Methanol carbonylation to methyl formate catalyzed by strongly basic resins

Marco Di Girolamo, Massimo Lami, Mario Marchionna [1], Domenico Sanfilippo
SNAMPROGETTI S.p.A., Research Division, Via F. Maritano 26, I-20097 San Donato Milanese, Italy

Marco Andreoni, Anna Maria Raspolli Galletti and Glauco Sbrana
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

Received 12 June 1995; accepted 18 December 1995

The liquid phase methanol carbonylation to methyl formate has been investigated both with homogeneous sodium methoxide, the industrial catalyst for this process, and with heterogeneous strongly basic resins. The strongly basic resins Amberlyst A26 and Amberlite IRA 400 displayed a higher activity than sodium methoxide. The activation procedure and the dependence of the reaction rate on CO pressure have also been investigated.

Keywords: methyl formate; methanol carbonylation; strongly basic anion exchangers

1. Introduction

Recently, increasing interest has been devoted toward methyl formate as a new building block in C_1 chemistry [1,2], because this ester is a useful chemical and a versatile intermediate for the production of chemicals such as formamide, N,N-dimethylformamide and, above all, formic acid [3].

Methanol carbonylation to methyl formate is an exothermic ($\Delta H_r^0 = -29.1$ kJ/mol) equilibrium reaction, industrially carried out in the liquid phase at 80°C under a CO pressure of 4.5 MPa using sodium methoxide (2.5% weight) as the catalyst. About 95% carbon monoxide but only 30% methanol are converted under process conditions [3]. Nearly quantitative conversion of methanol to methyl formate can, nevertheless, be achieved by recycling the unreacted methanol.

Relatively few studies are known about the homogeneous methoxide-catalyzed carbonylation of methanol to methyl formate. Kinetic aspects have been well described only in some recent papers [4–6].

Methanol carbonylation occurs through a two-step mechanism [5]: the alcoholate ion reacts with CO to form $MeOCO^-$ which then interacts with the alcohol producing methyl formate and restoring the active catalyst:

$$MeO^- + CO \rightarrow (MeOCO)^- \qquad (1)$$

$$(MeOCO)^- + MeOH \rightarrow HCOOMe + MeO^- \qquad (2)$$

Carbon dioxide and water are undesirable feed impurities because the formation in side reactions of sodium formate and methyl carbonate, which are insoluble in the reaction medium, causes clogging and fouling as well as catalyst loss.

In order to improve the current technology, alternative catalysts, both homogeneous and heterogeneous, have been investigated. As regards the homogeneous systems, studies of both basic catalysts [7,8] and transition metal complexes [9–13] have been reported: the latter catalysts are more resistant to poisoning by H_2O and CO_2 but are expensive and need drastic conditions. Heterogeneous strongly basic resins have also been explored but the few results reported to date are contradictory [14,15], probably due to the scarce experience in the use of strongly basic resins as catalysts, above all when compared to acid ones [16].

Otherwise, the use of a heterogeneous catalyst seemed to us very interesting as it could avoid solubility and plugging drawbacks and above all ease the separation and reactivation of the deactivated catalyst from methanolic solutions of methyl formate. Therefore, the aim of the present study is to re-investigate with much more care the methanol carbonylation by screening basic resins with different characteristics (degree of cross-linking, polymer matrices, functional groups).

2. Experimental

Anhydrous methanol (freshly distilled over Mg) was always employed under strictly inert atmospheres; pure CO was purchased by S.I.A.D. (99.9%; $CO_2 = 150$ ppm). MeONa was freshly prepared from methanol and

---

[1] To whom correspondence should be addressed.

sodium; the base was always titrated at the end of the preparation and the content of methanol, solvated or associated to MeONa, was determined. Amberlite IRA 400, Amberlite IRA 910 and Amberlyst A26 were purchased by Rohm & Haas. Basic resins were activated (or reactivated) by placing the resin into a column and passing through at first four bed volumes of a 10% aqueous NaOH solution at a rate of two bed volumes per hour, then distilled water up to neutral pH and finally anhydrous methanol. Demineralized, CO_2 free water was always employed.

Catalytic experiments were carried out using a 300 ml stirred autoclave at a constant CO pressure (1–5 MPa). In a typical experiment, 50 ml of anhydrous methanol and the desired amount of catalyst were charged under nitrogen atmosphere in the stirred autoclave, equipped with an internal thermocouple for temperature control. Then the autoclave was pressurized with CO and the reaction was started by plunging the autoclave in a thermostated oil bath. The reaction products were periodically removed for GC analyses from the autoclave to capped bottles cooled at ca. −70°C. At the end of the run the autoclave was cooled in a water–ice bath.

Analyses of the products were performed with a Hewlett Packard gas chromatograph equipped with FID as the detector and a 50 m capillary column (Hewlett Packard, HP5 5% cross-linked methyl-phenyl-silicone). IR spectra were performed with a Perkin Elmer FTIR 1750 spectrometer. The infrared cell was interfaced to a gas mainfold to maintain the recovered resin under dry nitrogen.

3. Results and discussion

The first aim of this study was to compare the activity of sodium methoxide with that of strongly basic resins having different polymer matrices and functional groups. The characteristics of the tested resins are reported in table 1.

As a few preliminary carbonylation runs pointed out the relevance of the procedure of the resin activation, at the beginning of our investigation more attention was devoted to this aspect.

3.1. Activation of the resin

In the activation phase an exchange reaction occurs between the OH^- ions in solution and Cl^- ions on the resin. The reaction is influenced by many parameters:

- characteristics of the resin;
- type and amount of ions to exchange;
- kind of regenerating agent and presence of CO_2 in the regeneration cycle;
- regeneration flow rate;
- type of exchange reactor;
- temperature.

We observed that the exchange process is often incomplete and, for instance, the operating capacity of Amberlyst A26 is always lower than its declared total capacity (2–2.5 compared to 4.4 meq OH^-/g resin dry). To increase the efficiency of the exchange reaction, growing regenerant concentrations (2.8, 5.5 and 7.7 mol NaOH/ℓ) were employed, pointing out the non-linear dependence of the operating capacity on the amount of regenerant. A huge amount of regenerant would be required to remove all the Cl^- ions from the resin; triplicating the concentration of regenerant results in an, in fact, only 15% higher operating capacity value (2.35 vs. 2.02 meq OH^-).

Column exchange operations were preferable to slurry batch operations because using the same quantity of resin, regenerating agent and contact time, a higher operating capacity was achieved (2–3 times higher). A better operating capacity was also achieved with successive alkaline treatments on the same resin sample. Batch runs showed that the catalytic activity of the resins used (not only Amberlyst A26) remarkably rose after the first regeneration but remained nearly unchanged after successive treatments.

3.2. Catalytic runs

Batch experiments were carried out at different temperatures and at a constant CO pressure of 5 MPa to compare the catalytic activity of the homogeneous MeONa with those of strongly basic resins (twice activated). The results are reported in table 2.

MeONa. The homogeneous catalyst MeONa showed a very low catalytic activity at 45°C. It rapidly increased

Table 1
Characteristics of basic ion exchangers

Resin	Type	Functional group[a]	Moisture (%)	Declared exchange capacity (meq/g)	Maximum declared operating T[b] (°C)
Amberlyst A 26	macroporous	I	45	4.4	60
IRA 910	macroporous	II	52	3.8	40
IRA 400	gel	I	46	4.4	60

[a] Functional group I = Ⓟ$-CH_2N(CH_3)_3^+Cl^-$; functional group II = Ⓟ$-CH_2N(CH_3)_2(CH_2CH_2OH)^+Cl^-$.

[b] For the resin in the OH^- form.

Table 2
Methanol carbonylation with basic resins: effect of temperature [a]

T (°C)	Catalyst	Base (meq)	MF (mmol)		DME/base [b]	Conv. (%)	TOF [c] (h^{-1})
			3 h	5 h	5 h	5 h	
45	CH_3ONa	10.0	174	249	–	20	5
	IRA 910	5.4	125	191	–	15	7
	A26	5.4	467	913	–	70	34
57	CH_3ONa	10.0	379	678	0.01	55	13
	IRA 910	5.4	121	187	–	14	7
	A26	4.7	1103	1188	0.08	91	78 [d]
	IRA 400	5.0	1104	1184	0.07	91	73 [d]
67	CH_3ONa	10.0	731	953	0.10	78	19
	IRA 910	5.4	221	309	–	26	11
	A26	4.7	1031	1068	0.22	83	73 [d]
	IRA 400	5.0	1029	1070	0.19	83	69 [d]

[a] Reaction conditions: MeOH: ca. 50 ml; P_{CO}: 5 MPa; MF: methyl formate; DME: dimethyl ether.
[b] DME/base (molar ratio).
[c] TOF (turnover frequency) = MF mol/(eq.-cat h).
[d] TF after 3 h.

with temperature: the equilibrium value was attained for temperatures around 70°C; at higher temperature ($T > 80$°C) a partial deactivation of the catalyst was observed together with the formation of dimethyl ether (DME).

AMBERLYST A26. This catalyst was very active, also at temperatures as low as 45°C, and much more able than MeONa to approach the equilibrium values in a large range of temperatures (see fig. 1). Furthermore, this resin was surprisingly very active also at temperatures (67°C) higher than the maximum declared operating temperature (see table 1).

AMBERLITE IRA 400. The gel resin Amberlite IRA 400 was also tested to verify how this reaction is influenced by the matrix morphology. It showed activity and selectivity values quite analogous to those of the macroporous Amberlyst A26 for temperatures up to 67°C.

AMBERLITE IRA 910. Amberlite IRA 910, a macromolecular resin with different catalytically active groups, displayed very poor catalytic performances also at 67°C and only low methanol conversions (maximum 25%) were reached with resulting methyl formate concentrations far from equilibrium values. Otherwise, the

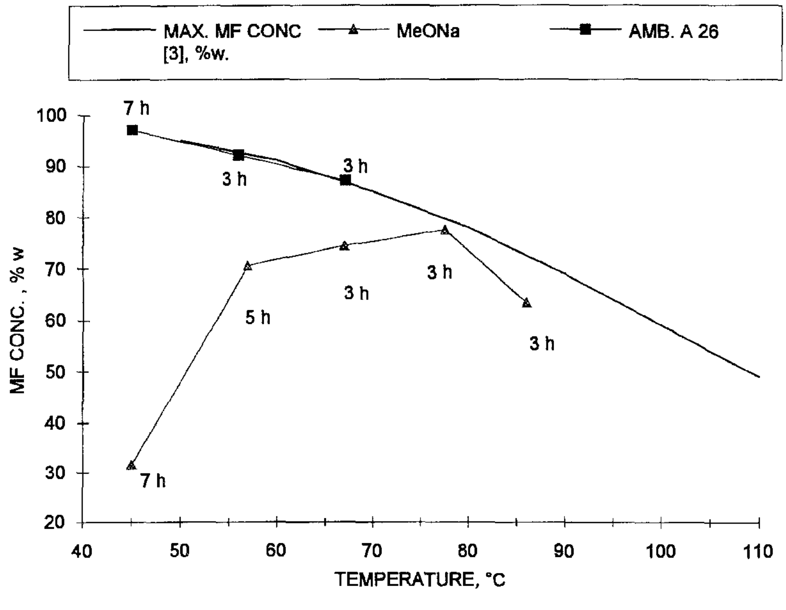

Fig. 1. Dependence of the approach to equilibrium methyl formate concentrations ($P = 5$ MPa) on temperature and on the catalytic performances (reaction conditions as in table 2; equilibrium data from ref. [3]).

claimed maximum operating temperature for this resin is lower (40°C) than for the other resins.

A more detailed investigation of the effect of the reaction conditions was then performed with the very active resin Amberlyst A26: this macroreticular resin was preferred to gel IRA 400, which offered analogous performances, because of its easier handling in practical use.

3.3. Dependence of the reaction rate on CO pressure

The effect of CO pressure on methanol carbonylation carried out with Amberlyst A26 is shown in table 3.

At 52°C the conversion sharply dropped (35% vs. 93%) when the CO pressure was lowered at 2 MPa; under these conditions the reaction rate increased only for higher temperatures (62°C) reaching ester concentrations next to the equilibrium value. With a CO pressure of 1 MPa, the system is far and far from the equilibrium values. For low CO pressures the reaction rate can be increased by increasing temperature; however, higher temperatures correspond to lower thermodynamic conversions and lower equilibrium concentrations of methyl formate in solution.

3.4. Catalyst deactivation

Methanol carbonylation, in the presence of MeONa or basic resins, was found to be a very selective reaction to methyl formate (98–100%) and the only byproduct formed at a low extent during these catalytic runs was DME (table 2).

DME is formed through the reaction between the methoxide (with either Na^+ or the resin as the counterion) and methyl formate,

$$\textcircled{P}-CH_2N(CH_3)_3^+MeO^- + HCOOMe \rightarrow \textcircled{P}-CH_2N(CH_3)_3^+HCOO^- + DME \quad (3)$$

where $\textcircled{P}-$ is the polymer matrix. The formate co-product is catalytically inactive. The contribution of this reaction is more relevant at higher temperatures and higher HCOOMe concentrations (see the different DME/base ratio in table 2).

A preliminary experimentation of continuous flow runs (which will be described in detail in a future work) showed that the strongly basic resins were thermally stable also at higher temperature (70°C) although a slow deactivation with time was observed.

Table 3
Methanol carbonylation with Amberlyst A26: effect of CO pressure

CO pressure (MPa)	Temp. (°C)	MF mmol		Conv. (%)
		3 h	5 h	
5	52	1313	2187	93.1
2	52	450	797	35.5
2	62	640	964	44.1
1	62	293	448	19.2

[a] Reaction conditions: MeOH: ca. 80 ml; Amberlyst A26: 12.8 meq OH^-.

Besides the contribution of eq. (3), the loss of activity of the resin under our reaction conditions is likely due to water, an unavoidable impurity of methanol, which produces formate after hydrolysis reaction:

$$\textcircled{P}-CH_2N(CH_3)_3^+MeO^- + H_2O \rightleftharpoons MeOH + \textcircled{P}-CH_2N(CH_3)_3^+OH^- \quad (4)$$

$$\textcircled{P}-CH_2N(CH_3)_3^+OH^- + HCOOMe \rightarrow \textcircled{P}-CH_2N(CH_3)_3^+HCOO^- + MeOH \quad (5)$$

$$\textcircled{P}-CH_2N(CH_3)_3^+OH^- + CO \rightarrow \textcircled{P}-CH_2N(CH_3)_3^+HCOO^- \quad (6)$$

The progressive deactivation of the catalyst was evidenced by the modification of the infrared spectrum of the Amberlyst A26 resin (fig. 2): the band at 1080 cm^{-1} due to the methoxy anion decreased with the contemporary rising of the absorptions at 1590 and 1340 cm^{-1} due to the asymmetric and symmetric stretching mode of the formate species [17]. Also carbon dioxide, an impurity of CO (ca. 150 ppm), can partially contribute to catalyst deactivation with formation of methyl carbonates. Reactions with poisons produced thus formate and methyl carbonate groups on the resin but, confirming this deactivation mechanism, it was observed that the exhausted resins can be regenerated simply through caustic washing.

The thermal stability of the active functional groups (also at about 70°C) was surprising as this kind of resins is claimed to be stable only for $T \leqslant 60°C$. Further work is in progress to clarify this phenomenon.

4. Conclusions

This study allowed us to assess that strongly basic resins, such as Amberlyst A26 or Amberlyst IRA 400, are more active catalysts than MeONa in the methanol carbonylation to methyl formate. On these heterogeneous systems the equilibrium concentrations were reached in shorter times and at lower temperatures (50–70°C) where higher conversions can be achieved.

A preliminary experimentation with continuous flow runs has shown that the catalyst loses its activity with time but the deactivation process seems to be reversible and the activity can be completely restored by regeneration with caustic washing. These preliminary results show that the use of a heterogeneous catalyst, with respect to the homogeneous methoxide, can simplify the procedure of catalyst separation and reactivation avoiding the typical problems of scarce solubility and plugging of the homogeneous catalyst and could represent a

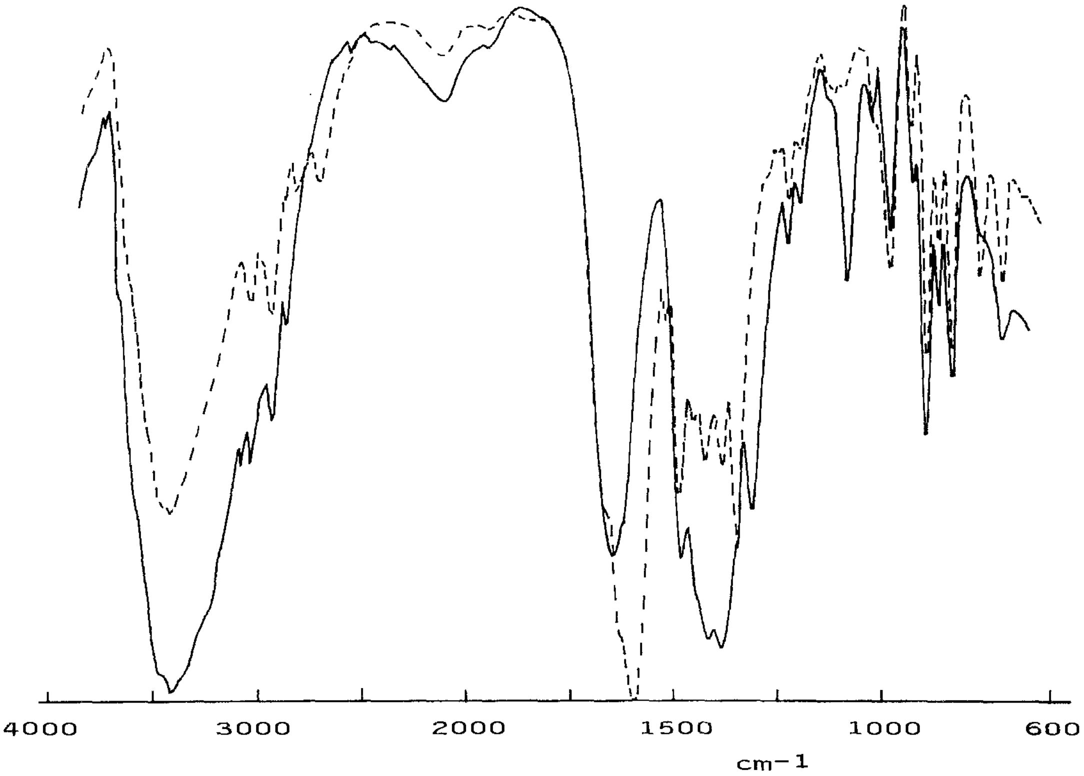

Fig. 2. IR spectra of Amberlyst A26 catalyst. (——) Freshly activated resin; (- - -) deactivated resin.

good choice to improve the industrial synthesis of methyl formate.

Finally, this work points out that in the near future strongly basic resins can represent a valuable substitute for homogeneous catalysts in base-catalyzed reactions.

Acknowledgement

Special thanks to G. Micheletti for technical support and to E.G. Lundquist (Rohm & Haas Co.) for interesting discussions. Rohm & Haas Co. is also gratefully acknowledged for having furnished the basic resins.

References

[1] J.S. Lee, J.C. Kim and Y.G. Kim, Appl. Catal. 57 (1990) 1.
[2] G. Jenner, Appl. Catal. A 121 (1995) 25.
[3] W. Reutmann and M. Kieczka, *Ulmann Encyclop. of Ind. Chem.*, 5th Ed., Vol. A12 (1989) p. 13.
[4] Z. Liu, J.W. Tierney, Y.T. Shah and I. Wender, Fuel Proc. Technol. 18 (1988) 185.
[5] S.P. Tonner, D.L. Trimm, M.S. Wainwright and N.W. Cant, J. Mol. Catal. 18 (1983) 215.
[6] R.J. Gormley, A.M. Giusti, S. Rossini and V.U.S. Rao, *9th Int. Congr. on Catalysis*, Vol. 2, Calgary 1988, eds. M.J. Phillips and M. Ternan (Chem. Inst. of Canada, Ottawa, 1988) p. 553.
[7] J. Green, EP 104 875 (1984) (BP).
[8] F. Piacenti, M. Bianchi, P. Frediani, G. Menchi and U. Matteoli, J. Mol. Catal. 83 (1993) 83.
[9] R.A. Head and M.I. Tabb, J. Mol. Catal. 26 (1984) 149.
[10] G. Jenner and G. Bitsi, J. Mol. Catal. 45 (1988) 235.
[11] B.H. Chung, A.R. Grimm and B.C. Trivedi, US 4 661 623 (1987) (Ashland Oil).
[12] D.J. Darensbourg, M.-L. Gray and C. Ovalles, J. Mol. Catal. 41 (1987) 329.
[13] S.J. Choi, J.S. Lee and Y.G. Kim, J. Mol. Catal. 85 (1993) L109.
[14] D.L. Smathers, US Patent 4 100 360 (1978) (du Pont).
[15] G. Sbrana, G. Braca, P. Antognoli and S.D'Antone, *VI Simp. It. Cec. Catal.*, Sanremo (1987) p. 76.
[16] A. Chakrabarti and M.M. Sharma, React. Polym. 20 (1993) 1.
[17] S. Bailey, G.F. Froment, J.W. Snoeck and K.C. Waugh, Catal. Lett. 30 (1995) 99.