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Catalytic Ketonisation over Oxide Catalysts. Part VII.[*] Ketonisation and Cross-Ketonisation of Aliphatic Esters over CeO_2 and ZrO_2 Supported on Alumina

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Catalysts of general formula xwt% MO_2/Al_2O_3, where x = 10, 20 or 30 and M = Ce or Zr have been studied in the ketonisation and cross-ketonisation of aliphatic esters under flow conditions between 548–723 K. Ketonisation of ethyl pentanoate, heptanoate and nonanoate has led to nonan-5-one, tridecan-7-one and heptadecan-9-one, respectively. The conversion of esters increased with temperature and at 698 K a quantitative conversion was observed, irrespective of the type of ester used. A maximum yield of ketone (46% for nonan-5-one, 60% for tridecan-7-one and 50% for heptadecan-9-one) was observed at 673 K. As a result of the cross-ketonisation of a mixture of ethyl pentanoate and ethyl nonanoate (3:1 molar ratio), three ketones were formed: nonan-5-one, tridecan-5-one and heptadecan-9-one. At 698 K, maximum yields of ketones were noted (37, 46 and 8%, respectively) together with a 90% conversion of esters. The catalysts were characterized by XRD, TPR and surface area measurements.

Key words: cerium and zirconium catalysts, synthesis of aliphatic ketones, ketonisation of esters

Carboxylic acids are very convenient starting materials in organic synthesis, due to their natural occurrence and variety of their transformations. A large scale catalytic hydrogenation of carboxylic acids has been the main source of long chain fatty alcohols for the last seventy years. Carboxylic acids are also frequently used in the synthesis of a popular group of compounds – ketones and aldehydes. Since 1895 the direct transformation of carboxylic acids into ketones in the presence of solid catalysts under flow conditions has been known to be superior to the old method – pyrolysis of salts of carboxylic acids [1]. Aliphatic esters may be employed as precursors of acids, when the use of free acid is not feasible. Tricosan-12-one (laurone) and heneicosa-1,20-diene-11-one (undecylenone) were obtained in the ketonisation of the appropriate ethyl alkanoates under diminished pressure over thoria [2]. The synthesis of cycloalkanones in the cycloketonisation of diethyl alkanodiates over oxide catalysts has also been studied [3,4]. The activity of MnO_2,

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CeO_2 and ZrO_2 containing catalysts in the cross-ketonisation of esters of aliphatic and aromatic acids has been recently determined by us [5].

Since 1995 we have studied the activities of inorganic catalysts based on many metallic oxides in transformations of carboxylic acids [6]. The most promising catalytic systems were those containing oxides of manganese, cerium and zirconium [7]. This work is focused on the activity of the last two systems in the ketonisation and cross-ketonisation of aliphatic esters of monocarboxylic acids. We intend to determine the dependence of the type of the active phase and reaction temperature on the conversion of esters, yields, and ratios of products and their composition. A study of the activity of manganese catalyst in the mentioned reaction and the structure-reactivity relationship of various alkyl heptanoates will be the subject of our forthcoming publication [8].

EXPERIMENTAL

Catalysts. Commercial alumina (Degussa C) was used as a support. The dust of oxide was mixed with redistilled water until thick paste was obtained. The resulting gel was dried at 333 K and at 393 K for 24 h in air. The sieved fraction of grains (0.4–0.6 mm diameter) was calcined at 873 K in air for 6 h before preparation of catalysts. The following compounds were used as precursors of active phase of catalysts: $Ce(NO_3)_3 \cdot 6H_2O$ (pure, UMCS Lublin, Poland) and $ZrO(NO_3)_2 \cdot 2H_2O$ (pure, Hf content 1%, Biddle, Sawyer Co.). Catalysts were prepared by impregnation of the supports with aqueous solutions of precursors of active phases using incipient wetness technique. The dried samples (393 K, 12 h) were calcined in a stream of air at 723 K for 3 h. Three samples of different MO_2 content (10, 20 and 30 wt%) were prepared for each of the CeO_2/Al_2O_3 and ZrO_2/AlO_3 systems. The surface area of the support and catalysts was measured using a Gemini instrument (Micromeritics). 20wt% CeO_2/Al_2O_3 89 m^2/g, 20wt% ZrO_2/Al_2O_3 106 m^2/g, Al_2O_3 104 m^2/g.

Reagents. Ethyl pentanoate (pure, Fluka), ethyl heptanoate (99%, Aldrich) and ethyl nonanoate (97%, Aldrich) were washed with a saturated $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. Esters were fractionally distilled under normal/reduced pressure. Ethyl pentanoate, n_D^{20}= 1.4004 (exp), purity 98.7% (gc); ethyl heptanoate, n_D^{20}= 1.4129 (exp), purity 99.5% (gc); ethyl nonanoate, n_D^{20}= 1.4217 (exp), purity 98.2 % (gc).

Temperature programmed reduction (TPR). Temperature programmed reduction was carried out in a flow system with linearly increased temperature. A sample of catalyst was placed in a heated quartz reactor. A solution of hydrogen in argon (6% v/v) was used as reductant. The TPR profiles were recorded between 323–973 K. The temperature of the sample was measured by a thermocouple and controlled by Omega 2010 temperature controller. Changes in hydrogen concentration were monitored by a Gow-Mac thermal conductivity cell. Analog signals from the thermocouple and TCD were passed through digital voltmeters and monitored using an 8255 I/0 card in a microcomputer.

Catalytic activity measurements. The reactions were performed in a typical fixed bed tubular quartz reactor with 1.000 g of catalyst. The activity measurements were performed between 598–723 K and the reaction products were collected after keeping the catalyst bed at the lowest reaction temperature in a stream of reactants for 60 min.

Analytical determinations. The composition of reaction products was analyzed by gc (Tracer wax capillary column, 15 m long, i.d. 0.25 mm, FID, chromatograph KONIK HRGC 4000 B, Spain) and identified by gc-ms (Hewlett-Packard 5971). n-Octane or n-decane were used as internal standards.

RESULTS AND DISCUSSION

Characterization of catalysts: XRD measurements of all catalysts revealed that ZrO_2 and CeO_2 active phases deposited on the surface of alumina support exhibit a very low crystallinity, due to the mild conditions of transformation of precatalyst into catalyst (723 K, 3 h). Under these conditions, the sintering of the active phase as well as the formation of compounds between the active phase and the support is strongly limited. Both groups of catalysts were characterized by TPR method. The hydrogen uptake as a function of temperature is shown in Fig. 1 and 2. As pure ZrO_2 is not reduced by hydrogen at temperatures below 973 K, only 20wt% ZrO_2/Al_2O_3 was selected for TPR measurements (Fig. 1). A small consumption was noted at 700 and 950 K.

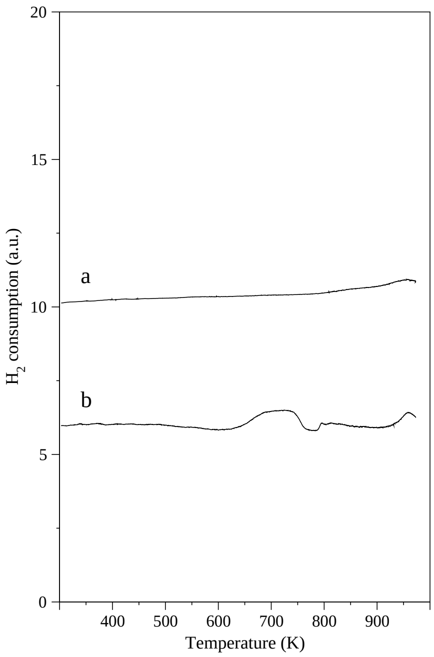

Figure 1. TPR profiles of ZrO_2/Al_2O_3 catalysts: a – pure ZrO_2; b – 20wt% ZrO_2/Al_2O_3.

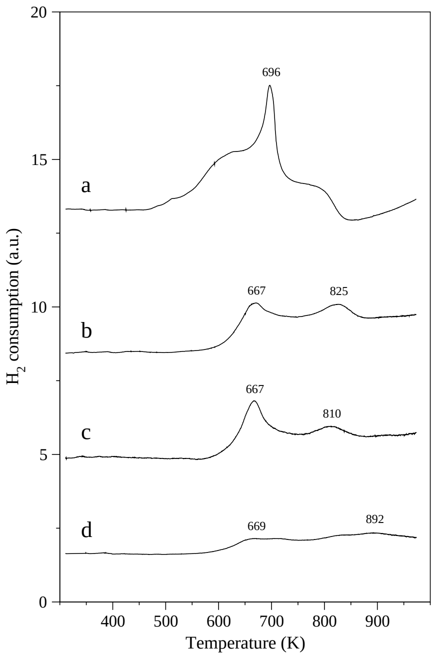

Figure 2. TPR profiles of CeO_2/Al_2O_3 catalysts: a – pure CeO_2; b – 30wt% CeO_2/Al_2O_3; c – 20wt% CeO_2/Al_2O_3; d – 10wt% CeO_2/Al_2O_3.

Much more interesting were the TPR profiles of CeO_2 containing catalysts (Fig. 2). The reduction of pure CeO_2 starts around 460 K and four peaks are detected at approximately 640, 696, 780 and above 940 K, of which the first three are not well resolved. The peak at 696 K is probably associated with the reduction of the surface oxygen of CeO_2 [9]. The last peak above 940 K, which is attributed to the total reduction of CeO_2 to Ce_2O_3 [9,10], is not complete, due to the termination of the ramp at 973 K. The negative peak around 850 K is suspected to originate from a release of

CO, formed during the reduction of carbonates present on the surface of ceria [11], or a release of hydrogen accumulated on the surface of ceria during the TPR experiment [12]. TPR profiles of CeO_2/Al_2O_3 catalysts revealed two not well resolved peaks, whose maxima depend on the concentration of the active phase. For all CeO_2/Al_2O_3 catalysts the reduction starts above 500 K, the first peak is around 670 K and the second at about 815 K, followed by a small peak at 890 K in the case of 10wt% CeO_2/Al_2O_3 catalyst only. The hydrogen consumption values and the degree of reduction for all cerium catalysts are collected in Table 1.

Table 1. The results of TPR measurements of CeO_2 and xwt% CeO_2/Al_2O_3 catalysts (x = 10, 20 and 30).

Catalyst	H_2 consumption[a] [μmole]	Ce_2O_3 content after TPR[b] [%]
CeO_2	25	20
$30CeO_2/Al_2O_3$	63	50
$20CeO_2/Al_2O_3$	66	53
$10CeO_2/Al_2O_3$	69	55

[a] Related to the presence of 250 μmoles of CeO_2 in samples; [b] on assumption that CeO_2 is selectively reduced to Ce_2O_3 only.

The CeO_2 active phase deposited on the surface of support shows a higher reducibility than that of pure CeO_2 under the same reduction conditions. A weak inverse dependence of the active phase concentration on its reducibility is also found.

Catalytic activity: Ketonisation of the ethyl ester of straight chain aliphatic acid in the presence of MO_2/Al_2O_3 catalyst (M = Ce and Zr) proceeds according to:

$$2\ RCOOC_2H_5 \rightarrow RCOR + 2\ C_2H_4 + CO_2 + H_2O$$

In preliminary experiments the activities of all catalysts have been measured in the transformations of pure ethyl pentanoate. The results are collected in Table 2.

Table 2. Ketonisation of ethyl pentanoate in the presence of xwt% MO_2/Al_2O_3 (x = 10, 20 or 30; M = Ce or Zr). LHSV = 3 $cm^3 \cdot g^{-1} \cdot h^{-1}$.

Active phase	Conversion of ester/ Yield of ketone[a] [%]/[%]				
	623 K	648 K	673 K	698 K	723 K
10 CeO_2	17/6	40/21	82/39	96/29	99/12
20 CeO_2	14/10	34/22	76/46	92/44	99/21
30 CeO_2	12/9	35/19	72/40	90/34	99/17
10 ZrO_2	16/3	44/16	90/30	98/20	99/3
20 ZrO_2	11/6	36/20	84/38	96/28	99/7
30 ZrO_2	12/4	30/22	78/27	92/22	99/6
–[b]	4/1	16/3	35/14	52/10	74/4

[a] Nonan-5-one; [b] activity of pure Al_2O_3.

The conversion of ester increased with temperature and at 723 K became quantitative in the presence of all catalysts. The catalysts based on cerium dioxide were more selective than those based on ZrO_2. The highest yields of ketones (46% for CeO_2/Al_2O_3 and 38% for ZrO_2/Al_2O_3) were observed at 673 K for 20wt% catalysts. These catalysts were chosen for further studies.

In Table 3 the results of the ketonisation reaction of pure ethyl esters of pentanoic, heptanoic and nonanoic acids over 20wt% MO_2/Al_2O_3 catalysts (M = Ce or Zr) are collected.

Table 3. Ketonisation of ethyl alkanoates in the presence of 20wt% MO_2/Al_2O_3 (M = Ce and Zr). LHSV = 3 $cm^3/(g \cdot h)$.

Alkanoate	T [K]	Conversion / Yield of ketone[a] [%]/[%]	
		CeO_2/Al_2O_3	ZrO_2/Al_2O_3
Pentanoate[b]	623	14/10	11/6
	648	34/22	36/20
	673	76/46	84/38
	698	92/44	96/28
	723	99/21	99/7
Heptanoate[c]	623	18/15	20/13
	648	50/44	46/39
	673	80/60	84/54
	698	98/47	98/23
	723	99/26	99/4
Nonanoate	623	19/14	22/13
	648	52/34	56/30
	673	86/50	86/42
	698	98/41	99/19
	723	99/30	99/6

[a] Nonan-5-one, tridecan-7-one and heptadecan-9-one were the observed products, respectively; [b] data taken from Table 2; [c] for pure Al_2O_3 the highest yield of ketone (34%) was observed at 673 K (85% conversion).

The conversions of all esters increased with temperature. The heaviest ester-ethyl nonanoate was the most reactive under the adopted conditions, below 698 K its conversion being higher than that of ethyl pentanoate and ethyl heptanoate at the same temperature. The cerium containing catalyst was more selective than the zirconium catalyst in the formation of ketones. The highest yields of ketones were obtained over it. A maximum yield of ketone (46% for nonan-5-one, 60% for tridecan-7-one and 50% for heptadecan-9-one) was observed already at 673 K. At the highest temperature (723 K), a quantitative conversion of all esters was noted, together with the lowering of the yields of ketones due to their thermal decomposition.

Cross-ketonisation of a mixture of ethyl pentanoate and ethyl nonanoate (3:1 molar ratio) in vapor phase over 20wt% CeO_2/Al_2O_3 catalyst proceeds according to:

$$\begin{gathered} 3\,C_4H_9COOC_2H_5 + C_8H_{17}COOC_2H_5 \rightarrow (1+y)\,C_4H_9COC_4H_9\, + \\ +\,x\,C_4H_9COC_8H_{17} + y\,C_8H_{17}COC_8H_{17} + 4C_2H_4 + 2H_2O + 2CO_2 \end{gathered}$$

where: $x + 2y = 1$

Two symmetric ketones – nonan-5-one (valerone) and heptadecan-9-one (pelargone), and an unsymmetric ketone tridecan-5-one are formed. The results of cross-ketonisation of a mixture of ethyl pentanoate and ethyl nonanoate are summarized in Table 4.

Table 4. Cross-ketonisation of a mixture of ethyl pentanoate and ethyl nonanoate (3:1 molar ratio) in the presence of 20wt% CeO_2/Al_2O_3. LHSV = 3 $cm^3/(g \cdot h)$.

T [K]	Conversion of esters [%]		Yield of ketones[a] [%]		
	Pentanoate	Nonanoate	A-A[b]	A-B[c]	B-B[c]
598	4	6	3	3	2
623	10	15	5	7	4
648	26	40	11	22	6
673	63	78	28	37	10
698	87	92	37	46	8
723	99	99	21	32	6

[a] A-A = nonan-5-one; A-B = tridecan-5-one; B-B = heptadecan-9-one; [b] yield based on ethyl pentanoate; [c] yield based on ethyl nonanoate.

The conversion of both esters increased with temperature with a simultaneous drop in the selectivity to ketones from 100% to *ca.* 45%. Ethyl nonanoate was the more reactive ester, its quantitative conversion was noted already at 673 K. The composition of ketones changed sharply with temperature. At low conversions tridecan-5-one was the dominant ketone. Its molar fraction dropped from 67 to 40% with temperature (573–723 K). The same profile of changes was observed for heptadecan-9-one. In contrast, the molar fraction of nonan-5-one increased sharply between 573–598 K and then gradually above this temperature range, reaching a plateau (*c.a.* 56–57%) at 673–723 K.

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