*Catalysis Letters Vol. 80, No. 3–4, June 2002 (©2002)*

# Dehydration of alcohols by microporous niobium silicate AM-11

Paula Brandão [a], Andreas Philippou [b], João Rocha [a,*], and Michael W. Anderson [b]
[a] *Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *Department of Chemistry, UMIST, PO Box 88, Manchester, M60 1QD, UK*

Received 20 November 2001; accepted 5 February 2002

The dehydration of ethanol, 1-propanol and 1-butanol has been studied at atmospheric pressure using the novel microporous niobium silicate AM-11 (Aveiro–Manchester structure number 11) in the temperature range 150–300 °C. The selectivity for alkenes increases with temperature for all three alcohols and reaches 100% for 100% conversion at 250–300 °C. At lower reaction temperatures (~200 °C), ethers are also formed and their selectivity decreases markedly with the alcohol size.

**KEY WORDS:** microporous; niobium silicate; alcohol dehydration.

## 1. Introduction

Niobium oxide and niobium compounds catalyze a number of important reactions [1]. It has been demonstrated that niobium oxide catalysts in combination with various supports possess remarkable acidity and redox activity [2–7]. These catalysts have been used for dehydration of alcohols [8,9], oxidative dehydrogenation of alkanes [10], NO reduction by $NH_3$ [11] and oxidation of methanol [12]. The presence of niobium in molecular sieves has the potential of generating catalysts with size/shape selective properties and acidic or redox characteristics. Only a few reports are available on porous niobosilicates; they include work on the incorporation of niobium in micro/mesoporous materials, ETS-10 [13] denoted ETNbS-10, MFI [14] designated NbS-1, and MCM-41 [15]. Furthermore Antonelli and Ying [16] published the synthesis of the niobium oxide molecular sieve Nb-TMS-1, a hexagonally-packed mesoporous material. Recently, Clearfield and coworkers, prepared three new niobium silicates [17]. Moreover, the first organically templated open-framework niobium silicate denoted NSH-1 with chemical formula $(C_4N_2H_{11})Nb_3SiO_{10}$ was reported by Francis and Jacobson [18].

In 1998, we prepared a novel microporous niobium silicate, AM-11 [19]. Though the structure of this material has not been solved yet, a preliminary characterization indicates that octahedral niobium(V) and tetrahedral silicon are the main units of the AM-11 framework. The charge associated with framework niobium is balanced by $Na^+$ and $NH_4^+$ cations, and the as-prepared material possesses a substantial amount of Brønsted acidity at the internal surface whereas the external surface accommodates predominantly Lewis acid centres [20]. A textural analysis indicates that AM-11 exhibits a large nitrogen uptake (~0.15 g/g) whereas the accessibility of larger molecules to this structure is rather limited.

The catalytic activity of AM-11 has already been investigated by means of methanol conversion [20]. It was found that in continuous flow experiments, methanol reacts rapidly on external Lewis acid sites to produce dimethylether, whereas, in the batch reactor, methanol diffuses into the internal surface yielding a range of $C_1$–$C_5$ hydrocarbons. Furthermore, AM-11 catalyses the gas-synthesis of MTBE from *t*-butanol and methanol [21].

In this contribution the dehydration of ethanol, 1-propanol and 1-butanol are investigated under various experimental conditions. It is shown that this inorganic solid exhibits an excellent catalytic performance, yielding 100% selectivity for alkenes at 100% conversion at 250–300 °C.

## 2. Experimental

### 2.1. *AM-11 synthesis*

The AM-11 sample used in this work was synthesized as reported in the literature [19]. Briefly, AM-11 was prepared in Teflon-lined autoclaves under hydrothermal conditions. The AM-11 gel with a composition $1.0\,Na_2O:1.0\,SiO_2:0.15\,Nb_2O_5:240\,H_2O$ was autoclaved for 12 days at 200 °C. The gel pH (after a 1:100 water dilution) was adjusted to 10.2 by adding an ammonia solution (25%, Merck). The crystalline product was filtered, washed with distilled water and dried at room temperature, the final product being an off-white microcrystalline powder. The powder XRD

---

[*] To whom correspondence should be addressed.
E-mail: rocha@dq.ua.pt

1011-372X/02/0600-0099/0

pattern of as-synthesised AM-11 is identical to that published earlier [19].

### 2.2. Characterization

XRD data were collected on a Philips X'pert MPD diffractometer using Cu $K_\alpha$ radiation with a curved graphite monochromator and proportional detector. Bulk chemical analysis was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Surface area and pore volume measurements were performed on a Micromeritics ASAP 2010 V1.01 B automatic instrument by absorption of nitrogen gas at 77 K, after outgassing the sample overnight at 573 K.

### 2.3. Catalysis experiments

The gas-phase experiments were performed in a fixed-bed stainless steel reactor at atmospheric pressure. The reactor's length and internal diameter are 16.0 and 0.5 cm, respectively, and the reactor bed is 1.0 cm long with a diameter of 0.5 cm. The catalyst (50 mg) was activated at 400 °C in argon with a flow rate of 10 ml $\text{min}^{-1}$ for 3 h. The gas composition at reaction conditions and during activation was the same. The reactant mixture was fed and controlled by a syringe pump, and residence times were adjusted by keeping the catalyst weight constant and changing the volumetric flow rate of the reactant. The products were analyzed by means of gas chromatography with a 30 m long capillary column (DP1 fused silica phase) and a flame ionization detector.

For all reactions the AM-11 catalyst was used in the as-prepared form.

## 3. Results and discussion

The catalytic activity of AM-11 for ethanol, 1-propanol and 1-butanol reactions are depicted in table 1. The products formed during these catalytic reactions are ethene and diethylether from ethanol, propene and dipropylether from 1-propanol, and *n*-butenes, dibutylether and $C_8$ hydrocarbons from 1-butanol. The acidity of AM-11 is clearly manifested in these reaction processes, producing only alkenes and ethers, which are indicative of acid catalysis. No products from dehydrogenation of alcohols were observed. The selectivity to alkenes and ethers was markedly affected by the reaction temperature. In all three cases, low temperatures favor ether formation, whereas at high temperatures (250–300 °C) alkenes are produced with 100% selectivity. It must be noted that at lower reaction temperatures the smaller the alcohol size the higher the selectivity for the corresponding ether.

The deactivation of AM-11 for all reactions was monitored at different temperatures as a function of time on stream (TOS) (figure 1). At high temperatures (>200 °C), no deactivation was observed for up to 17 h on stream for all three reactions. However, at lower temperatures ($\leq$200 °C) the conversion of alcohols decays slowly. This deactivation must relate to acid-site poisoning by water molecules, which fail to desorb effectively at lower reaction temperatures. The deactivation follows the order 1-butanol > 1-propanol > ethanol. For ethanol and 1-propanol reactions, AM-11 was reused three times, always showing 100% conversion and 100% selectivity for the corresponding alkene at 300 and 250 °C, respectively. The AM-11 catalysts were analyzed by powder XRD after reaction and showed no significant crystallinity loss.

Figure 2 depicts the alkene selectivity as a function of TOS. For all reactions long TOS favors alkene selectivity.

Table 2 illustrates the effect of weight hourly space velocity (WHSV) on ethanol conversion and the product distribution at 200 °C. It is clearly seen that the shorter the residence time the higher the ethene selectivity. For 1-propanol and 1-butanol only alkenes were formed at 200 °C and no ethers were produced even at the longest residence times. As shown in figure 2, the conversion of

Table 1
Conversion of ethanol, 1-propanol and 1-butanol and product selectivities over AM-11[a] at different temperatures

| Reactant | Conversion, selectivity (wt%) | Temperature (°C) | | | | |
|---|---|---|---|---|---|---|
| | | 150 | 180 | 200 | 250 | 300 |
| Ethanol | Conversion | – | 12.5 | 22.1 | 98.1 | 100 |
| | Ethene | – | 55.4 | 59.1 | 97.8 | 100 |
| | Diethylether | – | 44.6 | 40.9 | 3.0 | 0 |
| 1-Propanol | Conversion | – | 6.1 | 23.2 | 100 | – |
| | Propene | – | 84.4 | 100 | 100 | – |
| | Dipropylether | – | 15.6 | 0 | 0 | – |
| 1-Butanol | Conversion | 5.6 | 24.7 | 65.0 | 100 | – |
| | Butenes | 85.3 | 100 | 100 | 100 | – |
| | Dibutylether | 7.5 | 0 | 0 | 0 | – |
| | $C_8$ hydrocarbons | 7.2 | 0 | 0 | 0 | – |

[a] TOS = 60 min; WHSV = 2 $\text{h}^{-1}$.

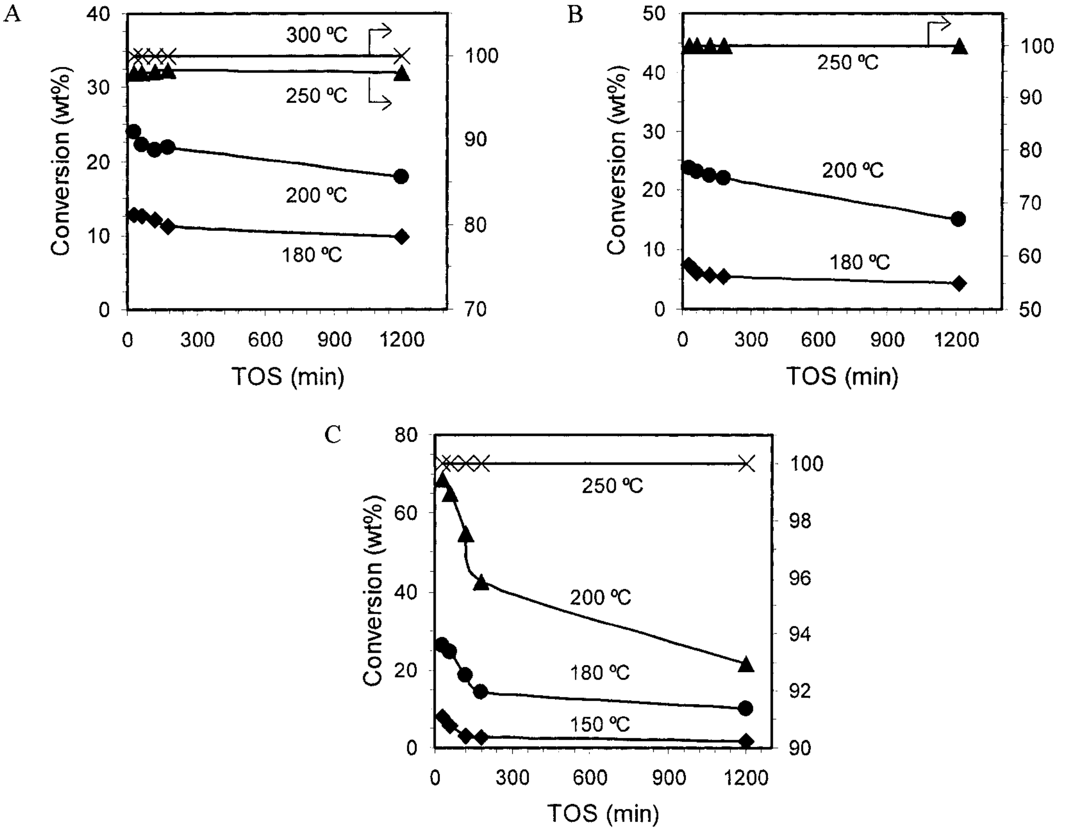

Figure 1. (A) Ethanol, (B) 1-propanol and (C) 1-butanol conversion as a function of TOS over AM-11 at various temperatures (WHSV = 2 h$^{-1}$).

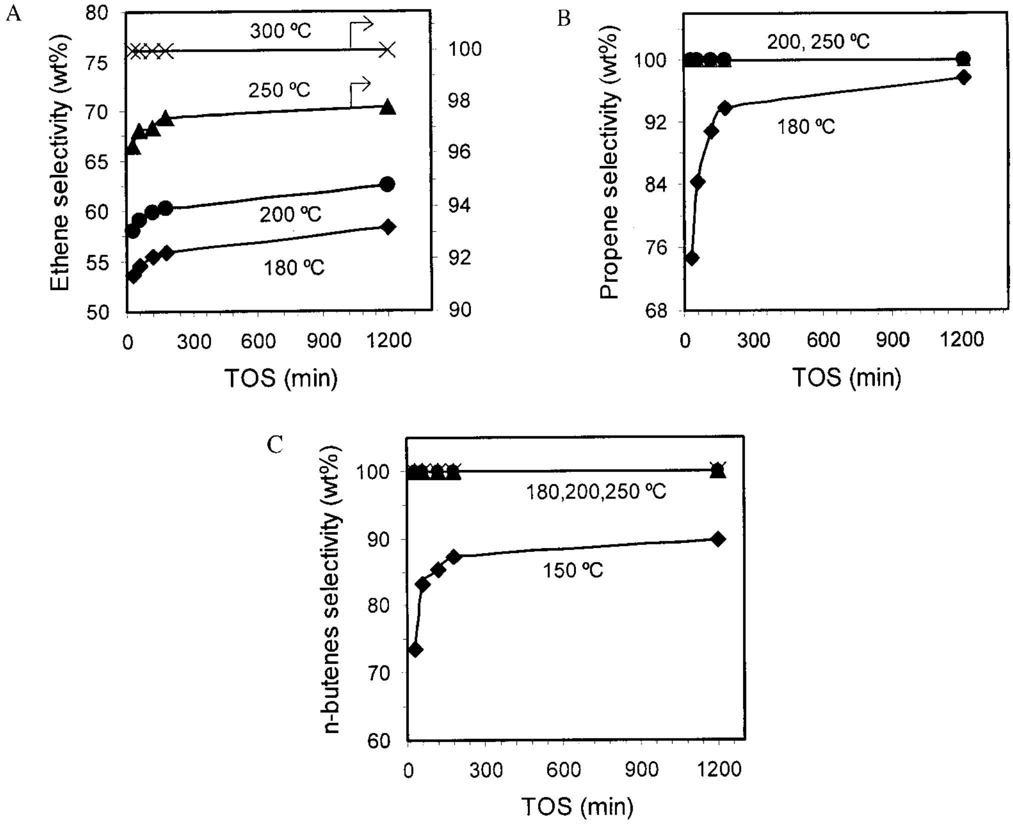

Figure 2. (A) Ethene, (B) propene and (C) *n*-butene selectivity as a function of TOS over AM-11 at various temperatures (WHSV = 2 h$^{-1}$).

Table 2
Conversion of ethanol, 1-propanol and 1-butanol and product selectivities over AM-11[a] at different WHSV

| Reactant | Conversion, selectivity (wt%) | WHSV ($h^{-1}$) | | |
|---|---|---|---|---|
| | | 0.4 | 2 | 4 |
| Ethanol | Conversion | 66.4 | 22.1 | 16.4 |
| | Ethene | 50.9 | 59.1 | 79.4 |
| | Diethylether | 49.1 | 40.9 | 20.6 |
| 1-Propanol | Conversion | 62.6 | 23.2 | 4.0 |
| | Propene | 100 | 100 | 100 |
| 1-Butanol | Conversion | 100 | 65 | 40 |
| | Butanes | 100 | 100 | 100 |

[a] TOS = 60 min; temperature = 200 °C.

both alcohols increases markedly as the WHSV decreases. These results show that although the product distribution depends on both temperature and WHSV, temperature is the parameter which determines the ether formation.

## 4. Conclusions

AM-11 is not only active in the intramolecular dehydration of alcohols but also catalyzes the intermolecular dehydration of alcohols to ethers. The reaction temperature has a strong effect on the product selectivities. Alkene formation is favored at high temperatures whereas low reaction temperatures promote ether yields. The catalyst deactivation is more profound at lower reaction temperatures (<200 °C) whereas no deactivation is observed at high temperatures (>200 °C).

## Acknowledgment

We acknowledge Fundação da Ciência e Tecnologia, PRAXIS XXI, POCTI and FEDER for financial support.

## References

[1] I. Nowak and M. Ziolek, Chem. Rev. 99 (1999) 3603.
[2] A. Florentino, P. Cartraud, P. Magnoux and M. Guisnet, Appl. Catal. A: General 89 (1992) 143.
[3] E.C. Decanio, V.P. Nero and E.I. Ko, J. Catal. 146 (1994) 317.
[4] K. Asakura and Y. Iwasawa, J. Phys. Chem. 95 (1991) 1711.
[5] P.A. Burke and E.I. Ko, J. Catal. 129 (1991) 38.
[6] S. Okazaki and N. Wada, Catal. Today 16 (1993) 349.
[7] J. Jehng and I.E. Wachs, Catal. Today 16 (1993) 417.
[8] T. Iizuka, K. Ogasawara and K. Tanabe, Bull. Chem. Soc. Jpn. 56 (1983) 2927.
[9] M. Shirai, N. Ichikumi, K. Asakura and J.I. Wasawa, Catal. Today 8 (1990) 57.
[10] O. Desponds, R.L. Keiski and G.A. Somorjai, Catal. Lett. 19 (1993) 17.
[11] K. Tanabe, Catal. Today 8 (1990) 1.
[12] J. Jehng and I.E. Wachs, Catal. Today 8 (1990) 13.
[13] J. Rocha, P. Brandão, J.D. Pedrosa de Jesus, A. Philippou and M.W. Anderson, Chem. Commun. (1999) 471.
[14] A.M. Prakash and L. Kevan, J. Am. Chem. Soc. 120 (1998) 13148.
[15] M. Ziolek and I. Nowak, Zeolites 18 (1997) 356.
[16] D.M. Antonelli and J.J. Ying, Angew. Chem. Int. Ed. Engl. 35 (1996) 426.
[17] M.A. Salvadó, P. Pertierra, S. García-Granda, S.A. Khainakov, J.R. García, A.I. Borton and A. Clearfield, Inorg. Chem. 40 (2001) 4368.
[18] R.J. Francis and A.J. Jacobson, Angew. Chem. Int. Ed. Engl. 40 (2001) 2879.
[19] J. Rocha, P. Brandão, A. Philippou and M.W. Anderson, Chem. Commun. (1998) 2687.
[20] A. Philippou, P. Brandão, A. Ghanbari-Siahkali, J. Dwyer, J. Rocha and M.W. Anderson, Appl. Catal. A 207 (2001) 229.
[21] P. Brandão, A. Philippou, J. Rocha and M.W. Anderson, Catal. Lett. 73 (2001) 59.