A new reaction for the synthesis of oxalic acid by the gas-phase partial oxidation of acetonitrile

N. Plint, N. J. Coville and V. D. Sokolovskii*

Applied Chemistry and Chemical Technology Centre, University of the Witwatersrand, Po WITS 2050, Johannesburg, South Africa

A new reaction of the direct selective oxidation of acetonitrile into oxalic acid by molecular oxygen over solid oxide catalysts at temperatures in the range 400–500 °C is disclosed.

Oxalic acid is currently produced by the liquid-phase oxidation of carbohydrates by nitric acid. With sugar as starting material the reaction requires the preliminary conversion of sugar to glucose and proceeds in the presence of concentrated sulfuric acid. In a second step the oxidation of glucose to oxalic acid is catalysed by vanadium pentoxide and iron(III) ions. This is a periodic process (rather than a continuous one) and requires utilization of dilute acid solution, the reaction media being highly corrosive.[1,2]

In our study, described below, we have found that acetonitrile can be directly converted into oxalic acid by a continuous process in which an acetonitrile–oxygen mixture is passed over magnesia-based catalysts.

Alumina, magnesia and magnesia doped with zinc, lead, calcium, lithium and phosphoric acid were used as catalysts for the reaction. The doped catalysts were prepared by coprecipitation (10% ZnO/MgO) or by impregnation (all other doped catalysts). All doped catalysts were dried at 120 °C overnight and calcined at 500 °C for 6 h. Three MgO catalysts of different origin have been tested: MgO (I) as supplied, MgO (II) prepared by thermal decomposition of magnesium hydroxide at 550 °C for 8 h and MgO (III) prepared by a similar procedure from magnesium carbonate.

Experiments were performed in a continuous plug-flow reaction system equipped with 'on line' GC. The catalyst (2.5 g, particle size 0.3–1.0 mm) was loaded into a quartz reactor equipped with a thermocouple. Acetonitrile was injected using a syringe pump into an oxygen stream prior to the reactor. Oxalic acid was collected in a trap, cooled by ice, situated at the outlet of the reactor. The analysis of gases formed in the reaction revealed the presence of carbon dioxide, ethylene, ammonia, nitric oxide and molecular nitrogen. The white solid crystalline material was analysed by ^{13}C NMR spectroscopy (Brucker AC 200 spectrometer) and IR spectroscopy (Brucker IFS 85 FTIR spectrometer).

The results of experiments with the different catalysts are presented in Table 1. It can be seen that under the reaction conditions all catalysts based on magnesia transform acetonitrile into oxalic acid with a high mass yield, comparable with that of the sugar-based process.[1] After 10 h on stream all catalysts show a decline of activity due to formation of a coke deposit on the catalyst surface. Catalytic activity was completely restored by regeneration under an oxygen flow for 1 h at 550 °C.

Taking into account the product compositions the following balance equations for selective [eqn. (1)] and non-selective oxidation [eqn. (2)] of acetonitrile under the studied conditions can be proposed. The best results in terms of oxalic acid yield and selectivity were obtained on pure MgO catalysts and for MgO doped with ZnO and PbO. Among pure magnesia catalysts the sample prepared by carbonate decomposition showed the best performance. CaO and Li$_2$O lowered the oxalic acid yield almost two-fold. A similar effect has been observed with catalyst modified by phosphoric acid. The lowest yield of oxalic acid was shown by alumina. It can be proposed that the moderate basic properties of magnesia are beneficial for the observed reaction: enhancement of the acidic properties of magnesia lead to a detrimental effect on oxalic acid formation.

$$\mathrm{MeCN} + 1.5\ \mathrm{O_2} + \mathrm{H_2O} = \mathrm{(COOH)_2} + \mathrm{NH_3} \quad (1)$$

$$2\ \mathrm{MeCN} + 3\ \mathrm{O_2} = \mathrm{C_2H_4} + 2\ \mathrm{CO_2} + 0.5\ \mathrm{N_2} + \mathrm{NO} + \mathrm{H_2O} \quad (2)$$

To summarize the performed study reveals that acetonitrile can be directly transformed into oxalic acid by gas-phase partial oxidation in the presence of magnesia based catalysts.

The FRD and Richard Ward Endowment Fond are greatly appreciated for financial support.

References

1 W. L. Faith, D. B. Leyes and R. L. Clark, *Industrial Chemicals*, Wiley, New York, 1970.

2 S. D. Deshpande and S. N. Vyas, *Ind. Eng. Prod. Res. Dev.*, 1979, **18**, 69.

Received, 4th September 1995; Com. 5/05842B

Table 1 Partial oxidation of acetonitrile into oxalic acid (OA)

Catalyst	T/°C	Flow rate (mmol min^{-1})		MeCN conv. (%)	OA yield^a (%)	OAD yield^b/ mass (%)
		MeCH$_3$CN	oxygen			
10% ZnO/MgO	500	1.55	1.79	80	19.4	59.5
10% PbO/MgO	450	0.95	1.79	92	19.4	59.5
10% CaO/MgO	500	0.95	1.79	95	9.4	28.9
10% Li$_2$O/MgO	500	0.95	1.79	97	9.3	28.5
5% H$_3$PO$_4$/MgO	500	0.95	1.79	99	12.9	39.6
MgO (I)	450	1.41	1.79	100	19.7	60.5
MgO (II)	450	1.41	1.79	100	15.5	47.5
MgO (III)	450	1.41	1.79	100	23.9	73.4
Al$_2$O$_3$	450	0.95	1.79	81	4.4	13.5

[a] Molar yield based on acetonitrile. [b] Yield of OAD [oxalic acid dehydrate; (COOH)$_2$·2H$_2$O], g per 100 g of acetonitrile.