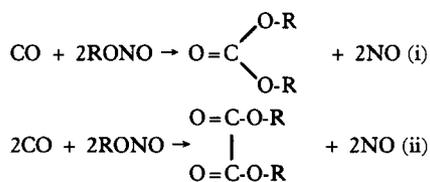


Palladium Supported Catalysts in CO + RONO Reactions

By X.-Z. Jiang

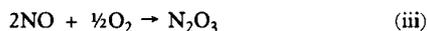
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In the past decade much effort has been directed towards the synthesis of dialkyl oxalates and dialkyl carbonates directly from carbon monoxide and alcohols over palladium supported catalysts, under mild reaction conditions (1-4). Although the mechanism of the reactions has not been fully elucidated, the key reactions can be illustrated by the following equations:



(where R represents an alcohol residue).

The conditions required for these chemical reactions to take place are quite mild; for example, dimethyl or diethyl carbonate and oxalate can be efficiently prepared in the vapour phase by bringing carbon monoxide into contact with methyl nitrite or ethyl nitrite, respectively, on a palladium fixed bed catalyst, at atmospheric pressure and at a reaction temperature between 80-120°C. The reason that this reaction can be carried out under such mild conditions could be rationalised on the basis of the iso-electronic structure of ^+NO and CO; leading to a strong synergistic catalytic effect on the active centre of palladium (5). On the other hand, the nitrogen oxide liberated from the reaction in Equations (i) or (ii) will generate alkyl nitrite in the presence of alcohol and oxygen, as indicated in the chemical Equations (iii) and (iv):



As a result, there is no loss of alkyl nitrite, which appears to play a role in circulating the reagent in the reaction system. It is therefore of great interest to investigate the applicability of these reactions to industrial processes.

This article is a summary of our recent studies on palladium supported catalysts in CO + MeONO (or EtONO) reactions at atmospheric pressure in the vapour phase (6-8). It was found that the carbonylation reactions of RONO, where R represents a methyl or ethyl group, were very sensitive to the support, and that the main product was particularly dependent on the nature of the support, as illustrated in Figure 1.

Monocarbonylation

The monocarbonylation of methanol or ethanol can be achieved by introducing the corresponding nitrites (methyl nitrite, MeONO, with b.p. -12°C, or ethyl nitrite, EtONO, with b.p. 17°C) which were prepared according to established procedures (9). The nitrite was then able to react directly with carbon monoxide to form dimethyl carbonate or diethyl carbonate over fixed catalyst beds of palladium supported on active carbon catalysts, in the gas phase and at atmospheric pressure. The reaction temperature varied from 80 to 120°C. Because the alkyl nitrites are fairly sensitive to heat and ultraviolet irradiation (10), they decompose rapidly above 130°C, but below 110°C they are quite stable for a long period of time. The optimum reaction temperature for the formation of dimethyl carbonate or diethyl carbonate from MeONO or EtONO, respectively, is in the region of 90 to 110°C, the selectivity being about 90 per cent and with a carbon monoxide conversion about 25 per cent in a flow system with a differential reactor. The formation of carbon dioxide was extremely low in the vapour phase.

The nature of the active carbon support, which was made from various kinds of raw materials, significantly affects the catalytic activity for dimethyl carbonate or diethyl carbonate formation (6, 7). Kinetic studies revealed that the 2 per cent palladium/carbon catalyst, in which the

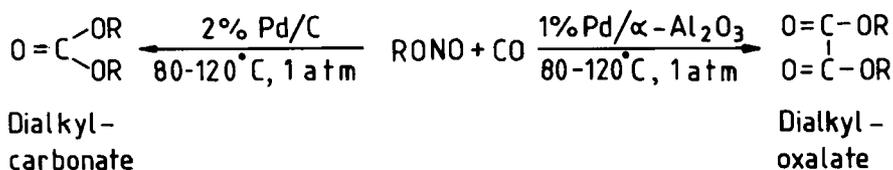


Fig. 1 The main product of the RONO + CO reactions was found to be dependent on the nature of the support. R represents a methyl or ethyl group

active carbon was made from coconut shell, exhibited relatively higher formation activities for dimethyl carbonate (DMC) or diethyl carbonate (DEC), for instance $r_{\text{DMC}} = 15$ mmol/gcat.h; while for an active carbon support made from coal $r_{\text{DMC}} = 9$ mmol/gcat.h, and for an active carbon support made from wood $r_{\text{DMC}} = 4$ mmol/gcat.h, all under the same reaction conditions. The main reason for these differences in the catalytic activity may be attributed to the dispersion of the palladium particles exposed on the surface of the catalyst. The average palladium particle sizes measured by transmission electron microscopy (TEM) can be ranked as follows: $d_{\text{TEM}} = 70$ Å for the coconut shell-made active carbon supported palladium catalyst; $d_{\text{TEM}} = 180$ Å for coal-made support and $d_{\text{TEM}} = 340$ Å for wood-made active carbon support. From a comparison of the dispersions of the palladium particles with the corresponding catalytic activity, it can be concluded that active carbon supported catalysts with higher dispersions of palladium particles demonstrate higher catalytic activity for the formation of dimethyl carbonate and diethyl carbonate from CO + MeONO, or EtONO, under the mild gas phase reaction conditions mentioned above.

In some cases, however, the competitive formation of dimethyl (or diethyl) oxalate with carbonate would occur, especially at reaction temperatures above 110°C. This competitive reaction gives rise to a selectivity problem. An attempt was made to direct the selectivity towards monocarbonylation, rather than carbon monoxide coupling, by the inclusion of a small amount of additive, such as a salt containing lithium, copper or iron (6). As a result of this additive selectivities greater than 90 per cent can

be achieved in the monocarbonylation of methanol and ethanol over the catalysts M + 2 per cent palladium/carbon (where M represents lithium, copper or iron) at a pressure of 1 atmosphere and temperature of 80 to 110°C.

Dicarbonylation

An alternative reaction which formed dialkyl oxalates from CO + RONO over a palladium catalyst supported on α -alumina under atmospheric pressure and at reaction temperatures between 80–120°C in the vapour phase, is illustrated in Figure 1. Where carbon monoxide coupling occurred to form carbon-carbon bonds, the occurrence of the dicarbonylation reaction was mainly attributed to a function of the support, therefore, α -alumina was utilised for the support instead of active carbon (8, 11). An important feature of palladium catalysts supported on α -alumina is a fairly low dispersion of the palladium particles exposed on the surface of the catalyst. It may be due to the very small surface area of the α -alumina support, for example, the surface area will be less than 8 m²/g, and the crystallites of α -alumina are quite large.

After a comparison of α -alumina-supported and active carbon-supported palladium catalysts a valuable conclusion could be drawn: α -alumina-supported palladium catalysts with a very low dispersion of the palladium particles favoured dicarbonylation reactions for the formation of alkyl oxalates from CO + RONO; while active carbon-supported palladium catalysts with a fairly high dispersion of palladium particles favoured the monocarbonylation reaction, forming dialkyl carbonates as the dominant product, under the same reaction conditions. No doubt this is due to the effect of the support.

The addition of a small amount of iron, gallium or titanium promoter will increase the catalytic activity for the formation of dimethyl (or diethyl) oxalate by 3 or 4 times (11). Therefore the synthesis of dimethyl and diethyl oxalates by carbon monoxide coupling in the vapour phase can be successfully achieved over catalysts of M + 1 per cent palladium/ α -alumina, with the selectivity of about 85 per cent, and with 35 per cent carbon monoxide conversion and 60 per cent RONO conversion in the integrated reactors.

The heat of reaction ($-\Delta H$) of the reaction of CO + RONO, Equation (ii), was estimated to be 47 kcal/mol at 100°C, therefore the design of an integrated reactor on an industrial scale must pay much attention to the heat effect.

So far the mechanisms of the reactions, Equations (i) and (ii), have not been established. We have proposed that a synergistic effect of the iso-electronic structure of ^+NO and CO might play an important role in the reaction procedure (6, 8, 11). Nishimura and colleagues assumed that an intermediate of alkoxy palladium, such as Pd(NO)₂(OR)₂ is formed during the reaction (1, 2); moreover Rivetti and Romano isolated alkoxy carbonyl complexes of palladium (12), such as Pd(COOCH₃)₂(PPh₃)₂. They reported that this complex was stable for several hours in methanol under carbon monoxide at room temperature, but quickly decomposed at 50°C, and then dimethyl oxalate was detected in the solution. Clearly further investigation will be required to explore the mechanisms for mono- or dicarbonylation of alcohols.

Conclusions

This article has briefly described novel ways for mono- and dicarbonylations of methanol and/or ethanol in synthesising the corresponding carbonates and oxalates over active carbon or α -alumina supported palladium catalysts in both academic and industrial research laboratories. The introduction of methyl or ethyl nitrite as a circulating reagent, which experienced almost no loss during the process, was a key feature of the novel method. In addition the mild reaction conditions and high catalytic activity and selectivity of these reactions have attracted a great deal

of attention for prospective industrial application. At present the production of diethyl oxalate from CO + EtONO over M + Pd/ α -Al₂O₃ catalyst is being developed in a plant in Shanghai. It will undoubtedly result in more industrial utilisation of palladium catalysts in the manufacture of valuable organic compounds, perhaps replacing existing production methods.

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Destruction of Organochlorines

Many organochlorine molecules are persistent environmental poisons, and after use they must be disposed of most carefully. Although high temperature incineration is the generally accepted method of destroying the polychlorinated biphenyls, for example, concern about incomplete oxidation remains.

Now, a report from the University of Sydney outlines a relatively low cost process for the electrocatalytic oxidative destruction of organochlorines (J. K. Beattie, *Pure Appl. Chem.*, 1990, **62**, (6), 1145-1146). Complete oxidation to carbonate and chloride is achieved using oxygen in alkaline solution, however, oxygen is too weak an oxidant to regenerate the ruthenium tetroxide which is the active catalytic species, but this can be achieved using a small applied voltage.