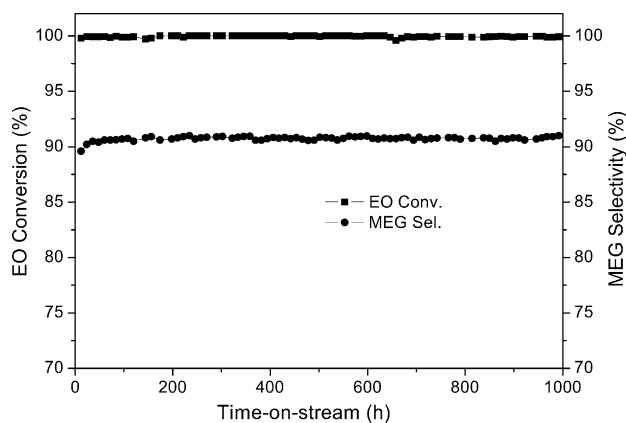
strength and density of the acidity of Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ that gives rise to an optimal catalytic performance.

### 3.5. Stability of supported niobium oxide catalyst

Durability test of the Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalyst was carried out over a period of 1000 h, as shown in Fig. 7. The selectivity of MEG remained almost unchanged at ca. 91% within 1000 h time-on-stream and no deactivation was observed during testing. The effluent was monitored with ICP to check whether there is the elution of niobia species or iron species of stainless steel reactor. No iron or niobia ion was found within the detection limit of $10^{-6}$ g/mL. This shows that the niobium oxide supported on MgAl$_2$O$_4$ modified α-Al$_2$O$_3$ had no leaching and no corrosion to the stainless reactor under harsh hydrothermal circumstance during EO hydration.

### 4. Conclusions

Modification of α-Al$_2$O$_3$ support with MgAl$_2$O$_4$ led to an increase in basicity and mechanical strength of the support. The catalyst prepared with MgAl$_2$O$_4$ modified α-Al$_2$O$_3$ support showed less density and strength of acidity than that of the pure α-Al$_2$O$_3$ supported catalyst. The acidity of the Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ decreased with increasing loading of MgAl$_2$O$_4$ and was much weaker than that of niobic acid. Catalytic test demonstrated that EO conversion decreased monotonously with increasing loading of MgAl$_2$O$_4$, whereas the selectivity to MEG showed a maximum of 90.6% at MgAl$_2$O$_4$ loading of 2.23%. In terms of MEG yield, optimal MgAl$_2$O$_4$ loadings should be around 2%. Durability test demonstrated that Nb$_2$O$_5$/MgAl$_2$O$_4$/α-Al$_2$O$_3$ catalyst exhibited excellent stability within 1000 h time-on-stream. The present investigation showed that there should be a compromise of the strength with density of the acidity of the catalyst to achieve the optimal catalytic performance.

## Acknowledgements

## References

[1] K. Tanabe, Catal. Today 78 (2003) 65.
[2] K. Tanabe (Ed.), Catal. Today 28 (1996).
[3] I. Nowak, M. Ziolek, Chem. Rev. 99 (1999) 3603.
[4] Y. Izumi, Catal. Today 33 (1997) 390.
[5] T. Okuhara, Chem. Rev. 102 (2002) 3641.
[6] T. Ushikubo, Catal. Today 57 (2000) 331.
[7] T. Hanaoka, K. Takeuchi, T. Matsuzaki, Y. Sugi, Catal. Today 8 (1990) 123.
[8] T. Hanaoka, K. Takeuchi, T. Matsuzaki, Y. Sugi, Catal. Lett. 5 (1990) 13.
[9] T. Hanaoka, K. Takeuchi, T. Matsuzaki, Y. Sugi, Jpn. Kokai Tokkyo Koho JP 6,179,633 (1994).
[10] Y.C. Li, S.R. Yan, W.M. Yang, Z.K. Xie, Q.L. Chen, B. Yue, H.Y. He, Appl. Catal. A: Gen. 272 (2004) 305.
[11] Y.C. Li, B. Yue, S.R. Yan, W.M. Yang, Z.K. Xie, Q.L. Chen, H.Y. He, Catal. Lett. 95 (2004) 163.
[12] G. Xanthopoulou, Appl. Catal. A: Gen. 182 (1999) 285.
[13] J. Sehested, A. Carlsson, T.V.W. Janssens, A.K. Datye, J. Catal. 197 (2001) 200.
[14] M. Ziolek, I. Nowak, J.C. Lavalley, Catal. Lett. 45 (1997) 259.
[15] S. Khabtou, T. Chevreau, J.C. Lavalley, Micropor. Mater. 3 (1994) 133.