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Carbonylation of Formaldehyde with Zeolite Catalysts

Sami A. I. Barri · David Chadwick

Abstract Carbonylation of formaldehyde with carbon monoxide over zeolite catalysts has been investigated. Compared with resins (Amberlyst-15 and Amberlyst-70), and phosphotungstic acid, the zeolite catalysts especially ZSM-5 showed very high selectivity to methyl glycolate. The selectivity of ZSM-5 was maintained to high temperature up to 200 °C.

Keywords Carbonylation · Zeolites · Glycolic acid · Formaldehyde

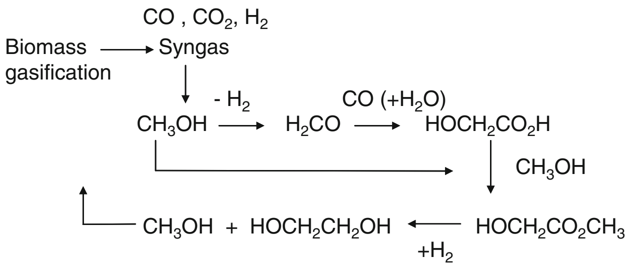
1 Introduction

Ethylene glycol is a major product of the chemical industry manufactured on a large scale. The current industrial process converts ethylene, which is obtained from hydrocarbon sources, to ethylene oxide which is hydrated to give ethylene glycol. Developing an alternative route to ethylene glycol is essential for a sustainable chemical industry. Synthesis gas (syngas, $CO + H_2$) is considered a building block for "green" chemicals because it can be produced from renewable sources such as biomass or organic agriculture waste in addition to the more traditional natural gas or coal [1, 2]. Furthermore, nitrogen and/or sulphur pollutants can be removed from syngas more easily than from fossil based hydrocarbon sources. Syngas can be converted to fuels and chemicals and in particular to methanol and its dehydrogenated derivative formaldehyde, which are important bulk chemicals. The syngas-based routes to ethylene glycol generally proceed via formaldehyde [2]. Carbonylation of formaldehyde with carbon monoxide produces glycolic acid which is esterified and hydrogenated to give ethylene glycol as shown in Scheme 1. Syngas can be used directly as the carbonylation reaction is not affected by the presence of hydrogen [3]. However, achieving high reaction rates and selectivity remains a challenge for the carbonylation step which is catalysed by solid or liquid acids [3–9].

Hydrogen fluoride, sulphuric acid, trifilic acid, heteropolyacid, and ion exchange acidic resins have been shown to be active and selective for the production of glycolic acid or methyl glycolate (after esterification with methanol). Utilisation of sulphuric acid as a catalyst was practiced commercially [8, 9], but the high temperature and pressure required resulted in an unacceptable corrosion rate in conventional commercial equipment. Furthermore the use of strong liquid acid was difficult to justify environmentally.

Lee et al. [5, 6] studied carbonylation of formaldehyde over various ion exchange resins up to 150 °C using several solvents. Addition of water gave a variable effect depending on the solvent. There was no clear advantage to adding water to the reaction. Drent et al. [7] claimed a process and catalysts with pK below −1 in the presence of sulfolane as a solvent for the carbonylation of formaldehyde (or a derivative) with CO. Conversions of 100% with high selectivity (75–90%) to methyl glycolate (after esterification with methanol) were reported. Trifilic acid and resins were demonstrated at a temperature range of 70–120 °C and 30–60 bar pressure of CO. More recently methyl formate was used as a source of CO and methoxy methanol as a source of formaldehyde producing methylglycolate directly [8–13] with heteropolyacids and liquid acids reported to be effective catalysts. The use of heteropolyacid and resins imposes temperature limitations on the application of this

S. A. I. Barri · D. Chadwick (✉)
Department of Chemical Engineering, Imperial College London,
South Kensington Campus, London SW7 2AZ, UK
e-mail: d.chadwick@imperial.ac.uk



Scheme 1 Ethylene glycol from syngas via carbonylation of formaldehyde

technology because of their relatively low thermal stability. Separation and/or thermal regeneration of the catalyst is complicated, if not impractical. Scope for increasing reaction rate by raising temperature is limited. In contrast, inorganic solid acid catalysts such as zeolites are known for their thermal stability and offer the potential for higher reaction temperatures with high acidity. Zeolites have been demonstrated as catalysts for carbonylation of dimethyl ether [14–16] and dimethoxymethane [17]. Furthermore, carbonylation of 1,3,5 trioxane (a precursor for formaldehyde) to 1,3-trioxlan-4-one over zeolites has been reported [18–20]. In this paper, we report on the catalytic performance of zeolites ZSM-5, Y, and mordenite for the carbonylation of formaldehyde to produce methyl glycolate (after esterification with methanol), and in particular demonstrate their high selectivity and intrinsic activity. Comparison is made with two resins (Amberlyst 15 and 70) and phosphotungestic acid. Amberlyst 70, which has not been studied previously in this context, has higher thermal stability than Amberlyst 15. The effect of temperature on catalytic performance is explored up to 220 °C, beyond the level reported previously (150 °C).

2 Experimental

Phosphotungstic acid, Sulfolane, and methanol were supplied by Sigma-Aldrich. Paraformaldehyde was supplied by Riedel-de-Haën. Amberlyst-15 and Amberlyst-70 were supplied by Rohm and Haas, France (code 69286 and 44355 respectively). Zeolites HY, ZSM-5 and mordenite were obtained from Zeolyst International (CBV 760, CBV 5524G, and CBV 21A, respectively).

Both Amberlyst-15 and Amberlyst-70 were ion exchanged with 0.1 M nitric acid solution several times at room temperature. The resins were then dried at 100 °C overnight before use. Phosphotungstic acid was used as supplied. The zeolites were calcined at 500 °C (slow heating rate 1 °C/min) immediately prior to use.

Catalytic tests were carried out in a stirred autoclave reactor at constant CO pressure of 80 bar and 100–220 °C. Sulfolane was used as solvent (100 g) and paraformaldehyde (7.5 g) was the source of formaldehyde. After adding the appropriate catalyst, the mixture was stirred at 950 rpm with a gas entrainment stirrer to enhance mixing and gas–liquid mass transfer. The resins were dried at 90 °C, whereas the phosphotungstic acid was used as supplied. The zeolites were calcined at 500 °C. At the end of the run, the products were refluxed with methanol (50 g) and 70% nitric acid (2 g) for 4 h to form methyl glycolate. The reaction product mixture was analysed by GC-FID using a HP-FFAP 30 m × 0.32 mm capillary column with a temperature programme from 60 to 220 °C to elute all the products and solvent. A blank run without catalyst showed no reaction.

3 Results and Discussion

The present results are concerned with the carbonylation step and esterification shown in Scheme 1. ZSM-5 and Y have been studied because of their high acidity and different pore structures which present not only varying diffusional paths to the reactants and products, but also influence the acidity of the framework. ZSM-5, with its medium pore size channels, has one of the strongest acidity offered by zeolites in general because of its acid site isolation, as the Si/Al ratio is normally high. Zeolite Y, on the other hand, has large pore size channels with supercages at the centre of the channel intersections and is normally synthesised at low Si/Al ratio, and then undergoes a dealumination process to increase its acid site strength. The acid site concentrations of the zeolites used were calculated based on their Si/Al ratios assuming all the aluminium were in the framework. Phosphotungstic acid and the resins were titrated with standard solution of sodium hydroxide to determine the concentration of acid sites. The values in mmol H^+/g of dry catalyst are given in Table 1.

Methyl glycolate (MG) in high yields was produced over all the catalysts. Table 1 gives maximum yields of MG after 2 h reaction time and the corresponding temperatures. SiO_2/Al_2O_3 ratios are given in parentheses. Dimethyl diglycolate (DMDG) and methoxy methyl acetate (MMAc) were produced as side products, Table 1. Minor amounts of methyl polyglycolate were also formed. In addition there were traces of unidentified products. Unreacted formaldehyde/paraformaldehyde was substantially converted by self reaction in the acid catalysed esterification step to methyl formate and small amounts of acetaldehyde and methyl acetate. Based on the major products, the carbon mass balance of all catalytic runs reported here was greater than 90%; the reproducibility of the methyl glycolate yield was within 5%.

The heteropolyacid and the resin catalysts produced a significant amount of DMDG, whereas the zeolite catalysts

Table 1 Catalysts and performance for carbonylation

Catalyst	Acid site concentration (mmole/g)	Wt catalyst per wt CH_2O	Temp. (°C)	Yield (%)			Yield of MG mole/mole of acid site
				MG	DMDG	MMAc	
ZSM-5(55)	0.64	0.20	200	47.7	<0.1	<0.1	120
ZSM-5(280)	0.012	0.20	180	18.4	0.4	<0.1	2500
Y (30)	0.54	0.20	180	27.8	<0.1	1.9	86
Y (5)	2.8	0.20	180	1.8	<0.1	1.2	1.1
Mordenite	2.2	0.20	180	5.3	<0.1	3.9	4.0
HPW	15	0.23	140	65.1	33.7	<0.1	6.3
Amberlyst-15	5.1	0.40	180	68.6	19.8	<0.1	11
Amberlyst-70	3.0	0.67	180	53.5	31.4	<0.1	8.9

especially ZSM-5 were highly selective for the production of MG. The high selectivity of the zeolites was due to their shape selectivity suppressing the formation of the bulky transition state of the dimerisation reaction that leads to the production of DMDG. Mordenite, on the other hand, showed very low conversion suggesting that diffusion of the products and reactants within the channels influence the overall activity of the catalyst. Unidirectional channels appear to be not suited for this reaction. The presence of the two reactants and most probably the solvent are essential for the formation of the glycolide intermediate, a situation where freely diffusing entities would be required. Configurational selectivity was achieved in zeolites Y and ZSM-5 to suppress the by-products as noted above. Further restriction in terms of diffusion as experienced in mordenite would appear to result in constraining the desired reaction of carbonylation. A low activity was also reported by Sano and co-workers [19] for the carbonylation of 1,3-dioxolan-4-one over mordenite.

The product yields after 2 h as a function of temperature are shown in Figs. 1 and 2. The activity generally increased with temperature up to a maximum which depended on the catalyst. Thermodynamic calculations show no equilibrium limitations on the production of methyl glycolate below 500 K. Although the reaction is moderately exothermic, the heat of reaction should have had no appreciable effect on the actual reaction temperature considering the amount of solvent used and the high stirring speed employed. The observed reductions in the yields of methyl glycolate at 180 °C for the Amberlyst resins and at 140 °C for HPW, therefore, was probably due to the relative low thermal stability of these materials and/or the rise in the yield of higher molecular weight products such as polyglycolate. Although coke formation was not sufficient to cause significant loss in the carbon balance, its effect on the accessibility of the acid sites might be appreciable. The thermal stabilities of the Amberlyst resins were checked and both were found capable of being stable for at least 2 h in all the reaction conditions used. The production of methyl glycolate over zeolite Y increased with temperature and dropped at 220 °C, probably due to coke formation as the zeolite has high thermal stability. Generally, zeolite Y produced lower levels of DMDG than the resins or HPW at the same reaction temperature. ZSM-5 was more active and selective than zeolite Y as shown in Fig. 2. The level of DMDG generally increased with increasing temperature per given type of catalyst as shown in Figs. 1 and 2.

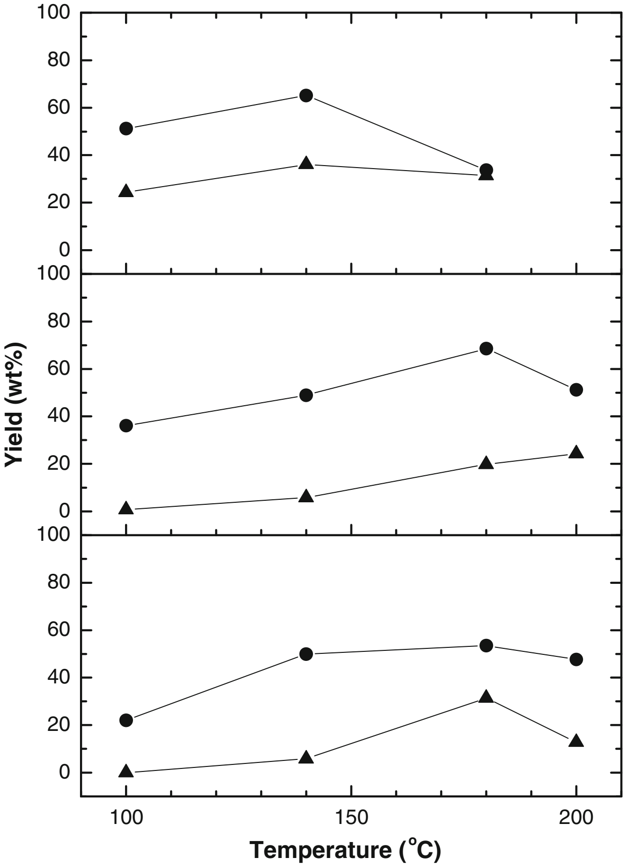


Fig. 1 Yields of MG (*closed circle*) and DMDG (*closed triangle*) with temperature. over HPW (top), Amberlyst-15 (middle), and Amberlyst-70 (bottom). Catalyst/CH_2O = 0.23, 0.4 and 0.67 respectively

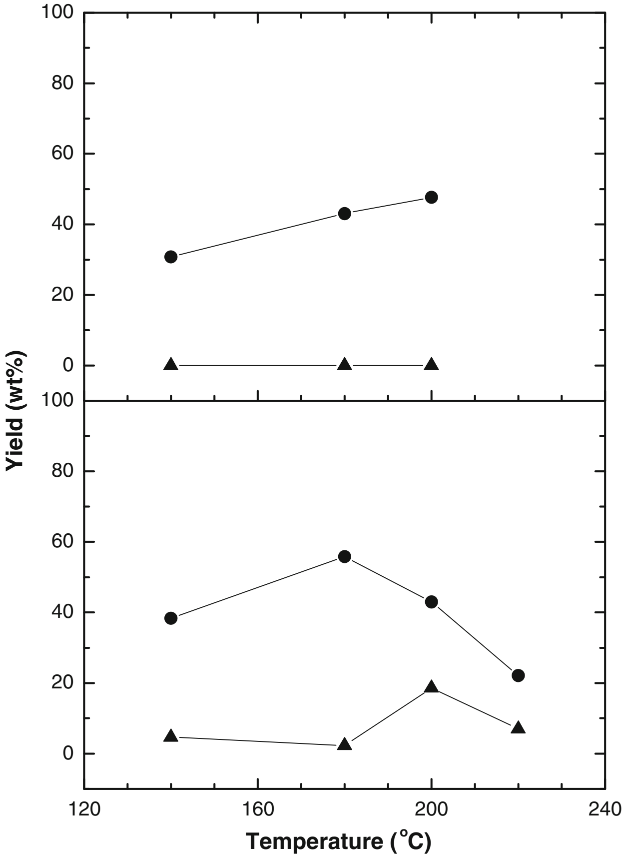
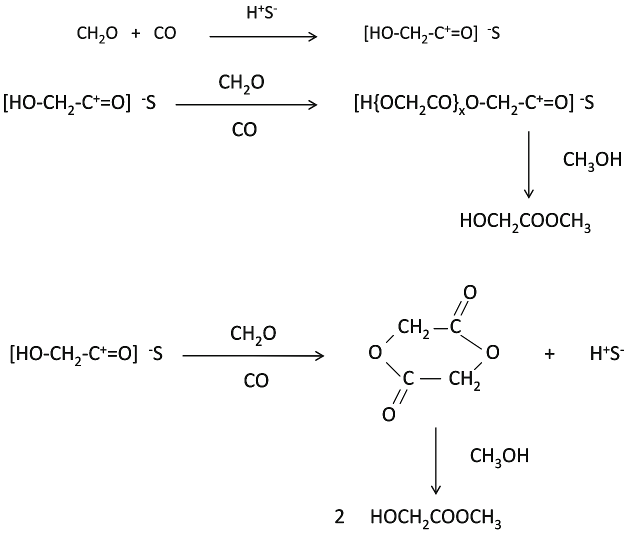


Fig. 2 Yields of MG (*closed circle*) and DMDG (*closed triangle*) with temperature. over ZSM-5(55) (top), and Y(30) (bottom). Catalyst/CH_2O = 0.2 and 0.4 respectively

Lee et al. [5, 6] have not reported DMDG but found high levels of unidentified products. Drent et al. [7] reported DMDG as the main by-product, in agreement with the present work.

Stoichiometrically, formation of glycolic acid requires one mole of water per mole. However, in this study no water was added to the reaction (and both solvent and zeolite were dry) and the most likely mode of stabilisation of the glycolide intermediate is via the formation of a glycolic acid cyclic dimer and/or chain oligomers [4]. Possible reaction pathways for the carbonylation reaction to produce methyl glycolate are shown in Scheme 2. An alternative could be the formation of 1,3-dioxolan-4-one in the initial step, as proposed by Sano and co-workers [18–20] using a different solvent and conditions from the present work, which is then converted to methyl glycolate during the acid catalysed esterification. Addition of water was studied by Lee et al. [5, 6] with mixed effect. It has been argued that an important effect of the solvent is in stabilising the hydroxyl carbonium ion and addition of water may interfere with this. Sano and co-workers [18–20] noted that the presence of water was detrimental for carbonylation of 1,3,5 trioxane.



Scheme 2 Possible reaction pathways [4] for methyl glycolate production by carbonylation of formaldehyde

Sun et al. [8, 9] reported that addition of excessive amount of water ($H_2O/HCHO > 2.0$) interfered with the stabilisation of the carbonium ion by the sulfolane solvent. We would argue also that formation of significant concentration of glycolic acid contributes to its further reaction and the loss in its selectivity. Formation of the cyclic dimer and oligomers stabilises the species, Scheme 2, and contribute to higher yields of MG as a product from the esterification step.

ZSM-5(55) and Y(30) were almost an order of magnitude more active per acid site than the HPW and Amberlyst resin catalysts, Table 1. This is most probably due to the higher acid strength of the zeolite frameworks and the concentration effect experienced in their micropores. The very low activity of the Y(5) is almost certainly due the low strength of its acid sites. Y zeolite with SiO_2/Al_2O_3 ratio of 5 have high population of $(SiOl)_2Si(OAl)_2$ and even $(SiO)Si(OAl)_3$ sites, which have lower acid strength than isolated aluminium sites, $(SiOl)_3Si(OAl)$. Similar considerations apply to ZSM-5 where ZSM-5(280) has much greater intrinsic activity that ZSM-5(55). High acid strength, however, was not translated into higher overall conversion because of the lower number of acid site per weight of the catalyst in the case of the zeolites.

The Amberlyst resins showed higher acid site strength than the HPW as reflected in their conversion per H^+. Lee et al. reported similar formaldehyde conversion per moles of H^+/h for the Amberlyst-15 as this study, but at lower temperature than in our work (135 vs. 180 °C). Their CO pressure, on the other hand, was higher (235 vs. 80 bars). As they reported first-order dependence of catalytic activity on CO pressure, the level of the activity reported here for the Amberlyst-15 resin catalyst is in general agreement the published result.

4 Conclusions

All the catalysts tested were active for the carbonylation of formaldehyde with carbon monoxide producing MG after esterification with methanol. Phosphotungstic acid was most active at 140 °C but produced the largest amount of DMDG side product. The resins, Amberlyst-15 and Amberlyst-70, were most active at 180 °C and produced moderate amounts of DMDG. ZSM-5 and Y zeolites gave high yields of MG at 180–200 °C comparable to the best yields produced by the other catalysts, and were the most selective producing only small amounts of DMDG. In particular, ZSM-5 was highly selective producing negligible amounts of DMDG. ZSM-5 and Y zeolites are thermally stable at severe conditions and expected to maintain their acidity during reaction and in the temperature range. The application of zeolites as catalyst provides several clear advantages: their high selectivity, high stability, regenerability, and ease of separation from the products.

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