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Direct synthesis of organic carbonates by oxidative carboxylation of olefins catalyzed by metal oxides: developing green chemistry based on carbon dioxide†

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In this paper we report on the 'oxidative-carboxylation' of olefins catalysed by either transition metal complexes or metal oxides. We discuss the oxidation mechanism under homogeneous and heterogeneous conditions. In the former case the process is driven by co-ordination to the metal centre, in the latter a radical reaction takes place. The yield of carbonate is strongly dependent on the catalyst used. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: carbon dioxide; catalysts; organic carbonates; oxidative carboxylation

INTRODUCTION

'Sinking carbon dioxide' has been included in international agreements as a technology for carbon dioxide mitigation following the 1997 Kyoto Conference on Climate Change. Recovery of carbon dioxide from power plant flue gases or industrial processes will make available very large amounts of carbon dioxide, either for disposal or for utilization.

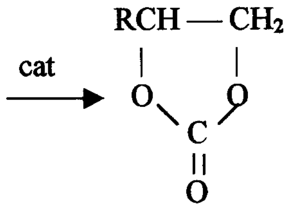
However, recycling carbon dioxide (technological utilization, fixation into chemicals or biomass) is now being assessed as a technology alternative to the disposal.[1]

As a matter of fact, the utilization of carbon dioxide as building block[2] for the synthesis of chemicals is now the object of several national and international research programmes worldwide, e.g. the EU-BRITE RUCADI project and the RITE programme in Japan; see also the proceedings of the 215th ACS National Meeting Symposium, held in Dallas, TX, in 1998. This approach can contribute to the development of clean synthetic methodologies, avoiding both the use of toxic substances[3,4] and the production of waste.

RESULT AND DISCUSSION

We have for a long time been developing new synthetic approaches to large-market (Megatonnes per year) chemicals, like carbamate- and carbonate-esters.[5] Relevant to the latter reaction is our study of the conversion of olefins into carbonates by carboxylation under oxidative conditions, (Eqn [1]) using rhodium catalysts under homogeneous conditions.[6]

$$\mathrm{RCH{=}CH_2} + \tfrac{1}{2}\,\mathrm{O_2} + \mathrm{CO_2}$$



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[1]

Such a reaction is of interest as it does not require pure (dioxygen free) carbon dioxide. This feature

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makes it attractive, as the CO_2 purification cost, which may be one of the aspects discouraging carbon dioxide utilization, is kept low. Moreover, the process uses low-priced organic substrates, like olefins, for the synthesis of valuable (molecular- or polymeric-carbonates) chemicals.

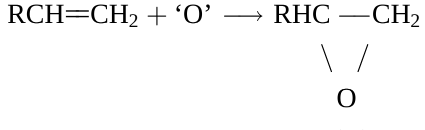
The limitation to the possible implementation of the rhodium-catalysed synthetic methodology lies in the low turnover number (TON), which is linked to the life of the catalyst under the homogeneous-phase oxidative carboxylation conditions.

In fact, we have demonstrated that if the catalyst is a rhodium complex stabilized by monodentate phosphanes, it can be destroyed because of the progressive oxidation of the ligand to phosphine oxide. We have also ascertained that the ligand oxidation is an inter-molecular, rather than an intra-molecular, process.[7]

Conversely, when unsaturated rhodium (I) complexes 'Rh(L—L)Cl' bearing a bidentate ligand (L—L = diphosphine, dipyridyl) are used, the mechanism of deactivation follows a different pathway. In this case, the coordinatively unsaturated 'Rh(L—L)Cl' moiety can be converted, by reaction with olefins, into a mixture of the penta-coordinated rhodium complex, $Rh(L—L)_2Cl$, which no longer shows catalytic properties,[7] and $Rh(olefin)_nCl$, which is inactive. Owing to these facts, the life time of the catalyst rarely exceeds a few hours, with a serious limitation on the potential application in synthetic chemistry.

As far as the reaction conditions are concerned, a low temperature is required in order to limit the decomposition of the catalyst and favour the oxidation of the olefin, which may occur either via a 'two-oxygen transfer' to the double bond, with subsequent cleavage and formation of aldehydes (Eqn [2]), or via a 'one-oxygen' transfer that affords oxidation products, among which is epoxide (Eqn [3]).

$$RCH{=}CH_2 + O_2 \longrightarrow RCHO + CH_2O \qquad [2]$$



$$RCH{=}CH_2 + \text{'O'} \longrightarrow \underset{\diagdown\ O\ \diagup}{RHC\text{—}CH_2} \qquad [3]$$

$$RHC(O)CH_3$$

$$RCH_2CHO$$

However, the synthetic methodology reported in Eqn [1] is of interest because it is based on easily available chemicals and couples two processes, epoxidation of olefins[8] and carbonation of epoxides,[9] which are already implemented at the industrial level.

Thus, we decided to explore further the potential of this reaction by operating under heterogeneous conditions. In principle, under these conditions the catalyst could have a longer life. However, metal oxides under heterogeneous conditions have been used both in the epoxidation of olefins (Ag_2O has been used to catalyse the epoxidation of ethylene for sometime, e.g. see Ref. 8) and the carbonation of epoxides (MgO is a good catalyst for the carbonation of styrene oxide[9]).

Therefore, we have tested a large number of oxides, either Group 1 and 2 or transition-metal oxides, and we present in this paper some selected results of the work we have done under batch-conditions in *N*,*N*-dimethylformamide as solvent. In our work we have used the catalyst either as a fine powder (this work) or supported on pumice,[10a] a natural alumino-silicate that has shown quite interesting properties as a support for hydrogenation catalysts.[10b–e] We discuss here the performance of our catalysts in comparison with Ag_2O and MgO, for the reasons given above.

As we have discussed in previous papers,[6,11] under our operating conditions olefins can undergo an oxidation according to a 'two-oxygen' or 'one-oxygen' transfer mechanism (see above).[12] We have also demonstrated that carbon dioxide can modulate the oxidative properties of dioxygen and that rhodium complexes enhance the 'one-oxygen' transfer reaction to olefins in the presence of CO_2/O_2 mixtures,[13] under homogeneous condition.

Table 1 summarizes the data for several heterogeneous catalysts. It lists, besides the conversion of styrene, the selectivity towards styrene epoxide, which is a product formed upon 'one-oxygen' transfer to the olefin, and styrene carbonate. The other majority products formed in the reaction are benzaldehyde (typical product of 'two-oxygen' transfer to styrene) and its oxidation derivative, benzoic acid. Among minority products, phenylacetaldehyde and acetophenone account for not more that 5% of the total.

Using heterogeneous catalysts, the oxidation process is not 'catalyst-driven'. More likely, it is a radical reaction started by the catalyst, as demonstrated by *ad hoc* studies. The role of the catalyst is quite important in the second phase of the reaction, i.e. the carbonation.

Noteworthy, silica, alumina and molecular sieves 5A show some catalytic properties for the synthesis of carbonate. It is worth noting that hydrated silica

Table 1 Conversion of styrene with CO_2–O_2 mixtures[a]

		Selectivity towards:			
Catalyst	Styrene conversion (%)	Styrene carbonate	Styrene oxide	Benzaldehyde	Benzoic acid
Molecular sieves 5A[b]	16	3.1	11.8	67.5	3.1
SiO_2 anhydrous[b]	23	9.1	15.2	45.6	19.1
SiO_2 hydrated[b]	22	1.1	17.3	50.9	24.1
Ag_2O[c]	28	—	16.4	50.8	24.5
MgO[b]	14	6.8	13.6	58.8	8.9
MgO[d]	—	—	—	—	—
Fe_2O_3[b]	28	10.3	1.8	46.4	33.9
MoO_3[b]	27	6.3	5.9	54.8	25.2
Ta_2O_5[b]	27	2.9	17	48.5	24.4
La_2O_3[b]	26	2.7	12.7	43	32.3
Nb_2O_5[b]	27	16.6	4.4	46.3	24.1
V_2O_5[b]	34	7.3	5	55.3	27
ZnO	12.5	1.3	14.2	41.1	36

[a] Each entry is the average of three tests. The average deviation is ±5%. The operating conditions were the same in all tests. Catalyst: 7×10^4 mol; styrene: 1.75×10^{-2} mol; *N,N*-dimethylformamide as solvent: 10 ml; temperature: 393 K; reaction time: 5 h.

[b] $P_{o_2} = 5$ atm; $P_{co_2} = 45$ atm.

[c] $P_{o_2} = 5$ atm.

[d] $P_{co_2} = 45$ atm.

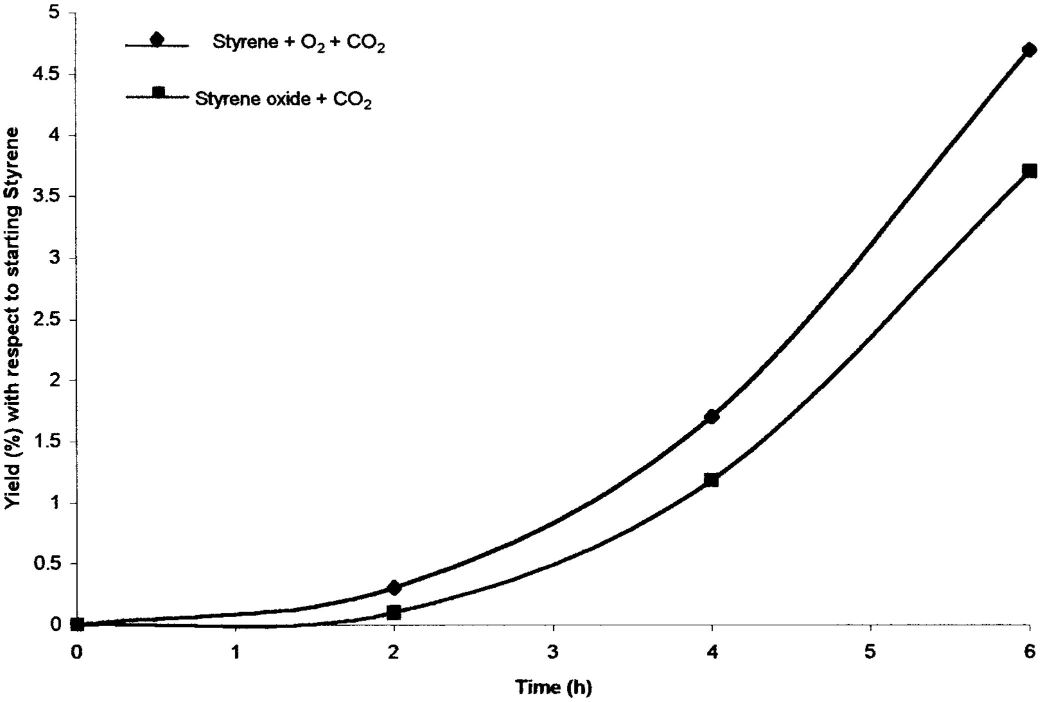


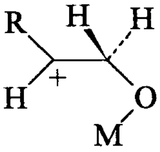
Figure 1 Formation trend of styrene carbonate.

is less active than anhydrous silica. This is due to the fact that surface OH groups destroy organic carbonates, as we have demonstrated in an *ad hoc* study.

A quite interesting behaviour is also shown by Nb_2O_5, which is not deactivated after several cycles.

Preliminary kinetic studies have demonstrated that the formation of carbonate is faster from olefins and CO_2–O_2 than from epoxide–CO_2, (Fig. 1) using the same catalyst under identical reaction conditions.

This could be explained by taking into account an intermediate like (**2**) that is likely to be formed under the reaction conditions. Such species avoid the ring-opening of epoxide that may be the limiting step from the thermodynamic and kinetic points of view.



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Further experiments are in progress to elucidate the reaction mechanism and improve the catalytic activity.

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