

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/ $\alpha$ -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)<sub>2</sub>(OR)<sub>2</sub> is formed during the reaction (1, 2); moreover Rivetti and Romano isolated alkoxy carbonyl complexes of palladium (12), such as Pd(COOCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. 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  $\alpha$ -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/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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.

## References

- 1 K. Nishimura, S. Uehiumi, K. Fujii and K. Nishihira, *Am. Chem. Soc., Prep. Div. Pet. Chem.*, 1979, **24**, (1), 355
- 2 K. Nishimura, S. Uehiumi, K. Fujii and K. Nishihira, *U.K. Patent* 2,003,872; 1979
- 3 U. Romano, R. Tesel, M. Massi Mauri and P. L. Rebori, *Ind. Eng. Chem., Prod. Res. Dev.*, 1980, **19**, 396
- 4 S. G. David and M. S. Staines, *European Appl.* 134,668; 1985
- 5 S.-Y. Xu, B. Xue, Z.-F. Lin and X.-Z. Jiang, *J. Catal. (Dalian, China)*, 1989, **10**, (2), 187 (Chinese)
- 6 X.-Z. Jiang, Y.-B. Zhu and S.-Y. Xu, *J. Catal. (Dalian, China)*, 1989, **10**, (1), 75 (Chinese)
- 7 Y.-B. Zhu and X.-Z. Jiang, *Chin. Sci. Bull.*, 1989, **34**, (10), 875
- 8 X.-Z. Jiang and Y. Chen, *Fine Chemicals*, 1989, **6**, (1), 37 (Chinese)
- 9 A. H. Blatt, "Organic Syntheses, Collective Volume", Wiley, London, 1950, Vol.2, p.363
- 10 K. Kornblum and E. P. Oliveto, *J. Am. Chem. Soc.*, 1949, **71**, 226; J. B. Levy, *Ind. Eng. Chem. (Ind. Ed.)*, 1956, **48**, 762
- 11 X.-Z. Jiang, *Chinese Patent Application* 90103093.7
- 12 F. Rivetti and U. Romano, *J. Organomet. Chem.*, 1978, **154**, 323

## 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.