Polish J. Chem., **76**, 1037–1039 (2002) **COMMUNICATION**

Catalytic Ketonisation over Oxide Catalysts. Part V[*]. Synthesis of Cyclopentanone over MnO_2/Al_2O_3 Catalysts

by M. Gliński[**] and M. Kaszubski

Faculty of Chemistry, Warsaw University of Technology (Politechnika),
Laboratory of Catalytic Synthesis, Noakowskiego 3, 00-664 Warsaw, Poland
E-mail: marekg@ch.pw.edu.pl

(Received January 10th, 2002; revised manuscript March 4th, 2002)

Cycloalkanones can be prepared according to two main sets of methods. In the first set, the existing ring is expanded, in the second the ring is formed. The first set consists of insertion of a methylene group originated from diazomethane into the cycloalkanone ring and reaction of nitrous acid with 1-hydroxy-1-aminomethyl-cycloalkanone [1]. Various cyclizations represent the second set of methods, cyclizations of esters of dicarboxylic acids [2,3], cyclization of dinitriles [3], cyclization of dichlorides of dicarboxylic acids [4] and cyclization of alkyl ω-haloacylacetates [5]. Vacuum pyrolysis of thorium, yttrium and cerium salts of dicarboxylic acids has been also used for the preparation of cycloalkanones containing up to 32 carbon atoms [6].

In the past we have studied the direct catalytic ketonisation of monocarboxylic acids under flow conditions [7–9]. Oxides of manganese, cerium and zirconium deposited on Al_2O_3, SiO_2 and TiO_2 exhibited the highest activity. Very recently, catalytic ketonisation has been applied in the synthesis of cyclopentanone over catalysts containing 20 wt% of MnO_2, CeO_2 and ThO_2 supported on alumina [10]. Liquid diethyl hexanodiate was used as a substrate instead of free acid, which is solid with a high melting point. Because of the rather low yields of cyclopentanone together with high conversions of ester [10], it was necessary to further examine the dependence of the concentration of active phase of the catalyst on its activity. The present work is focused on the MnO_2/Al_2O_3 system, whose representative (20 wt% MnO_2/Al_2O_3) has shown the highest yield of ketone together with a moderate activity in the mentioned reaction [10].

The same batch of commercial alumina (Degussa C, 100 m^2 g), over which our former works were performed [7–10], was used as a support and as a catalyst. The grains of alumina were impregnated by $Mn(NO_3)_2{\cdot}4H_2O$ solution using incipient wet-

---

[*] Part IV: Gliński M. and Kaszubski M., *React. Kinet. Catal.*, **70**, 271 (2000).

[**] To whom the correspondence should be addressed.

ness technique; the activation procedure was described in [8]. Reactions were carried out in a typical fixed bed tubular quartz reactor with 1.000 g of catalyst. As a preheater 1 g of fused quartz was placed on the top of the catalyst bed. Diethyl hexanodiate was dosed using a microdosing pump with a liquid hourly space velocity (LHSV) 2 cm^3 per 1 g of catalyst·hour. The composition of the reaction products was analyzed by GC (OV-101 column, FID, Chrom-4 chromatograph, n-tetradecane as internal standard) and identified by GC-MS (Hewlett-Packard 5971). Diethyl hexanodiate undergoes cycloketonisation in the presence of catalyst containing manganese oxide:

$$(CH_2)_4(COOC_2H_5)_2 \longrightarrow \text{cyclo}(CH_2)_4C{=}O + H_2O + CO_2 + 2C_2H_4$$

Ethanol, diethyl ether, 2-ethylcyclopentanone, cyclopent-2-en-1-one and cyclopentene were observed as by-products. Measurements of the activities of x wt% MnO_2/Al_2O_3 (x = 0, 5, 10, 15, 20 and 25) catalysts in the transformations of diethyl hexanodiate were performed. The results are summarized in Table 1.

Table 1. Influence of concentration of MnO_2 phase on activity of MnO_2/Al_2O_3 catalysts in cycloketonisation of diethyl hexanodiate. LHSV = 2 $cm^3/(g \cdot h)$.

Concentration of MnO_2 phase [%]	Ester conversion [%]/Yield of cyclopentanone [%]/T [K]			
	623	648	673	698
25	36/17	50/31	99/24	99/15
20[a]	30/14	53/33	99/26	99/19
15	16/7	53/26	98/27	95/22
10	14/8	60/33	97/30	98/13
5	12/5	56/31	98/37	98/14
0	49/39	89/60	97/40	98/31

a – data taken from [10].

Unexpectedly pure alumina was found to be the most active catalyst. Already at 623 K almost 40% yield of cyclopentanone was obtained at 50% conversion of ester. The maximum yield of product (60%) was found at 648 K. The deposition of MnO_2 phase on the surface of alumina lowered the yield of cyclopentanone as well as the conversion of ester. At 673 K the yield was inversely related to the concentration of MnO_2 in the catalyst. In the case of alumina, high selectivity in cyclopentanone formation seems to be dependent on the observed high conversions of diethyl hexanodiate at low temperatures. In the contrary, the same support was not very active in transformations of pure monocarboxylic acids studied earlier [7–9]. The MnO_2/Al_2O_3 catalysts were active at low temperatures in transformations of pure monocarboxylic acids [7–9], whereas their selectivity in the transformations of esters of dicarboxylic acids at high temperatures was strongly diminished due to the occurrence of consecutive reactions. Pure alumina was chosen for the measurements of catalyst activity *versus* time. The results are collected in Table 2.

Table 2. Activity of Al_2O_3 *versus* time in cycloketonisation of diethyl hexanodiate. T = 648 K. LHSV = 2 $cm^3/(g{\cdot}h)$.

Time-on-stream [min]	Ester conversion [%]	Yield of cyclopentanone [%]	Selectivity [%]
0	92	56	61
20	89	86	99
40	87	81	91
60	87	79	91
120	85	67	79
180	82	62	74
240	81	60	76
300	79	54	68
360	74	49	66
420	66	42	64

The maximum yield of cyclopentanone (86%) and ester conversion (89%) was found after 20 min. During the first 240 min, a small decrease in ester conversion from 89 to 81% was noted together with higher drop in the yield of ketone to 60%. After 420 min, the catalyst was found to be still active, because the ester conversion and the yield of ketone exceeded 65% and 40%, respectively.

REFERENCES

1. Smith P.A. and Baer D.R., *Org. Reactions*, **11**, 54 (1937).
2. Finley K.T., *Chem. Rev.*, **64**, 573 (1964).
3. Schaefer J.P. and Bloomfield J.J., *Org. Reactions*, **15**, 1 (1967).
4. Blomquist A.T., Holley R.W. and Spencer R.D., *J. Am. Chem. Soc.*, **70**, 34 (1948).
5. Hunsdiecker H., *Chem. Ber.*, **75B**, 1190 (1942).
5. RuHcka L. and Brugger W., *Helv. Chim. Acta*, **9**, 389 (1926).
7. Gliński M., Kijeński J. and Jakubowski A., *Appl. Catal. A: Gen.*, **128**, 209 (1995).
8. Gliński M. and Kijeński J., *Appl. Catal. A: Gen.*, **190**, 87 (2000).
9. Gliński M. and Kijeński J., *React. Kinet. Catal. Lett.*, **69**, 123 (2000).
10. Gliński M. and Kaszubski M., *React. Kinet. Catal. Lett.*, **70**, 271 (2000).