Efficient Synthesis of Acetone from Ethanol over ZnO–CaO Catalyst

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ZnO–CaO (molar ratio 9 : 1) exhibited a high catalytic activity (100% conversion) and selectivity (91%) for formation of acetone from ethanol at 673 K.

Ethanol produced from sugar cane and biomass is being utilized not only as an energy source in place of gasoline, but also as a raw material for synthesis of various chemicals. One of these, acetone, is important as a solvent and raw material for manufacturing methyl methacrylate, methyl isobutyl ketone, *etc.* The direct synthesis of acetone from ethanol has been investigated using catalysts such as ZnO–Cr_2O_3,[1] Fe_2O_3–CaO,[2,3] Cu,[4] and ZnO–Cr_2O_3–K_2O,[5] but the catalytic activities and selectivities are not satisfactory, and ZnO–Cr_2O_3–K_2O which gave the highest yield of acetone is unsuitable because it contains a toxic chromium ion. We now report an efficient catalyst, ZnO–CaO, in which we hoped the acidity (dehydration activity) would be controlled by addition of the basic CaO to the well established dehydrogenation catalyst, ZnO. The catalytic activity and selectivity were compared with those of ZnO–Cr_2O_3–K_2O and some commercially available catalysts containing Zn, Cr, Cu, *etc.*

ZnO and Cr_2O_3 were prepared by hydrolysis of aqueous solutions of their nitrates with aqueous ammonia, followed by drying and calcining in a nitrogen stream at 773 K for 2 h.

Table 1. Activities and selectivities of various mixed oxide catalysts for acetone formation from ethanol at 673 K for 30 min.

Catalyst	Surface area /$m^2 g^{-1}$	Conversion /%	Selectivity/% Acetone	Hydrocarbon	Acetaldehyde
ZnO	7.3	98.6	41	51	8
ZnO–CaO (9 : 1)[a]	13.1	100	91	9	0
ZnO–Na_2O (198 : 1)[a]	6.3	56	66	2	32
ZnO–Na_2O (9 : 1)[a]	4.3	6.2	0	8	92
ZnO–MgO (9 : 1)[a]	19.5	100	63	37	0
CaO	20.3	4.0	45	22	33
ZnO–Cr_2O_3–K_2O (60 : 30 : 1)[b]	23.9	100	88	12	0
ZnO–Cr_2O_3	45.7	100	34	66	0
CuO–ZnO–Cr_2O_3	63.3	100	19	81	0
CuO–ZnO–Al_2O_3	85.9	100	66	34	0
CuO–ZnO	39.4	100	68	32	0

[a] Molar ratio. [b] Weight ratio.

ZnO–CaO, ZnO–MgO, ZnO–Na_2O, and ZnO–Cr_2O_3–K_2O were prepared by kneading a mixture of $Zn(OH)_2$ and, respectively, $Ca(OH)_2$, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$, Na_2CO_3, or $Cr(OH)_3$ and K_2CO_3, followed by drying and calcining as above. $Zn(OH)_2$ and $Cr(OH)_3$ were prepared by hydrolysis of aqueous solutions of their nitrates with aqueous ammonia. The other reagents were all commercial samples of 'guaranteed' quality. ZnO and CaO were prepared by calcining their hydroxides as above. ZnO–Cr_2O_3, CuO–ZnO–Cr_2O_3, CuO–ZnO–Al_2O_3, and CuO–ZnO were commercially available catalysts (Toyo CCI, KMA; Toyo CCI, KMB; Toyo CCI, MDC-02, and Nissan Girdler, G-66B).

Reactions were carried out at 673 K by use of a conventional flow reactor. A nitrogen stream, containing ethanol which was obtained by bubbling nitrogen through an aqueous solution of ethanol maintained at 313 K, was passed at a constant rate through the reactor which contained 0.5 g of catalyst, the residence time being 0.435 s. The partial pressures of EtOH and H_2O were 1.59 and 7.25 kPa, respectively. Products were analysed by gas chromatography. A steady state was reached about 20 min after the start of reaction and was well maintained except in the cases of ZnO and ZnO–MgO where the yields of hydrocarbon gradually decreased during the reaction (2—3 h). The results obtained are shown in Table 1. The ZnO–CaO (molar ratio of Zn : Ca 9 : 1) catalyst led to 100% conversion and 91% selectivity for acetone formation. The hydrocarbons formed as by-products were mainly ethylene and small amounts of methane, propene, and isobutene. The activity of ZnO–CaO was at a maximum for a molar ratio of 9 : 1; other molar ratios led to lower activity. The activities of ZnO–MgO (9 : 1), ZnO–Cr_2O_3–K_2O (60 : 30 : 1 w/w/w), and commercially available catalysts were high but their selectivities were inferior to that of ZnO–CaO (9 : 1). The ZnO–Cr_2O_3–K_2O catalyst whose selectivity is the second best has a disadvantage of containing a toxic chromium ion.

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References

1 M. Ya. Kagan, I. A. Sobolev, and G. D. Lyubarskii, *Ber.*, 1935, **68B**, 1140.

2 M. Ya. Kagan and V. C. Klimenkov, *Zh. Fiz. Khim.*, 1932, **3**, 244 (*Chem. Abs.*, 1933, **27**, 2232).

3 M. N. Goswami and K. P. Koley, *J. Indian Chem. Soc., Ind. and News Ed.*, 1953, **16**, 109 (*Chem. Abs.*, 1955, **49**, 1547e).

4 B. N. Dolgov, B. A. Bolotov, and L. A. Komissarova, *Zh. Prikl. Khim.*, 1955, **28**, 71.

5 G. Geiseler and R. Danneberg, *J. Prakt. Chem.*, 1964, **26**, 296.