ELSEVIER

Journal of Molecular Catalysis A: Chemical 165 (2001) 275–281

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

The catalysed synthesis of symmetrical ketones from alcohols

N.D. Plint, N.J. Coville*, D. Lack, G.L. Nattrass, T. Vallay

Department of Chemistry, Applied Chemistry and Chemical Technology Centre, University of the Witwatersrand, P.O. Wits, Johannesburg 2050, South Africa

Received 22 December 1999; accepted 4 September 2000

Abstract

Reaction of a series of primary and secondary alcohols (1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 1-hexanol and 1-heptanol) with O_2 over CeO_2/MgO (1 atm, 450°C) produced the symmetrical ketone with $2n-1$ carbon atoms in 5–45% yield. The ketones were characterised by a combination of GC-MS and ^{1}H NMR spectroscopy. Aldehydes and aldol condensation products were the main products produced in competing reactions. No ketone was produced from the reaction of 2-methyl-2-propanol with oxygen. Reaction of a 1:1 mixture of 1-hexanol and 1-heptanol over the CeO_2/MgO catalyst produced a statistical yield of the three expected ketones. The data are consistent with oxidation of the alcohol to the acid followed by coupling of two acid molecules to give the symmetrical ketone. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ketone; Magnesium oxide; Cerium oxide; Alcohol oxidation; Base catalysis

1. Introduction

The catalysed synthesis of ketones from aldehydes and acids by the ketonisation reaction has been of interest since its original discovery [1]. In the reaction, two molecules of acid combine to form a symmetrical ketone with $2n-1$ carbon atoms, CO_2 and water. Numerous catalysts have been found to be active for the ketonisation reaction. For example, the conversion of acetic acid to acetone has been achieved over catalysts which include oxides of thorium, cerium, manganese, zirconium, rare earth metals, alkaline earth metals and metal oxides supported on alumina, silica, titania, and pumice [2–7].

The reaction is not restricted to acids. For example, in a recent paper by Wang and Davis, it was noted that a range of primary alcohols were converted to symmetrical ketones with $2n-1$ carbon atoms over iron oxide and iron carbide catalysts under Fischer–Tropsch synthesis conditions [8].

The possibility of using base catalysts [9,10] has also received attention. Indeed, in a previous paper [11], we observed that a mixture of 1-butanol and oxygen (1:3) when passed over a 40% CeO_2/MgO catalyst at 450°C produced 4-heptanone (17% yield). This reaction indicated that alcohols could be converted to ketones under oxidising conditions over a basic catalyst. To further explore this chemistry, the generality of the above reaction has been studied by investigating the effect of primary alcohol chain length (C_3–C_7) and the effect of secondary and tertiary alcohols, on the ketonisation reaction.

2. Experimental

2.1. Reagents

Reagent grade 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 1-hexanol, 1-hepta-

---

* Corresponding author. Tel.: +27-11-717-6738;
fax: +27-11-339-7967.
E-mail address: ncoville@aurum.chem.wits.ac.za (N.J. Coville).

1381-1169/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(00)00445-3

nol and 2-methyl-2-propanol from Sigma Chemicals were used without further purification. Magnesium oxide ('lite' and 'heavy') and cerium nitrate from BDH and oxygen from AFROX were used as received.

2.2. Catalyst synthesis

MgO 'lite' (MgO(1)) and MgO 'heavy' (MgO(2)) were pelletised by pressing the powdered MgO to 20 tonnes using a pneumatic press. The pellets were crushed and screened with the 300–1000 μm fraction being collected. The MgO was impregnated with a solution of $Ce(NO_3)_3 \cdot 6H_2O$ dissolved in distilled water to yield 5 and 40% loaded catalysts (by mass). The catalysts were then dried in air at 180°C for 16 h followed by air calcination at 550°C for 8 h.

2.3. Reactor studies

Catalytic reactions were performed in a fixed bed reactor. The reactor was made of quartz glass and was heated by means of an external heating jacket. The temperature was controlled by means of a thermocouple (type J) in contact with the catalyst. The alcohol was loaded into a Hamilton series 1010 gastight syringe and added by means of a syringe pump (Sage instruments, model 355) to an oxygen stream prior to the reactor. Both oxygen and alcohol were passed through a pre-heated section of the reactor such that the carrier gas was added to the reactor at 110°C. Typically 5 g of catalyst was placed in the reactor. The catalyst bed was maintained at $450 \pm 1°C$ for the duration of the experiment. The gaseous product stream from the reaction was passed directly through an on-line column (poropak Q) and the course of the reaction was monitored directly. The macroscopic amounts of the liquid products produced were collected at room temperature, and analysed off-line (see below).

Gas flows, temperatures, catalyst loading and reagents, were varied in the experiments. The yield of ketone was calculated as follows:

$$\text{Yield of ketone (\%)} = \frac{\text{Ketone (produced)} \times 100}{\text{Ketone (theoretical)}}$$

2.4. Characterisation studies

Liquid products were condensed in a cold trap attached to the reactor outlet and analysed using a GC with a 30 m megabore capillary column (DB1) manufactured by J&W (nitrogen carrier gas at a flow rate of 10 ml/min) and detected by means of a FID detector. They were also analysed using a Brucker AC 400 NMR spectrometer, a VG70 SEQ mass spectrometer with a VG11-250J data system and a Finnigan TSQ-7000 GC-MS system comprising of a Finnigan MAT GCQ Gas Chromatograph and a Finnigan GCQ Quadrupole ion trap mass analyser.

The off-gases were analysed on line using GC. A 2 m Porapak column was used for hydrocarbon analysis (nitrogen carrier gas at a flow rate of 30 ml/min and an FID detector). CO, CO_2, and O_2 were analysed using a packed 2 m × 1/8 in. Porapak Q column (helium carrier gas at a flow rate of 20 ml/min and a TCD detector).

The BET surface area, pore diameter and pore volume of MgO and the 40 and 5% CeO_2/MgO catalysts were determined using a Micromeretics ASAP2010 porosimeter (Table 1). Addition of CeO_2 to the MgO resulted in the expected decrease in surface area and pore volume of both MgO samples used (MgO 'lite' (MgO(1)) and MgO 'heavy' (MgO(2); Table 1). The 40% loaded CeO_2/MgO catalysts differed by about 25% in terms of their respective surface areas (28 and 21 m^2/g). Although the Ce dispersion was not measured, it is anticipated that at the high loadings used the Ce surface area will also increase with an increase in MgO surface area.

Table 1
Surface area analysis of supports and catalysts

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
MgO (1)	54	0.350	262
MgO (2)	25	0.169	272
5% CeO_2/MgO (1)	33	0.056	69.0
40% CeO_2/MgO (1)	28	0.041	59.3
40% CeO_2/MgO (2)	21	0.032	61.2

2.5. Carbon balance

Carbon balances were calculated by summing the number of moles of carbon deposited on the catalyst, the carbon in the liquid fraction products, the carbon in CO and CO_2, and the carbon in the hydrocarbon gas fractions. The mass balance was found to be to $100 \pm 10\%$ for the conversion of the C_2–C_7 normal

Table 2
Carbon balances for selected reactions, using different catalysts and reagents

Reactant	CeO_2 loading (%)	Alcohol		Aldehyde[a]	Ketone[a]	Aldol[a]	CO_2[a]	H/carbons[a,b]	Coke[a]	C total[c]	Mass balance (%)
		In	Out								
Ethanol	5.00	75.3	22.8	1.2	1.8	12.9	0.7	32.4	4.0	75.7	100.5
1-Propanol	5.00	96.0	25.0	4.7	3.1	5.8	7.8	34.0	6.8	87.2	90.9
1-Butanol	5.00	85.4	30.5	3.7	8.3	1.5	4.5	23.5	5.0	77.0	90.2
1-Pentanol	5.00	105.1	45.5	5.9	11.6	2.5	3.9	30.7	4.5	104.6	99.5
1-Hexanol	5.00	105.0	44.1	6.2	13.1	2.7	4.0	31.2	4.7	105.9	100.9
1-Heptanol	5.00	109.0	44.5	6.8	18.2	5.4	3.3	7.1	16.8	102.0	93.6
Ethanol	40.00	92.0	4.3	2.9	5.7	3.0	9.8	55.8	5.0	86.4	93.9
1-Propanol	40.00	92.5	8.5	0.4	13.9	0.9	11.4	41.7	7.2	84.2	91.1
1-Butanol	40.00	91.5	7.7	0.6	35.1	2.9	8.5	37.0	5.7	97.4	106.5
1-Pentanol	40.00	105.1	3.4	0.6	41.7	2.1	7.4	51.9	5.6	112.6	107.1
1-Hexanol	40.00	105.6	3.9	0.9	43.2	4.9	7.9	33.6	3.1	97.5	92.4
1-Heptanol	40.00	100.8	3.2	0.9	40.9	4.2	4.4	25.0	13.1	91.8	91.0

[a] Measured in mmol of carbon.
[b] H/carbons refers to hydrocarbons.
[c] This is the total amount of carbon (mmol) for all C containing species.

alcohols over both the 5 and 40% CeO_2/MgO catalyst (Table 2).

3. Results and discussion

3.1. Product identification

Reaction of a series of alcohols (ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 1-hexanol, 1-heptanol) and oxygen over 40% CeO_2/MgO (450°C) gave a wide range of products as indicated by GC analysis. Identification of these products, in particular the major products, was achieved by use of GC-MS and ^{1}H NMR spectroscopy. For example, reaction of 1-hexanol/O_2 over the catalyst gave a product mixture, as indicated by GC, which was dominated by the presence of two major components (Fig. 1). Use of GC-MS and standards permitted these two peaks to be identified as the starting material, 1-hexanol (m/z = 101 (4.6%), 69 (46.1%)) and the symmetrical ketone, 6-undecanone (m/z = 172 (11.5%), 171 (97%), 99 (100%)). NMR spectroscopy also confirmed the identity of these major components. Other products were also formed in the reaction and included minor amounts of aldehyde (hexanal, <5%), various hydrocarbons (e.g. methane, propane, butane, etc.) and the aldol condensation reaction product (2-butyl-3-octenal). These products were also identified by GC-MS, as described above (data not shown). Similar results were obtained for the other straight chain alcohols that were studied (Table 2). As can be seen from Table 2, the amounts of the different products varied with the alcohol chain length.

3.2. Effect of surface area

To evaluate the effect of surface area on the reaction, 1-butanol was passed over both 40% loaded

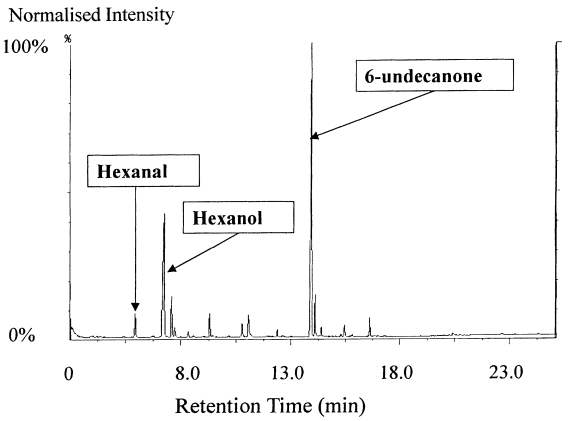

Fig. 1. A GC trace of the products obtained from the passage of 1-hexanol and oxygen over a 40% CeO_2/MgO catalyst at 450°C.

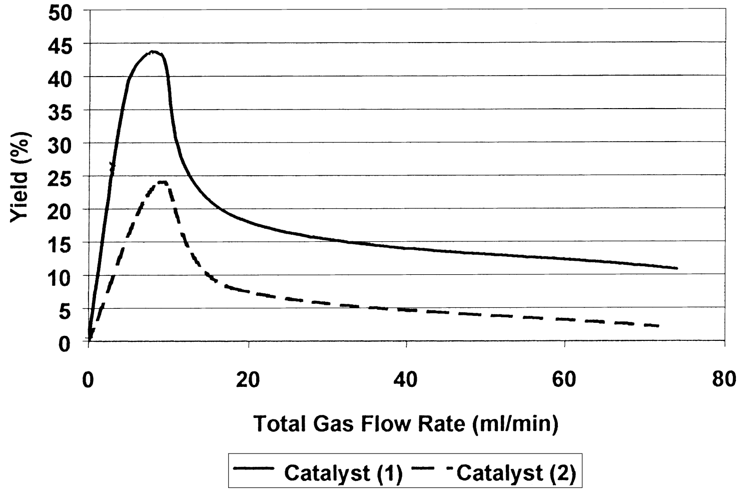

Fig. 2. The yield of 4-heptanone when 1-butanol was passed over the two 40% CeO_2/MgO catalysts with different surface areas.

CeO_2/MgO materials and the results are shown in Fig. 2. As can be seen the amount of ketone formed is markedly higher at all flow rates for the catalyst with the higher surface area. The product spectrum and trends in activity, however, remained the same for both catalysts, with the maximum yield being achieved at a flow rate of 7 ml/min (see also [11]). This suggests that the reaction is related to the number of surface active sites (available to the reactant).

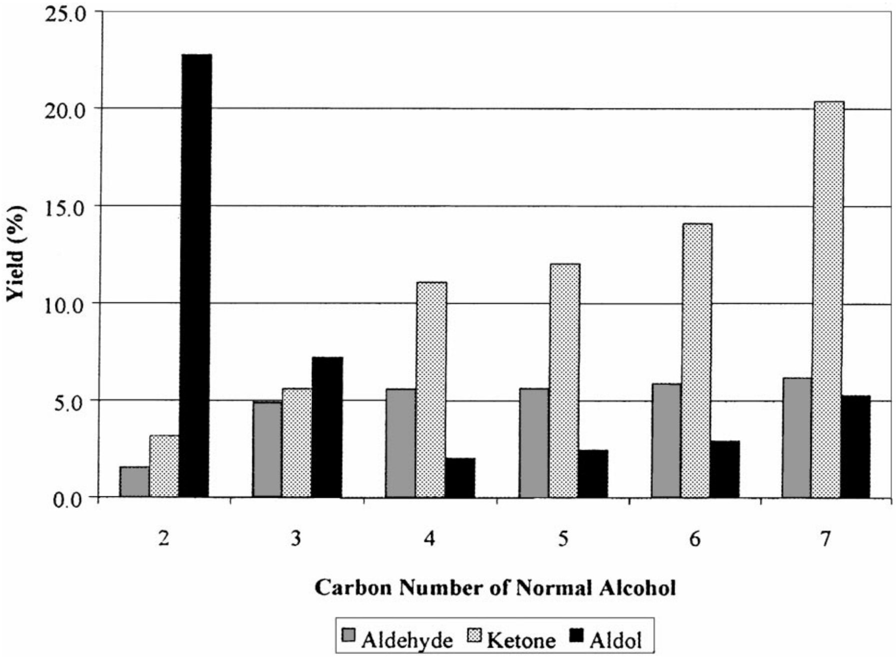

Fig. 3. The yield of ketone, aldol products and aldehyde produced after the passage of C_2–C_7 normal alcohols over a 5% CeO_2/MgO catalyst.

Table 3
The conversion of 1-hexanol over 40% CeO_2/MgO at different flow rates

Flow rate (ml/min)	CO_2 (%)[a]	Hydrocarbons (%)[a]	Deposited carbon (%)[a]	Ketone (%)	Conversion (%)
5.4	4.2	8.6	16.5	31.78	84.3
20.1	7.5	20.1	4.0	23.10	75.2
43.0	4.8	22.0	1.5	8.27	52.5

[a] Reaction conditions: alcohol flow rate 0.024, 0.092 and 0.192 ml/min and oxygen flow rate varied to maintain a 3:1 alcohol to oxygen ratio, temperature 450°C, 60 min reaction time. The amount of carbon for each species is given as a percentage of carbon in.

3.3. Effect of alcohol chain length

Oxygen and a range of the alcohols (C_2–C_7) were passed over the 40% CeO_2/MgO(1) (28 m^2/g) and 5% CeO_2/MgO(1) (33 m^2/g) catalysts at a flow rate of 0.024 ml/min and the appropriate oxygen flow rate to maintain the alcohol to oxygen flow rate at 3:1 at 450°C.

Use of the 5% cerium on magnesia loaded catalyst revealed that the yield of ketone increased significantly with chain length while the amount of aldehyde increased only marginally (Table 2, Fig. 3). The aldol condensation products were the predominant products obtained from the ethanol oxidation reaction (22.7%) with the ketonisation reaction being less significant for this reactant. This trend is reversed for the longer chain alcohols (C_4–C_7) where the yields of aldol products (<6%) were less than the yields of ketonisation products (>11%).

The yield of ketone increased with chain length from C_2–C_4 and then reached a maximum for the C_4–C_7 reactants over the 40% CeO_2/MgO. At the high CeO_2 loading (40%), the conversion is consistently high (>90%) for all the alcohols (C_2–C_7) irrespective of chain lengths. The yield of aldehyde is greater for C_2 than for the C_3–C_7 alcohols.

For the reaction of 1-hexanol over the CeO_2/MgO catalyst the amounts of hydrocarbons and CO_2 produced were monitored with respect to flow rate (Table 3). As the flow rate increases, the yield of hydrocarbon increases with a corresponding decrease in carbon deposited on the surface.

Data suggest that it is important to oxidise the reactant but if surface species are accessible to O_2, then further oxidation occurs. It is possible that the longer the chain the more protected the surface entity to over-oxidation.

A competing reaction to the coupling of the acid is loss of CO_2 to give a surface alkyl. According to the data it appears that any alkyl species are eliminated from the surface prior to coupling. Furthermore, fragmentation occurs, to yield hydrocarbons with less than six carbon atoms. Data for 1-heptanol reactions (5 and 40%) suggest that if surface species are trapped on the surface then coke and not hydrocarbons are obtained. It is, thus, clear that competition between a range of reactions occurs to give the final products formed in the oxidation reaction.

A consideration of the above shows that:

1. over-oxidation of the alcohol to CO_2 or coke accounts for less than 20% of the carbon balance;
2. in general, the formation of hydrocarbons (20–55%), presumably by loss of CO_2 from the surface RCO_2 species, is a significant competitive reaction. High temperatures would favour this reaction;
3. in general, the aldol condensation reaction is not a major competing reaction. This suggests that conversion of alcohol to acid is a rapid reaction that occurs prior to aldehyde coupling on the surface;
4. a reduction in reaction temperature results in a decrease in the reactant conversion.

3.4. The reaction of branched alcohols over 40% CeO_2/MgO

The alcohols 2-propanol, 2-methyl-1-propanol and 2-methyl-2-propanol were passed over a 40% CeO_2/MgO catalyst at a flow rate of 0.024 ml/min and the appropriate oxygen flow rate to maintain the alcohol to oxygen flow rate at 3:1, at 450°C. The resultant products were analysed by GC (Table 4).

2-Methyl-1-propanol coupled to form the symmetrical ketone with a reduced yield (12.7%) when

Table 4
The reaction of 1-butanol, 2-methyl-2-propanol, 2-methyl-1-propanol and 2-propanol over 40% CeO_2/MgO

	Yield (%)[a]			Conversion (%)
	Aldehyde	Ketone ($2n-1$)	Aldol	
1-Butanol	0.7	43.8	3.6	91.6
2-Methyl-1-propanol	8.1	12.7	5.7	39.7
2-Methyl-2-propanol	ND	ND	ND	4.4
2-Propanol	ND	ND[b]	ND	73.9

[a] Major product detected for 2-propanol was acetone (35.73% yield).

[b] Not detected.

compared to the 1-butanol (43.8%). Also of importance is the observation that a high yield of aldol (5.7%) was detected in the reaction. As expected 2-methyl-2-propanol did not give ketones or aldehydes. The reaction of 2-propanol gave acetone (36%) as the only ketone/aldehyde product produced in any noticeable yield.

In a previous study, we noted that a temperature of 450°C was optimal for producing the highest yield of 4-heptanone [11]. This temperature was also used in this study and no further investigation of temperature on the reaction was undertaken.

The proposed reaction mechanism requires that the alcohol be oxidised to the aldehyde and then the carboxylic acid, and that two acid molecules couple to form the symmetrical ketone, CO_2 and water (Fig. 4) [11]. The low ketone yield obtained for the 2-methyl-1-propanol reaction is consistent with this picture and can be rationalised in terms of both a higher steric interference of the reactant methyl group with the surface of the catalyst and the difficulty of coupling of two bulky reactants on the catalyst surface.

3.5. Mixed alcohol systems

A mixture of 1-hexanol (C_6) and 1-heptanol (C_7) were passed over the 40% CeO_2/MgO catalyst under standard reaction conditions. From this reaction mixture, three possible ketonisation coupling reactions are possible, viz. C_6+C_6, C_7+C_7, C_6+C_7 (or C_7+C_6) and the GC data recorded showed that indeed all three ketones were produced. The yields obtained indicate that there is no preference for the $C_7 + C_7$ (8.7%) coupling reaction over the $C_6 + C_6$ (8.7%) coupling

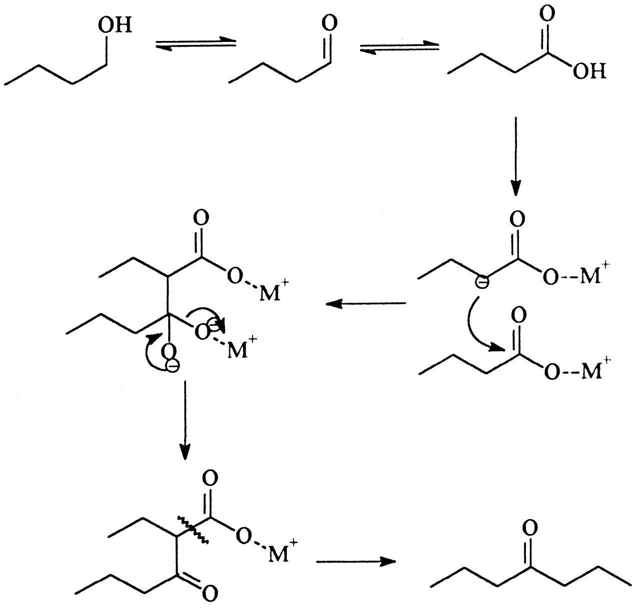

Fig. 4. The proposed mechanism for the coupling of 1-butanol to yield 4-heptanone.

reaction and this finding is consistent with the data given in Table 2. As predicted from a statistical product distribution, twice the yield (21.4%) of the mixed alcohol coupled product ($C_6 + C_7$) over either of the self-condensation products was observed. The data imply that the alcohol reacts with the catalyst surface and that the intermediate acid moiety is mobile on this surface.

The above proposal was confirmed by analysis of the reaction products obtained after passing a mixture of 1-propanol and 1-heptanol over the 40% CeO_2/MgO catalyst using standard conditions. The separate reactions do not give similar yields of ketone (Table 2). The yields obtained show that the $C_7 + C_7$ (15.0%) product is achieved in a higher yield than the $C_3 + C_3$ (4.0%) product. The yield of $C_7 + C_3$ (15.3%) coupled ketone is similar to the yield for the coupling of 1-heptanol on its own. This data suggests that the C_7 and C_3 moieties are available on the surface in equal abundance, but that C_3 does not couple as easily to another C_3 entity as does a C_7 to another C_7 moiety.

4. Conclusions

Our results show that the products formed in the alcohol oxidation reaction are determined by the type of reactant and the surface area of the MgO. By manipulation of reactant variables, it is, thus possible to obtain aldehydes, ketones via the ketonisation reaction, aldol condensation products, hydrocarbons, CO_2 and coke. While many features of the reaction are to still to be ascertained in detail, a picture is emerging of a range of surface species that are generated from alcohols on the CeO_2/MgO catalysts. It is the concentration, stability and mobility of these intermediates that determine the final product.

Further studies to gain a better understanding of these reaction intermediates are underway in our laboratories.

Acknowledgements

We wish to thank the University, THRIP and the NRF for financial support.

References

[1] H. Idriss, C. Diagne, J.P. Hindermann, A. Kinnemann, M.A. Barteau, J. Catal. 155 (1995) 219.

[2] K. Parida, H.K. Mishra, J. Mol. Catal. A: Chem. 139 (1999) 73, and references therein.

[3] R. Pestman, R.M. Koster, A. van Duijne, Z.A. Pieterse, V. Ponec, J. Catal. 168 (1997) 265, and references therein.

[4] R. Pestman, A. van Duijne, Z.A. Pieterse, V. Ponec, J. Mol. Catal. A: Chem. 103 (1995) 175.

[5] K. Okumura, Y. Iwasawa, J. Catal. 164 (1996) 440.

[6] S. Sugiyama, K. Sato, S. Yamasaki, K. Kawashiro, H. Hayashi, Catal. Lett. 14 (1992) 127.

[7] M.A. Barteau, Chem. Rev. 96 (1996) 1413.

[8] Y. Wang, B.H. Davis, Appl. Catal. A 180 (1999) 277.

[9] H. Hattori, Chem. Rev. 95 (1995) 537.

[10] U. Meyer, H. Gorzawski, W.F. Hölderich, Catal. Lett. 59 (1999) 201.

[11] N. Plint, D. Ghavalas, T. Vally, V.D. Sokolovski, N.J. Coville, Catal. Today 49 (1998) 71.