Catalysis Today 145 (2009) 163–168

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

# Oxygenated fuel additives: The formation of methyl vinyl ether and 1,1-dimethoxyethane by the catalysed reaction of acetylene with methanol

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ARTICLE INFO

*Article history:*
Available online 13 June 2008

*Keywords:*
Methyl vinyl ether
Methanol
Acetylene
1,1-Dimethoxyethane
$ZnO/SiO_2$
NaOH/C
KOH/C

ABSTRACT

Optimisation of the performance of fuels has focused attention on the use of oxygen containing additives to improve octane or cetane numbers. A systematic study of the synthesis of one such additive (1,1-dimethoxyethane) from the catalysed reaction between acetylene and methanol has been carried out. An amorphous catalyst prepared from zinc oxide on silica has been found to be an efficient catalyst with excellent catalytic life. Methyl vinyl ether is the primary product, reacting further via an equilibrium reaction to form dimethoxyethane. The reaction kinetics of the first reaction has been measured at various temperatures as a basis for process optimisation.

## 1. Introduction

The use of oxygenated fuel additives to improve the octane rating of gasoline or the cetane rating of diesel is now well established [1–3]. Ethanol and methyl *tert*-butyl ether are well known additives for gasoline [1,2], while acetals have been recommended as additives to diesel [3]. More efficient combustion leads to improved emission performance in both cases.

Methanol, although easily prepared from synthesis gas [4], is not a good additive for gasoline, and there is significant interest in using the alcohol to produce higher molecular weight oxygenated additives. One possible reaction was described by Hinton and Nieuwland [5], in which alcohols were reacted with acetylene over a soluble boron trifluoride/mercuric oxide catalyst to produce acetals. The reaction was suggested to proceed via the formation of a vinyl ether

$$HC{\equiv}CH + ROH \rightarrow CH_2{=}CH{-}O{-}R \qquad (1)$$

$$CH_2{=}CH{-}O{-}R + ROH \rightarrow CH_3CH(OR)_2 \qquad (2)$$

A few years later Reppe [6], in one of his many patents, reported that the reaction halted at the ether stage if the catalyst was a strong base (e.g. sodium hydroxide or sodium alcoholate). Vinyl ethers are important industrial intermediates and the process for their production has been continuously improved, a recent innovation being the development of catalysts based on combinations of CsF and NaOH with dimethylsulfoxide as a solvent [7].

Reppe also patented a process for the continuous production of vinyl ethers by passage of gaseous mixtures of acetylene and low boiling alcohols over solid base catalysts such as soda lime (NaOH/CaO) [8]. There have been few subsequent studies of this reaction. Ghosh et al. [9], in a study of the reaction between acetylene and methanol to make methyl vinyl ether (MVE), came to the conclusion that KOH/C was the most active catalyst but that deactivation was a problem. Subsequent work showed that KOH/MgO was more stable but that catalyst life was still confined to day or so [10,11].

All the above authors mention only vinyl ethers as the products over alkali-based catalysts. However, a recent study of Anderson et al. [12] reports 1,1-dimethoxyethane (DMOE), as the sole oxygenated product from the reaction between acetylene and methanol over soda lime at temperatures of 100 and 150 °C. DMOE was stated to be usable as a cetane enhancer but its boiling point (101 °C) may be too low for that purpose. By analogy with 1,1-diethoxyethane, the flash point of DMOE is also expected to be too low for such applications.

In a recent development, workers at BASF have described a very stable $ZnO/SiO_2$ catalyst for the reaction of methanol with a mixture of methylacetylene and allene to produce the vinyl ether, 2-methoxypropene, and the corresponding acetal, 2,2-dimethox-

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doi:10.1016/j.cattod.2008.04.015

ypropane [13,14]. The catalyst was prepared from zinc acetate or nitrate on silica, but was found to undergo activation when first brought on line as a result of a methanol-facilitated reaction between zinc oxide and silica. The resulting solid was very difficult to characterise but independent synthesis of various zinc-silica compounds showed that hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$) was the only material that could be synthesised that was catalytically active [13].

The aim of the present work was to compare the reaction of acetylene with a range of alcohols over both alkali catalysts and the zinc silicate material and to study the reaction pathway over the best catalyst. The kinetics of the production of methyl vinyl ether (MVE) and dimethoxyethane (DMOE) from the reaction of methanol with acetylene over the best promoter have also been explored.

## 2. Experimental

Catalyst testing was carried out using a continuous flow system with 2.5 or 5.0 g samples of catalysts held between quartz wool plugs in a stainless steel reactor of internal diameter 10 mm. The gaseous components of the feed, acetylene and nitrogen as diluent, were fed via Brooks 5850 mass flow controllers, with methanol added subsequently in a preheating stage at 130 °C using an Isco high-pressure syringe pump. Products passed though lines held at 150 °C to sampling valve(s) located inside one, in some cases two, gas chromatograph(s) for on-line analysis. Liquid samples were collected subsequently in two Pyrex receivers arranged in series, one in an ice bath (~0 °C), the second in dry ice (−78 °C). The acetylene used contained ~0.25% acetone as fed from a cylinder (BOC, Australia, instrument grade). The acetone could be largely removed by passage through a dry ice trap. However, comparison experiments with and without the trap cooled gave identical extents of reaction and the trap was dispensed with in most experiments.

On-line analyses were carried out using a Shimadzu GC8A chromatograph fitted with a Porapak N column (2 m long, 2 mm i.d.). Experiments with DMOE as the reactant (fed from the Isco pump in place of methanol) were carried out with duplicate on-line analyses made using a second Shimadzu GC8A chromatograph with a FID detector and capillary column (Restek Rtx®-1, 60 m long, 0.53 mm i.d.) arranged in series. Liquid products were identified by injection into a GC-MS (Shimadzu Model QP-5050) equipped with another Rtx®-1 capillary column, also 60 m long but of 0.25 mm diameter.

The NaOH/C and KOH/C catalysts were prepared as described by Ghosh et al. [9]. This involved the repeated impregnation of an activated carbon (Calgon Type F-400, BET area of ~400 $m^2/g$), pre-dried in vacuum at 150–200 °C, with small volumes of saturated solutions of the hydroxides until the total weight of hydroxide deposited reached 30% of that of the starting carbon. Vacuum-drying was repeated after each deposition.

The $ZnO/SiO_2$ catalyst, 20 wt% loading, was prepared as described in claim 1 of the patent by Teles et al. [14]. This comprised two successive impregnations of silica gel (Davison grade 62, 285 $m^2/g$, 60–200 meshes) with a solution of zinc nitrate followed by calcination in air at 330 °C. The surface area of the catalyst, after 48 h activation [13] and some use, was found to be 155 $m^2/g$.

## 3. Results and discussion

### 3.1. Comparison of alkali and zinc oxide-based catalysts

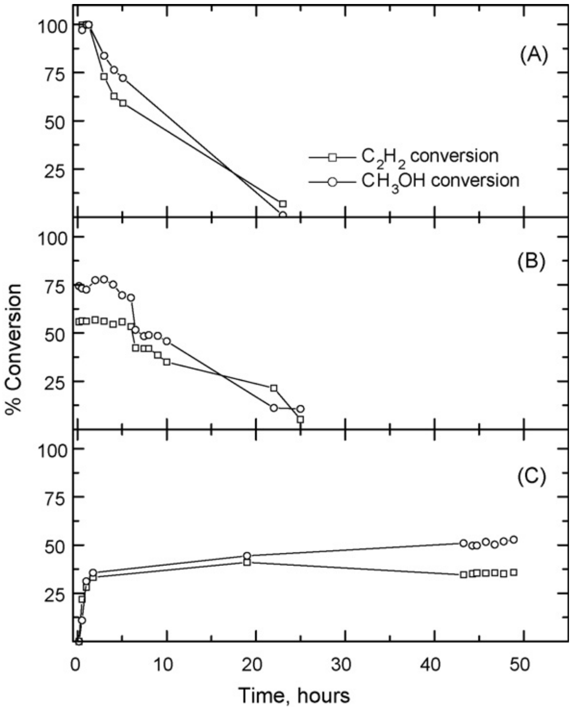


**Fig. 1.** Conversion versus time on stream for the reaction between acetylene and methanol, each with partial pressure of 0.23 atm, in $N_2$ over 5 g of catalyst when using a total feed rate of ~35 mL/min and at a temperature of 220 °C. (A) 30 wt% KOH/C, (B) 30 wt% NaOH/C and (C) 20 wt% $ZnO/SiO_2$.

Fig. 1 shows the behaviour of the three catalysts in terms of conversion (calculated from loss of reactant) versus time. The KOH/C catalyst showed complete conversion initially but the activity started to decline immediately with less than 10% conversion after 24 h on stream. The NaOH/C showed reasonably constant activity for ~6 h (~75% conversion) but activity then fell, reaching ~10% conversion after overnight operation. Tests with feeds containing $H_2O$ (2.3%) and/or $CO_2$ (2%) showed faster deactivation of both catalysts indicating that the formation of hydroxides and carbonates are probable contributors to activity loss. The deposition of heavier hydrocarbons on the surface ([9] and Table 1) also contributed to deactivation.

The $ZnO/SiO_2$ catalyst behaved quite differently. Using the reaction conditions suggested by Breuer et al. [13] (2.5–5 g

**Table 1**
Reaction products in terms of normalised % of total GC-MS peak area[a]

| | KOH/C | NaOH/C[b] | $ZnO/SiO_2$ |
|---|---|---|---|
| Collection period (h) | 0.5–5.5 | 0.5–5.5 | 5–21 |
| Volume collected (mL) | 6 | 8.3 | 25 |
| % Products in volume | 81 | 70 | 50 |
| Products (% of total) | | | |
| Methyl vinyl ether | 76 | 89 | 68 |
| 1,1-Dimethoxyethane | 0.6 | 2.4 | 30 |
| Dimethyl ether | 3.6 | – | 1.0 |
| Ethanol | 0.5 | 0.9 | 0.8 |
| Isopropanol | 0.3 | 0.4 | |
| Isobutanol | 0.3 | | |
| $C_4$ unsaturates | 2.8 | 0.1 | |
| $C_5$ oxygenates | 3.8 | | |
| $C_5$ oxygenates and/or $C_6$ unsaturates | 6.1 | | |
| $C_6$ unsaturates | 1.7 | | |
| $C_7$ oxygenates | 2.8 | | |
| $C_8$ unsaturates | 1.0 | | |

[a] Reaction conditions: 215–220 °C, $CH_3OH:C_2H_2$ mole ratio = 1:1, total flow rate 30–35 mL/min, catalyst weight = 2.5 g.

[b] Several small unidentified products were observed over NaOH/C.

catalyst; 300–700 $h^{-1}$ GHSV), the as-prepared catalyst required activation for ~48 h in the feed mixture before reaching steady state (ca 50% conversion). Once activated the $ZnO/SiO_2$ catalyst was remarkably stable. In long-term tests here, the activity was constant for many months despite repeated shutdown and start-up procedures, occasional use above 270 °C and feed ratios that varied by a factor of 20.

The importance of catalyst activation was confirmed by the lack of activity of zinc oxide, alone or supported on silica. However, characterisation of the active catalyst proved as difficult as reported by Breuer et al. [13].

The products detected by GC-MS analysis of liquids collected during the runs are summarised in Table 1. As reported by Ghosh et al. [9] reaction over KOH/C produced mainly methyl vinyl ether (MVE) with dimethyl ether (DME), originating from methanol dehydration, as a minor product. The yield of 1,1-dimethoxyethane (DMOE), the acetal expected for the further reaction of MVE with methanol, was very small (less than 1% of that of MVE). Correspondingly, passage of DMOE over KOH/C gave negligible amounts of MVE and methanol. MVE was also the dominant product for the methanol plus acetylene reaction over NaOH/C. The yield of DMOE was somewhat higher than for KOH/C but that of DME was below the detection limit (~1%).

Both alkali catalysts and especially KOH/C gave rise to small amounts of a multitude of higher products. These included $C_4$–$C_8$ unsaturates resulting from acetylene oligomerisation (e.g. 1,2-butadiene, divinylacetylene, 1,5-hexadiyne, 3-methyl-2-pentene, 1,7-octadiyne and dimethylfulvene) and $C_5$ and $C_7$ oxygenates attributable to their subsequent reaction with methanol (e.g. 2-methyl-2-vinyloxirane, cyclohexadien-1-yl methyl ether). It is likely that deposition of even higher molecular weight material on the catalyst was a factor in the observed rapid deactivation. Separate experiments showed that hydrocarbons became the major products of the reaction at temperatures above 250 °C.

$ZnO/SiO_2$ catalysts produced MVE and DMOE, together with some DME (Table 2). The utilisation rates are low in absolute terms but in line with the data of Breuer et al. [13] for the corresponding reaction of allene. Increasing the temperature increased rate but decreased selectivity. It will be shown that the conversion of MVE to DMOE is an equilibrium reaction and, as a result, lower conversions of methanol to MVE (Table 1) would result in higher concentrations being available to react with MVE. However, comparison of the amounts of DMOE produced over KOH/C and $ZnO/SiO_2$ indicates that the forward reaction from MVE is catalysed by the zinc catalyst and not by the hydroxides.

Given the superior stability of the zinc-based catalyst, further attention was focused on reactions over this system. Table 2 shows the effect of temperature on product distribution at various $C_2H_2$:$CH_3OH$ molar ratios with GHSV held constant at 120 $h^{-1}$, As may be seen, production of DMOE was favoured relative to MVE at low temperatures and low $C_2H_2$:$CH_3OH$ ratios (i.e. excess methanol). This suggested that DMOE was formed by the successive reactions

$$HC{\equiv}CH + CH_3OH \rightarrow CH_2{=}CH{-}O{-}CH_3 \tag{3}$$

$$CH_2{=}CH{-}O{-}CH_3 + CH_3OH \Leftrightarrow CH_3CH(OCH_3)_2 \tag{4}$$

with the possibility that the second reaction was in partial or full equilibrium. Production of the only other significant product, dimethyl ether (DME), increased with temperature and with methanol pressure, indicating that it was probably formed by dehydration:

$$2CH_3OH \rightarrow CH_3{-}O{-}CH_3 + H_2O \tag{5}$$

On the above basis, the conversions ($X$) of $C_2H_2$ and $CH_3OH$ can be calculated from partial pressures in the exit stream using

$$X_{C_2H_2} = \frac{P_{MVE} + P_{DMOE}}{P_{C2H2} + P_{MVE} + P_{DMOE}} \tag{6}$$

$$X_{CH_3OH} = \frac{P_{MVE} + 2P_{DOME} + 2P_{DME}}{P_{CH_3OH} + P_{MVE} + 2P_{DOME} + 2P_{DME}} \tag{7}$$

Methanol conversions as high as 97% were possible with acetylene in large excess (Table 2). Acetylene conversions reached 64% with methanol in four-fold excess but such conditions were associated with the production of the highest amounts of DME. The peak productivity in terms of acetylene usage (~1.0 mol $g^{-1}$ $h^{-1}$ for a temperature of 250 °C) was largely independent of the feed ratio in the range used. In general terms, excess acetylene is to be preferred since it would minimise production of undesired DME as a byproduct and make for easier recycle in a continuous process.

Tests using 1:1 feeds at 270 °C led to high $C_2H_2$ and $CH_3OH$ conversions, but a further increase in temperature to 300 °C resulted in rapid deactivation with decreased selectivity to MVE and DMOE and the appearance of yellowish acetylene-derived oligomers in the liquid product.

## 3.2. Equilibrium between MVE and DMOE

The data in Table 2 show that formation of DMOE was favoured by a low temperatures and high partial pressures of methanol. This implied that the yield was controlled more by the thermodynamics of the reaction between MVE and $CH_3OH$ (Eq. (4)) rather than by

**Table 2**
Effect of feed ratio and temperature on product distribution and conversion using the $ZnO/SiO_2$ catalyst[a]

| P(in), atm | | T (°C) | Product distribution (mole%) | | | Conversions (%) | | Utilisation rate (mmol($C_2H_2$)$g^{-1}$ $h^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $C_2H_2$ | $CH_3OH$ | | MVE | DMOE | DME | $C_2H_2$ | $CH_3OH$ | |
| 0.14 | 0.64 | 200 | 52.1 | 47.0 | 0.9 | 30 | 12 | 0.58 |
| | | 220 | 58.2 | 40.3 | 1.5 | 37 | 15 | 0.79 |
| | | 250 | 70.5 | 26.0 | 3.5 | 51 | 17 | 0.87 |
| | | 270 | 68.0 | 25.7 | 6.3 | 64 | 17 | 0.99 |
| 0.28 | 0.20 | 200 | 62.4 | 37.3 | 0.3 | 19 | 37 | 0.62 |
| | | 220 | 64.3 | 35.1 | 0.6 | 28 | 53 | 0.90 |
| | | 250 | 75.5 | 23.4 | 1.1 | 36 | 58 | 1.04 |
| | | 270 | 76.8 | 21.6 | 1.5 | 39 | 65 | 1.06 |
| 0.62 | 0.16 | 200 | 69.2 | 30.5 | 0.3 | 11 | 64 | 0.75 |
| | | 220 | 75.7 | 23.9 | 0.4 | 15 | 73 | 0.98 |
| | | 250 | 86.3 | 13.2 | 0.6 | 17 | 97 | 1.01 |

[a] For 5 g of catalyst with a total input flow rate of ~30–35 mL/min.

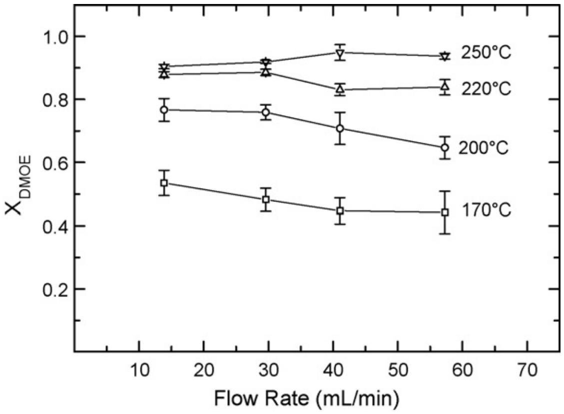


**Fig. 2.** DMOE conversion as a function of total flow rate when using 5 g of $ZnO/SiO_2$ and an input DMOE pressure of 0.07 atm.

kinetics. The characteristics of the forward step could not be studied directly since pure MVE was not available, but it was possible to study the reverse reaction

$$CH_3CH(OCH_3)_2 \rightarrow CH_3OH + CH{=}CH_2{-}O{-}CH_3 \tag{8}$$

The system was studied at temperatures from 170, 200, 220 and 250 °C by feeding ~7 kPa DMOE, carried in pure $N_2$, at different flow rates. Based on the on-line analyses, the conversion of DMOE could be calculated in several ways—from the partial pressure in the product stream, $P_{DMOE}$, relative to that in the feed, $P^{\circ}_{DMOE}$, i.e.

$$X_{DMOE} = \frac{P^{\circ}_{DMOE} - P_{DMOE}}{P^{\circ}_{DMOE}} \tag{9}$$

or from analyses of the product stream alone based on DMOE and the partial pressure of either of the products, MVE or $CH_3OH$ ($P_P$), i.e.

$$X_{DMOE} = \frac{P_P}{P_{DMOE} + P_P} \tag{10}$$

In principle Eq. (9) should be the more accurate at high conversions and Eq. (10) at low conversions.

The data obtained are shown in Fig. 2, where the error bars represent one standard deviation in the average conversion. In some cases, the analyses were carried out using both the on-line FID system as well as the TCD-equipped chromatograph, thus giving six values for each conversion. The apparent conversion of DMOE is clearly independent of flow rate (and hence contact time) at 250 °C indicating that reaction (8) has fully equilibrated. The data for the three lower temperatures shows a slight decrease in conversion with flow rate (i.e. shorter contact time) but the trend is barely outside the range of uncertainty.

The apparent thermodynamic equilibrium constant, $K_{app}$, is given by

$$K_{app} = \frac{P^{\circ}_{DMOE} X^2_{DMOE}}{P^{\circ}(1 - X_{DMOE})} \tag{11}$$

where $P^{\circ}$ is the standard pressure. Plots of ln $K_{app}$, calculated for all points in Fig. 2, versus $1/T$ (K) gave

$$\Delta H^{\circ} = 82 \pm 5\,\mathrm{kJ\,mol^{-1}}, \quad \Delta S^{\circ} = 156 \pm 10\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Direct comparison with the literature is not possible since, to our knowledge, neither $\Delta H^{\circ}_f$ nor $\Delta S^{\circ}$ for MVE, nor $\Delta S^{\circ}$ for DMOE, has been measured. If these quantities are estimated using Benson's group additivity method [15], and combined with known quantities, then the expected values for reaction (8) are

$$\Delta H^{\circ} = 80.2\,\mathrm{kJ\,mol^{-1}}, \quad \Delta S^{\circ} = 173\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

The agreement is quite good bearing in mind the uncertainties present.

Overall it seems likely that $ZnO/SiO_2$ has sufficient catalytic activity to achieve equilibrium between DMOE, MVE and $CH_3OH$ at temperatures from 170 to 250 °C and hence that the DMOE formed during the reaction between $C_2H_2$ and $CH_3OH$ arises by a fast reversible reaction between MVE + $CH_3OH$.

Gandi et al. [16] have improved the yield the reversible reaction producing DMOE from reacting methanol with acetaldehyde by the use of a suitable resin. The present reaction conditions are too extreme to test the same approach here.

### 3.3. Reaction kinetics

On the basis of the above findings, consumption of acetylene is a true measure of the kinetically determined rate of reaction between $C_2H_2$ and $CH_3OH$, but methanol consumption is not,

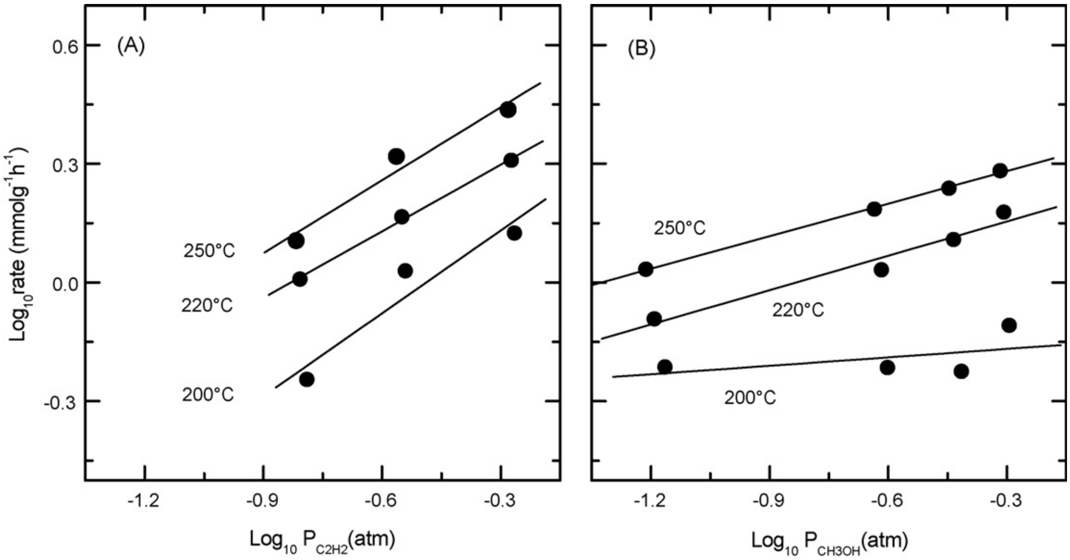


**Fig. 3.** Log–log plots of the rate of acetylene consumption versus partial pressure for the reaction of $C_2H_2$ with $CH_3OH$ over 2.5 g of $ZnO/SiO_2$ with an input flow rate of 30–35 mL/min. (A) Dependence on $C_2H_2$ pressure with input $CH_3OH$ pressure held at 0.14 atm; (B) dependence on $CH_3OH$ pressure with input $C_2H_2$ pressure held at 0.19 atm.

since it is also influenced by the thermodynamics of reaction (4). Thus, the dependence of rate on temperature and reactant pressure was determined for a range of partial pressures of $C_2H_2$ from 0.19 to 0.55 atm and $CH_3OH$ from 0.08 to 0.54 atm using 2.5 g samples to minimise production of DME. Over the range of conditions investigated (temperature from 200 to 250 °C), the average conversion calculated using Eq. (6) was 22% with only three values above 50%.

Fig. 3 shows log–log plots of rate, calculated from conversion using

$$\text{rate of } C_2H_2 \text{ loss } (\text{mmol h}^{-1}\text{ g}^{-1}) = \frac{X_{C_2H_2} N_{C_2H_2}(\text{in})}{W} \qquad (12)$$

where $N_{C_2H_2}$ is the flow of acetylene into the reactor in mmol/h, $X_{C_2H_2}$ the conversion and $W$ is the weight of $ZnO/SiO_2$, versus reactant pressure (the average of inlet and outlet values) at three temperatures. Clearly the order in acetylene (0.7, 0.56 and 0.61 from the slopes at 200, 220 and 250 °C) is higher than that in methanol (0.07, 0.29 and 0.24, respectively). The dependence of rate on methanol partial pressure at 200 °C was subject to most error due to low conversions, but the results reported were as reproducible as could be measured.

Non-linear regression of the entire measured data set against the power rate equation

$$\text{rate } (C_2H_2 \text{ loss}) = k P^{a}_{C_2H_2} P^{b}_{CH_3OH} \exp\left(-\frac{E_a}{RT}\right) \qquad (13)$$

using the Excel program Solver with statistics (one standard deviation) assessed by the program Solvstat [17] gave

$$a = 0.71 \pm 0.07;\ b = 0.24 \pm 0.05;\ E_a = 36 \pm 3\ \text{kJ mol}^{-1} \text{ and } k = 2.9 \times 10^4\ \text{mmol g}^{-1}\text{ h}^{-1}\text{ atm}^{-0.95}$$

The orders differ slightly from those given above because they correspond to the best fit to actual rates and pressures for the entire data set, rather than to logarithmic fits carried out separately for each temperature. Rates calculated according to Eq. (13), using the parameters obtained by the non-linear fitting, matched actual rates with an average deviation of 12%.

### *3.4. Reaction pathways*

The above kinetic orders (between zero and unity for both reactants with the order in acetylene higher than that in methanol) carry little mechanistic implications. They simply suggest that the adsorption of methanol is stronger than that of acetylene which is consistent with the displacement experiments of Spitz et al. [18] using ZnO alone.

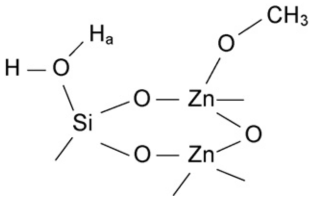
According to the molecular modeling of Breuer et al. [13], the reaction between methanol and allene over $ZnO/SiO_2$ proceeds through an initial dissociation of methanol on a cationic zinc site adjacent to a silanol group leading to the following surface arrangement.

Partial charges are not specified but the $H_a$ is stated as being protonic, in which case dissociation may be represented as

$$CH_3OH\,(\text{gas}) + (zs) \Leftrightarrow CH_3O^-(z) + H^+(s) \qquad (14)$$

where (z) and (s) are the zinc and silanol components of the dual-site (zs). There is also good experimental evidence that $ZnO/SiO_2$ combinations possess many more, and stronger, acid sites than present on either oxide alone but the method used (amine titration) does not distinguish between Bronsted and Lewis acidity [19].

Two schemes for the reaction of surface species with acetylene to form MVE can then be envisaged. The methoxide formed in Eq. (14) could add first, as occurs in strongly basic solutions



Scheme 1.

[20,21], with proton transfer occurring subsequently to form the acetal

$$CH_3O^-(z) + C_2H_2(x) \rightarrow CH_3OCH{=}CH^-(z) + x \qquad (15)$$

where $x$ is a surface site,

$$CH_3OCH{=}CH^-(z) + H^+(s) \rightarrow CH_3OCH{=}CH_2 + (zs) \qquad (16)$$

Alternatively, the proton could be added first as in conventional acid catalysis

$$H^+(s) + HC{\equiv}CH \rightarrow H_2C{=}CH^+(s) \qquad (17)$$

$$H_2C{=}CH^+(s) + CH_3O^-(z) \rightarrow H_2C{=}CHOCH_3 + (zs) \qquad (18)$$

The molecular modeling of Breuer et al. [13] for allene implies an intermediate course with the molecule first adsorbing with one double bond bridged across the $CH_3O$ and $H_a$ in Scheme 1 and then undergoing direct conversion to the vinyl ether in a concerted fashion.

Although the kinetic orders measured here cannot distinguish between the above possibilities, the existence of a rapid equilibrium between MVE, methanol and DMOE rules against the base-catalysed route (reactions (15) and (16)). This is because acetals are only minor products in that process [20], as is exemplified here by the data for KOH/C and NaOH/C in Table 1. By contrast, the addition of alcohols to vinyl ethers to form acetals is strongly catalysed by $H^+$ [22].

## 4. Conclusions

It is clear that amorphous $ZnO/SiO_2$ catalyst is very efficient at promoting the reaction between methanol and acetylene to give MVE and DMOE. MVE was found to be the primary product, DMOE being formed by a fast equilibrium reaction between methanol and MVE. As opposed to alternative catalysts for the reaction, minimal deactivation was observed over long periods of operation. The rate of the reaction producing MVE was found to depend on the partial pressures of acetylene and methanol, with a low activation energy. The catalysed reaction appears to offer a low energy selective route to vinyl ethers and acetals, to be used as chemical intermediates or octane improvers. Corresponding reactions with higher alcohols are now under study, with the object of producing improved cetane enhancing molecules.

## Acknowledgements

One of us (D.L.T.) is most grateful to the Australian Research Council for the award of a Federation Fellowship and to the CSIRO and the University of New South Wales for the provision of the associated research funding that supported this project.

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