ELSEVIER

Catalysis Today 81 (2003) 623–629

CATALYSIS TODAY

www.elsevier.com/locate/cattod

On the activity, longevity and recyclability of Mn(II) and Co(II) substituted AlPO-18 catalysts for the conversion of methanol to light olefins

Ilona L. Franklin, Andrew M. Beale, Gopinathan Sankar*

Davy Faraday Research Laboratory, The Royal Institution of GB, 21 Albemarle Street, London W1S 4BS, UK

Abstract

The influence of the degree of substitution of the cobalt and manganese ions into AlPO-18 structure was investigated for the conversion of methanol to light olefins (MTO) at 350 °C. The results show that the activity for methanol conversion increases with transition metal content up to 2 at.% for conversion of methanol after 2 h on stream. These catalysts show good stability for this reaction after regeneration suggesting that there is no leaching of the active metal centres.

Keywords: Acid catalysis; MTO reaction; MAPO; Microporous materials; Shape selective catalysis; EXAFS

1. Introduction

It has been well established in recent years that hetero-atom substituted small pore microporous aluminophosphate materials are extremely efficient shape selective catalysts [1,2]. For example, it is well-known that SAPO-34 (structure related to chabazite), and its nickel substituted analogue are very effective in converting methanol to both ethylene and propylene [1,3–5]. Similarly, it has been established in our laboratory that the transition metal ion substituted AlPO-18 and AlPO-34 materials, in particular manganese or cobalt, can be employed to selectively (regio-selective) oxidise the terminal carbon atoms in *n*-hexane and other linear alkanes [6]. In light of these unique catalytic properties there is considerable interest in the study of hetero-atom substituted, small pore aluminophosphates for a variety of reactions. Among the various small pore structures, AlPO-18 and AlPO-34 (the main difference being the way in which the double six rings are stacked, otherwise their pore dimensions are identical) based systems have shown good thermal stability upon calcination, and excellent activity and selectivity towards the conversion of methanol to light olefins [1,2,7,8]. The majority of synthesis and catalytic studies in the literature are concerned with SAPO-34 and a variety of metal substituted analogues, such as CoAlPO-34, NiSAPO-34 and FeSAPO-34 [9,10]. Therefore it is somewhat surprising to see that only a few studies have been devoted to the hetero-atom substituted AlPO-18 structure since although the overall architecture and thermal stability of both AlPO-34 and AlPO-18 related structures are very similar, a greater number of different hetero-atom compositions are possible. For example, it has been shown that SAPO-18 can be prepared with Si/Al ratio ranging from 0.0 to at least 0.1, whereas in contrast SAPO-34 can only be prepared over a much smaller composition range of between 0.09 and 0.11 [11,12].

---

* Corresponding author. Tel.: +44-20-7409-2992; fax: +44-20-7629-3569.
E-mail address: sankar@ri.ac.uk (G. Sankar).

0920-5861/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00160-3

Because of this flexibility in the composition of the MAlPO-18 structure, we have carried out a systematic investigation of two transition metal ion substituted AlPO-18 materials for the production of light olefins from methanol. To do so, we synthesised pure AlPO-18 as well as cobalt and manganese substituted analogues (CoAlPO-18 and MnAlPO-18) with a concentration of metal substituent ranging from 0.05 to 4 at.% of the total aluminium content, and carried out detailed catalytic studies to investigate the nature of selectivity and activity as a function of both transition metal incorporation and reaction temperature. The results clearly show that manganese and cobalt substituted systems are very good catalysts for the selective conversion of methanol to both ethylene and propylene and that the catalytic conversion improved with increasing amounts of metal substitution.

2. Experimental

Both AlPO-18 and its transition metal ion (Mn(II) and Co(II)) substituted analogues were synthesised using a previously reported procedure [2] employing *N*,*N*-diisopropylethylamine (Aldrich) as the structure directing agent (SDA). In a typical synthesis aluminium hydroxide hydrate (Aldrich) was added to a solution of 85% phosphoric acid (Aldrich) and water. Appropriate amounts of the Mn(II) acetate (Aldrich) was then added prior to the addition of the SDA with vigorous stirring in order to form a homogeneous mixture. The final gel, with a pH of 8, was introduced into a Teflon lined stainless steel autoclave and was subjected to hydrothermal treatment at 150 °C for 96 h. The recovered solid was filtered, washed with distilled water then dried at approximately 100 °C. The M/P ratios (in the precursor gel) used in this study were 0.005, 0.01, 0.02, and 0.04.

The as-prepared catalysts were characterised for phase purity and crystallinity, by X-ray diffraction (XRD) and X-ray absorption spectroscopy. XRD studies were carried out at room temperature using a Siemens D500 diffractometer equipped with copper target. The metal K-edge X-ray absorption spectroscopy data were collected at station 8.1 of the Daresbury synchrotron radiation source that operates at 2 GeV with a typical current in the range of 150 and 250 mA. The experimental station consists of a Si(1 1 1) double crystal monochromator, ion chambers for measuring incident and transmitted beam intensity and a fluorescence detector. For systems containing less than 2 at.% metal ions we have employed the florescence detection mode and for the other materials data was collected employing the transmission mode. EXAFS data were processed using a suite of programs available at the Daresbury laboratory, namely EXCALIB, EXBROOK and EXCURV98.

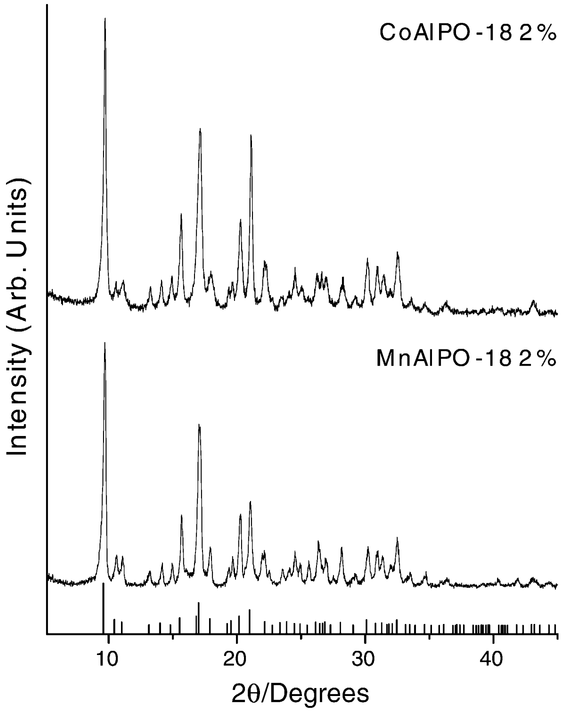

Fig. 1. XRD patterns of the as-synthesised CoAlPO-18 (top) and MnAlPO-18 (bottom) materials. The vertical lines represent the calculated 2θ positions using the structure reported previously.

Table 1
Structural parameters determined from Co and Mn K-edge EXAFS of as-synthesised and calcined CoAlPO-18 and MnAlPO-18

Catalyst	M–O distance (Å)	Oxidation state of metal ion
CoAlPO-18 as-prepared	1.94	2+
CoAlPO-18 calcined	1.83	3+
MnAlPO-18 as-prepared	2.03	2+
MnAlPO-18 calcined	1.85	3+

Each methanol conversion reaction was carried out using a custom built continuous flow reactor. In a typical experiment, 200 mg of the as-prepared catalyst was palletised then crushed using a 20 μm mesh sieve prior to being loaded into a quartz reactor tube. The catalyst was activated by heating in a nitrogen atmosphere at 1 °C/min to 530 °C and then held for 8 h prior to oxygen being introduced for 1 h at the same temperature in order to remove the organic template. The sample was then cooled to a specific temperature, again in a nitrogen atmosphere, before methanol was injected at a fixed flow rate of 0.05 ml/min using

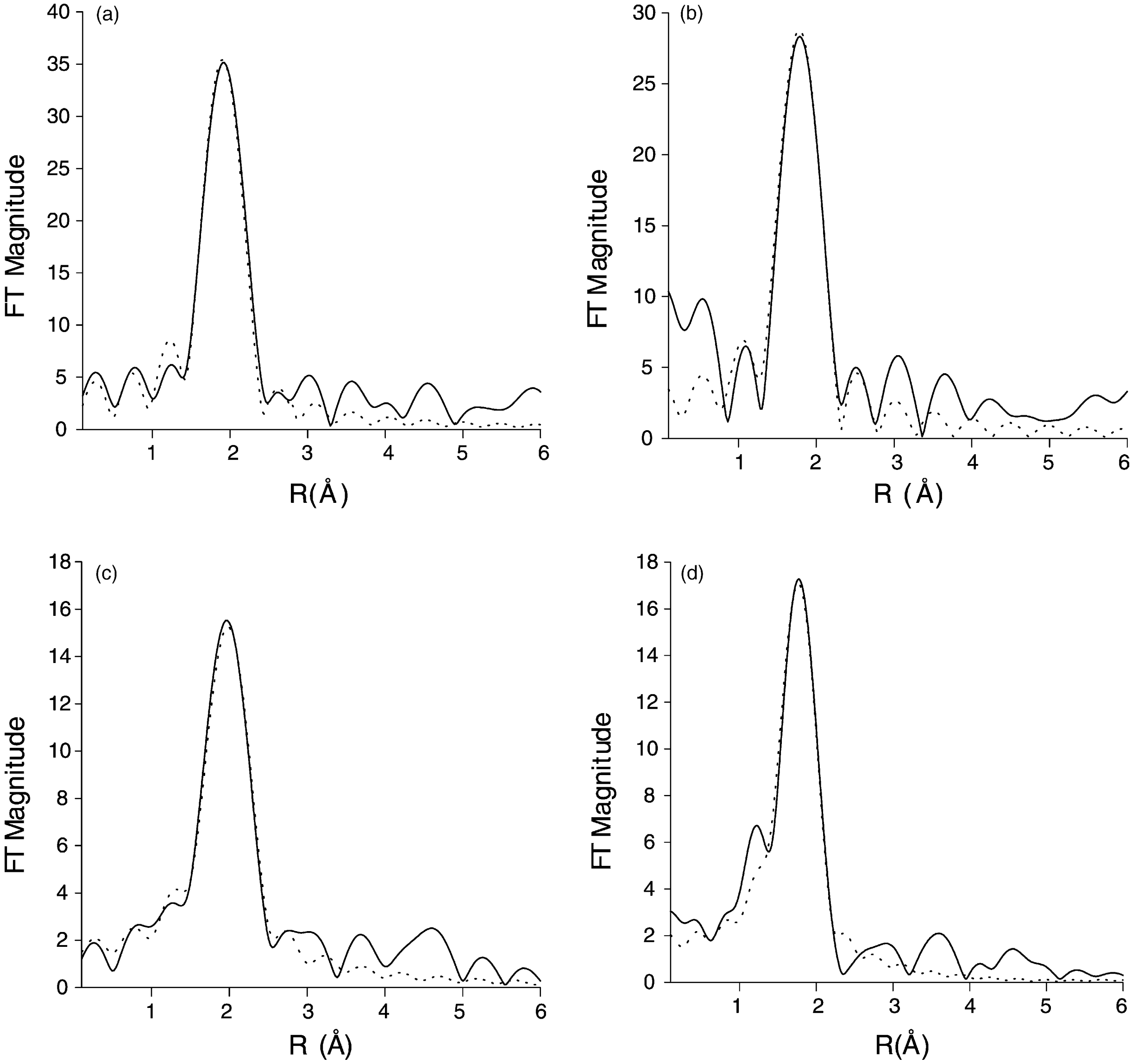

Fig. 2. Co and Mn K-edge EXAFS data and the associated Fourier transforms of (a) as-prepared CoAlPO-18, (b) as-prepared MnAlPO-18, (c) calcined CoAlPO-18 and (d) calcined MnAlPO-18 along with the best fit (the dotted line represents the calculated EXAFS and the solid curves the experimental data) to the data. The results are very similar to previously reported data for cobalt and manganese substituted microporous aluminophosphate structures suggesting that the metal ions are incorporated as tetrahedral Co(II) and Mn(II) [13–15].

a syringe pump. The products were analysed using a Porapak N column in a Perkin Elmer 3010 gas chromatograph equipped with an FID detector.

3. Results and discussion

The XRD patterns of the as-synthesised phase pure AlPO-18 containing 2 at.% Co and Mn are shown in Fig. 1. Although the XRD patterns could not reveal directly the extent of incorporation of the metal ions, analysis of the respective K-edge EXAFS data of the as-prepared materials yielded a Co–O and Mn–O distances of ca 1.94 and 2.03 Å (see Table 1) with coordination number of ca 4, respectively, suggesting that high-spin Co(II) and Mn(II) ions are present in the tetrahedral sites of the AlPO-18 structure in the respective systems [13–15]. The best fit to the Co and Mn K-edge EXAFS data and the associated Fourier transforms of the as-prepared material are

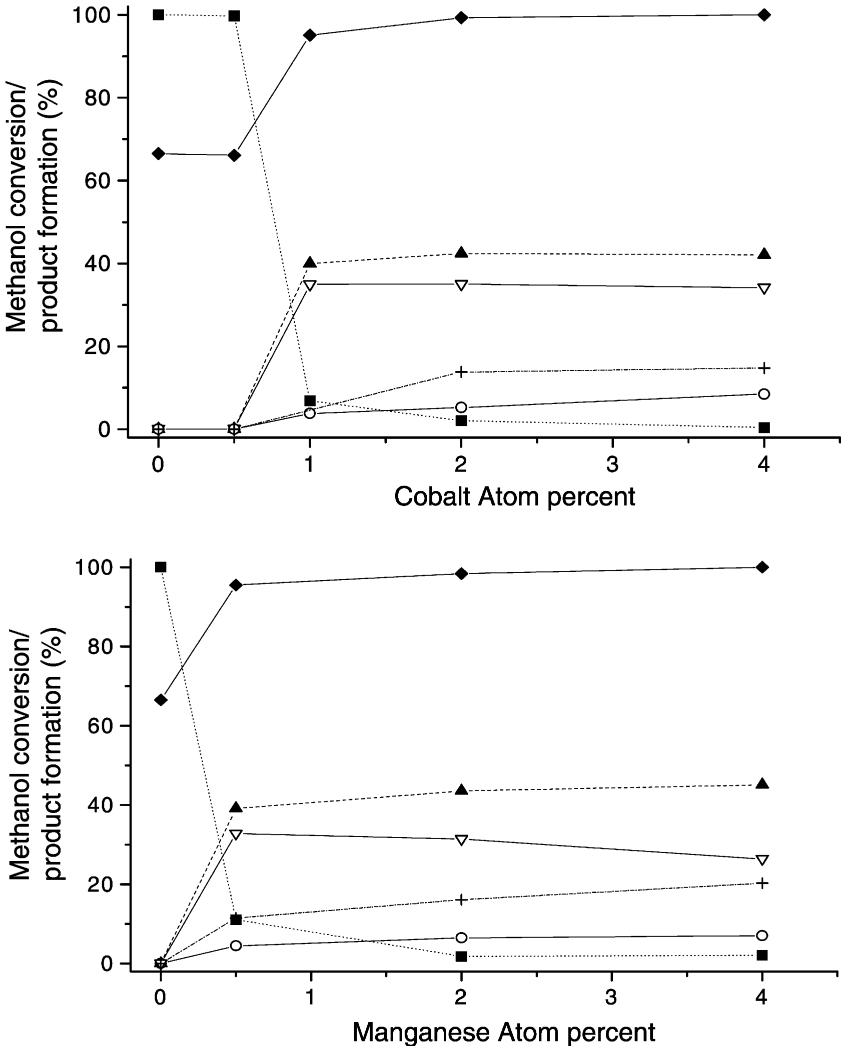

Fig. 3. Effect of percent metal atom incorporation on methanol conversion (◆), selectivity to DME (■), selectivity to ethylene (▽), selectivity to propylene (▲), selectivity to C4/C5 (+) and selectivity to C6+ (○), for the MTO reaction at 350 °C over CoAlPO-18 (top) and MnAlPO-18 (bottom), TOS = 30 min.

shown in Fig. 2. It has been well-established from several detailed EXAFS studies [6,13,14,16,17] of cobalt and manganese ions, when substituted into AlPO-18 materials, that respective Co–O or Mn–O distances decrease upon calcination (an important process carried out prior to the catalytic testing, to remove the organic template which occlude the channels and pores available for shape selective catalysis) which is indicative of changes in the oxidation state from 2+ to 3+ (see Table 1 and Fig. 2). Similarly, EXAFS studies of cobalt and manganese substituted microporous aluminophosphate catalyst, measured after reduction with either hydrogen or reaction with methanol showed that the bond distance of both Co–O and Mn–O increase (compared to the calcined one) and suggesting the conversion of 3+ back to 2+ [13]. In situ FTIR studies, reported elsewhere, clearly supported this oxidation–reduction behaviour of cobalt ions in CoAlPO-18 and CoAlPO-34 catalysts; a distinct OH stretching frequency was seen around 3600 cm^{-1} in the reduced catalyst due to the presence of the charge compensating proton (when 2+ oxidation state is present) [2,16,18,19].

It is known from earlier catalytic studies that 4 at.% containing cobalt, zinc and magnesium AlPO-18 catalysts are highly active for the conversion of methanol to hydrocarbons with conversions reaching nearly 100% and with very good selectivities to light olefins [2]. The origin of such catalytic activity has been attributed to the presence of Brönsted acid sites (consistent with the IR observation) when divalent species such as Co(II) and Zn(II) substitute for Al(III) or the tetravalent Si(IV) substitutes for P(V) [11]. However it has been shown from previous work conducted on SAPO-18 that beyond 8 at.% of silicon there is no significant change in activity. This has been explained as due to the nature of substitution of Si(IV) ions in place of both P(V) and Al(III) sites, forming so-called silicon islands resulting in charge neutral sites [11]. In order to establish whether there is similar such concentration dependence on the catalytic performance in other metal ion substituted MAlPOs, we carried out a systematic study with catalysts containing 0.5, 1, 2 and 4 at.% of either cobalt or manganese ions. The plot showing methanol conversion versus concentration (Fig. 3) clearly shows that methanol conversion reaches almost 100% for catalysts containing only 2 at.% of the metal substituents and hence there is no significant change in the conversion for either catalysts containing more than this. Hence, subsequent studies were conducted using catalysts containing 2 at.% of Mn or Co ions.

In order to determine the extent to which the catalysts continued to convert methanol feed, we carried out a time on stream (TOS) experiment and the results of this are shown in Fig. 4. Clearly, there appears to be no significant decline in either activity or selectivity for both catalysts, for up to 2 h. This catalytic performance is also tested after regeneration of the catalyst. In a typical experiment, we calcined the as-prepared catalyst and subjected the activated catalyst for methanol reaction at 350 °C for 1 h. The same catalyst was calcined again at 550 °C before carrying out the catalytic reaction with methanol. This procedure was repeated three times and the results are given in Table 2. The catalytic results suggest that there is no significant decline in the conversion level. However, with increasing time there appears a slight decrease in the conversion which is likely to be due to the formation of coke, which is known to occur in these materials [1,11]. Based on the initial conversion after each cycle and under the conditions employed in this study, we propose that there is no significant leaching of the active metal centres during reaction.

In summary, it has been possible to substitute into the microporous framework of the AlPO-18 structure between 0.5 and 4 at.% of the transition metal ions cobalt and manganese and this results in a highly active catalyst for the conversion of methanol to light olefins (C2, C3). We have shown that the catalytic activity increases with the degree of Co(II) and Mn(II) substitution up to 2 at.% but beyond this amount there

Table 2
Recyclability study showing the effect of TOS on the methanol conversion after three consecutive methanol conversion reactions over 2% MnAlPO-18 at 350 °C

Run	TOS (min)	Methanol conversion (%)
1	30	98.16
	70	98.80
2	30	100
	70	100
3	30	96.30
	80	91.74

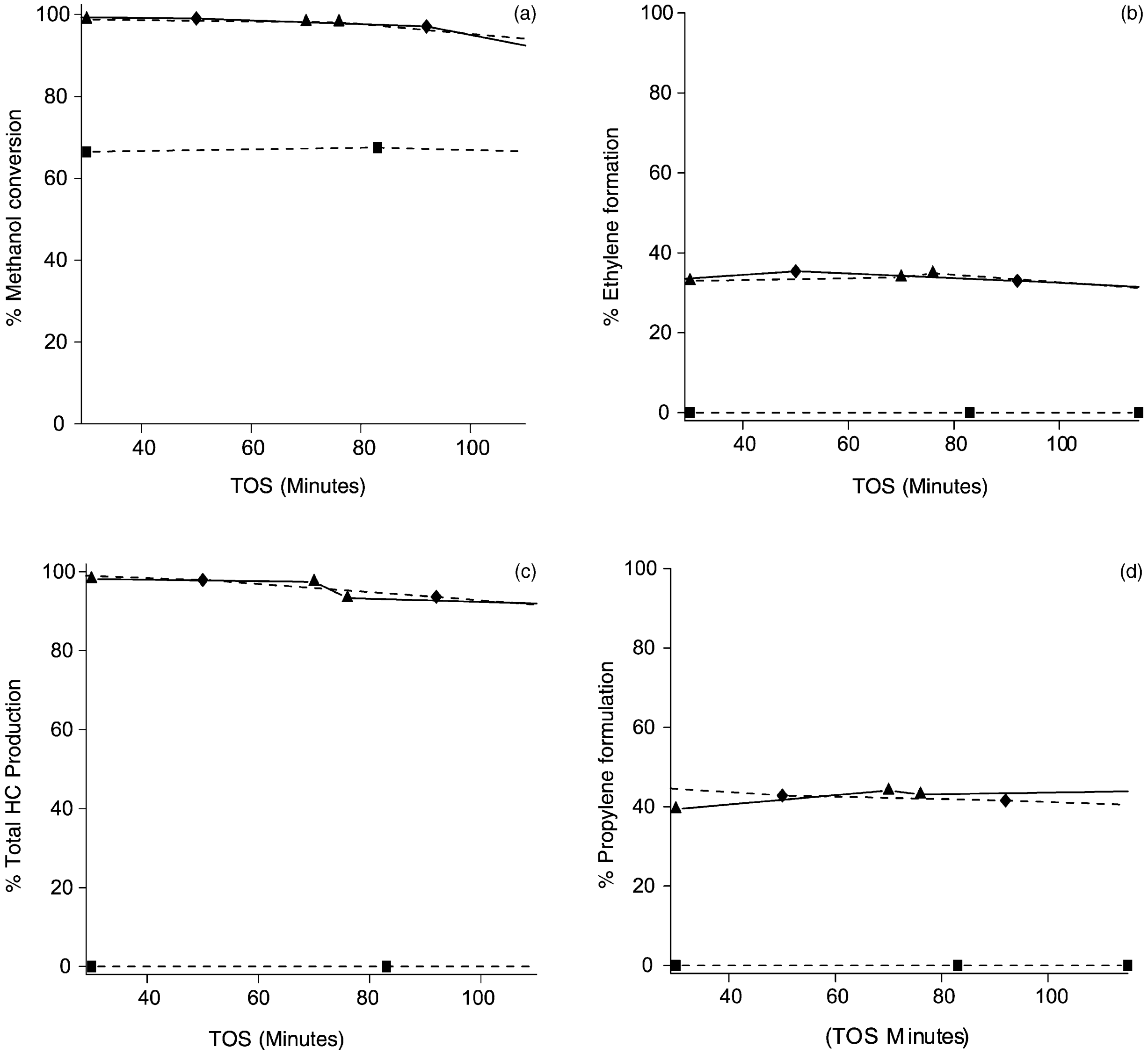

Fig. 4. Effect of TOS on (a) methanol conversion, (b) selectivity to ethylene, (c) total hydrocarbon production (HC) and (d) selectivity to propylene, for the MTO reaction over pure AlPO-18 (■), 2% CoAlPO-18 (▲) and 2% MnAlPO-18 (◆) at 350 °C.

is no significant improvement in the catalytic performance. Both systems show no sign of any significant decline in either selectivity or activity after 2 h on stream or after regeneration, which suggests that there is no leaching of the metal centres. From this study it is clear that 2 at.% of transition metal ion is sufficient to effect 100% conversion of methanol to hydrocarbons and in addition it appears that MnAlPO-18 is marginally better than CoAlPO-18 for this catalytic reaction.

Acknowledgements

The authors thank EPSRC for financial support and Daresbury Laboratory for the use of various facilities.

GS thanks the Leverhulme trust for a senior research fellowship.

References

[1] M. Stocker, Microporous Mesoporous Mater. 29 (1999) 3.
[2] J.S. Chen, J.M. Thomas, J. Chem. Soc., Chem. Commun. (1994) 603.
[3] T. Inui, H. Matsuda, H. Okaniwa, A. Miyamoto, Appl. Catal. 58 (1990) 155.
[4] T. Inui, S. Phatanasri, H. Matsuda, J. Chem. Soc., Chem. Commun. (1990) 205.
[5] J.M. Thomas, Y. Xu, C.R.A. Catlow, J.W. Couves, Chem. Mater. 3 (1991) 667.
[6] J.M. Thomas, R. Raja, G. Sankar, R.G. Bell, Accounts Chem. Res. 34 (2001) 191.
[7] R. Wendelbo, D. Akporiaye, A. Andersen, I.M. Dahl, H.B. Mostad, Appl. Catal. A 142 (1996) L197.
[8] S. Wilson, P. Barger, Microporous Mesoporous Mater. 29 (1999) 117.
[9] M. Inoue, P. Dhupatemiya, S. Phatanasri, T. Inui, Microporous Mesoporous Mater. 28 (1999) 19.
[10] M. Kang, J. Mol. Catal. A 160 (2000) 437.
[11] J.S. Chen, P.A. Wright, J.M. Thomas, S. Natarajan, L. Marchese, S.M. Bradley, G. Sankar, C.R.A. Catlow, P.L. Gaiboyes, R.P. Townsend, C.M. Lok, J. Phys. Chem. 98 (1994) 10216.
[12] J.S. Chen, J.M. Thomas, P.A. Wright, R.P. Townsend, Catal. Lett. 28 (1994) 241.
[13] P.A. Barrett, G. Sankar, C.R.A. Catlow, J.M. Thomas, J. Phys. Chem. 100 (1996) 8977.
[14] F. Cora, G. Sankar, C.R.A. Catlow, J.M. Thomas, Chem. Commun. (2002) 734.
[15] A. Tuel, I. Arcon, N.N. Tusar, A. Meden, V. Kaucic, Microporous Mater. 7 (1996) 271.
[16] J.M. Thomas, G.N. Greaves, G. Sankar, P.A. Wright, J.S. Chen, A.J. Dent, L. Marchese, Angew. Chem. Int. Ed. Engl. 33 (1994) 1871.
[17] G. Sankar, J.M. Thomas, C.R.A. Catlow, Top. Catal. 10 (2000) 255.
[18] J.S. Chen, J.M. Thomas, G. Sankar, J. Chem. Soc., Faraday Trans. 90 (1994) 3455.
[19] L. Marchese, J.S. Chen, J.M. Thomas, S. Coluccia, A. Zecchina, J. Phys. Chem. 98 (1994) 13350.