Direct production of hydrogen from ethanolic aqueous solutions over oxide catalysts†

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Steam-reforming of ethanol over ZnO gives highly effective production of CO-free H_2: 5.1 mol of H_2 per mol of reacted ethanol is formed at 723 K under 100% ethanol conversion.

There is growing interest in the use of H_2 as an alternative fuel mainly due to environmental aspects.[1,2] Alcohols could constitute a good supply of hydrogen, as they are efficient H_2-reservoirs and could avoid the difficulty of H_2-distribution. In this context, many efforts have been applied to the production of hydrogen from steam-reforming of methanol by using methanol synthesis-based catalysts;[3–5] however, there are fewer papers dealing with ethanol steam-reforming.[6] However, two considerations point to ethanol as an alternative to methanol: (i) the yield of H_2 is higher, (ii) ethanol is a renewable material which can be easily obtained from biomass. As regards the use of supported catalysts in the steam-reforming of ethanol, mainly copper- and cobalt-based catalysts have been studied.[7–9] In both cases the behaviour of supported catalysts was strongly affected by the support used. However, their role remains unclear and no exhaustive studies of transformations of ethanol over individual inorganic oxides under ethanol steam-reforming conditions have been reported.

Here we report the behaviour of several oxides, with a wide range of redox and acid–base properties, in the steam-reforming of ethanol. A high H_2O : ethanol ratio was used to explore the possibility of using ethanol as obtained from biomass (aqueous solutions of concentration *ca.* 15% in ethanol are obtained from sugar cane or starch-rich grains). In some cases total conversion of ethanol and high selectivity to the reforming reaction were attained.

The following oxides with the indicated BET surface area were used: MgO (prepared by adding ammonia to a $MgCl_2$ solution, 110 $m^2 g^{-1}$), γ-Al_2O_3 (Girdler, 188 $m^2 g^{-1}$), SiO_2 (Degussa–Hüls, 200 $m^2 g^{-1}$), TiO_2 (Degussa–Hüls, 45 $m^2 g^{-1}$), V_2O_5 (Merck, 22 $m^2 g^{-1}$), ZnO (1) (Asturienne New Jersey, 11 $m^2 g^{-1}$), ZnO (2) (prepared by decomposition of $3ZnO\cdot 2ZnCO_3\cdot 3H_2O$, 100 $m^2 g^{-1}$), La_2O_3 (Merck, 11 $m^2 g^{-1}$), CeO_2 (Aldrich, 17 $m^2 g^{-1}$), Sm_2O_3 (Merck, 9 $m^2 g^{-1}$). Steam-reforming of ethanol was carried out between 573 and 723 K, at atmospheric pressure, using a 1 : 13 : 70 $C_2H_5OH : H_2O : Ar$ stream (molar ratio) and 0.1 g of the appropriate oxide diluted with inactive SiC, under a gas hourly space velocity (GHSV) of 5000 h^{-1}. After periods of 2 h at each temperature, the temperature was increased consecutively from 573 to 623, 673 and 723 K; at the final temperature the reaction was conducted over a period of 20 h. Products were analysed on-line by gas chromatography. Hydrogen was analysed with a TCD using Ar as a carrier gas, CO and CO_2 were analysed with an FID after passing through a methanizer, and hydrocarbons as well as oxygenated products were separated with a capillary column and analysed with an FID.

Conversion of ethanol increased with temperature for all samples (see Fig. 1). However, significant differences between them in terms of activity, stability and selectivity were found. The temperature required for total conversion was lower for V_2O_5 and γ-Al_2O_3 (623 K) than for the other oxides, and even at 723 K, conversions of $< 10\%$ were obtained over MgO and SiO_2 and were *ca.* 20% over La_2O_3 and CeO_2. A comparison between conversion values, after 20 h of reaction at 723 K and initial values (after 2 h of reaction at 723 K), shows a high deactivation process for TiO_2 and Sm_2O_3. Conversion diminished from 100% to 3.9% for TiO_2 and from 67.2% to 37.9% for Sm_2O_3. After reaction these two oxides appeared black, and carbon deposition during reaction could be responsible for the drop in activity. Table 1 shows the product selectivity and the ethanol conversion values after 20 h at 723 K (GHSV = 5000 h^{-1}) under the steam-reforming conditions mentioned above for catalysts with conversion $> 5\%$. The values of selectivity obtained with the different catalysts can be explained in terms of the contribution of the following reactions: ethanol steam-reforming (1), ethanol decomposition to CH_4 (2), ethanol dehydration (3), ethanol dehydrogenation (4), ethanol decomposition to acetone (5) and water–gas shift reaction (WGSR) (6).

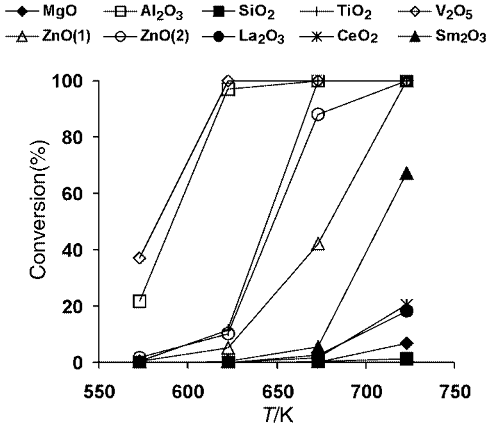

Fig. 1 Ethanol conversion as a function of temperature for different oxides. Reaction conditions: total pressure 1 atm, $C_2H_5OH : H_2O : Ar = 1 : 13 : 70$ (molar ratio), GHSV = 5000 h^{-1}.

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{1}$$

$$CH_3CH_2OH \rightarrow CO + CH_4 + H_2 \tag{2}$$

$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O \tag{3}$$

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2 \tag{4}$$

$$2CH_3CH_2OH \rightarrow CH_3COCH_3 + CO + 3H_2 \tag{5}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

Negligible steam-reforming of ethanol was observed over MgO and γ-Al_2O_3. Over γ-Al_2O_3 only the dehydration of ethanol to ethylene was observed and over MgO high selectivity to acetaldehyde was obtained. These findings are consistent with the acidic and basic characteristics of γ-Al_2O_3 and MgO respectively,[10] which in addition do not have redox properties.

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† Dedicated to Professor Rafael Usón on the occasion of his 75th birthday.

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Table 1 Catalytic performance on a C_2H_5OH–H_2O–Ar ($C_2H_5OH : H_2O = 1 : 13$ molar ratio) stream at 723 K and atmospheric pressure

			Product selectivity[a] (%)									
Sample	GHSV/h^{-1}	Conv.(%)	H_2	CO	CO_2	CH_4	C_2H_4	C_3H_6	CH_3CHO	CH_3COCH_3	mol H_2/ mol EtOH	mol CO_2/ mol EtOH
MgO	5000	6.9	45.9	—	0.4	0.9	6.8	1.7	44.3	—		
Al_2O_3	5000	100	—	—	—	—	100	—	—	—		
V_2O_5	5000	100	36.7	1.1	19.1	1.2	33.3	0.4	8.2	—		
ZnO (1)	5000	100	61.4	—	18.5	1.1	1.7	0.5	10.2	6.6		
ZnO (2)	5000	100	64.6	—	21.1	0.7	0.6	0.3	0.2	12.5		
La_2O_3	5000	19.9	44.4	—	17.7	4.5	33.0	0.4	—	—		
CeO_2	5000	24.4	52.4	0.2	15.9	1.1	18.9	0.1	—	11.4		
Sm_2O_3	5000	37.9	32.0	—	11.9	0.9	53.3	0.5	—	1.4		
ZnO (2)	2300	100	60.4	—	20.2	0.5	1.0	0.2	2.6	15.1	1.6	0.5
ZnO (2)	3800	100	63.2	—	21.0	0.4	1.0	0.2	3.4	10.8	2.0	0.7
ZnO (2)	9900	100	65.0	—	21.8	0.3	1.1	0.2	5.9	5.8	2.4	0.8
ZnO (2)	19000	100	72.0	—	23.8	0.3	1.6	0.2	0.9	1.2	4.3	1.4
ZnO (2)	22000	100	73.4	—	24.3	0.5	1.0	0.1	0.4	0.3	5.1	1.7

[a] Water not included.

The product distribution for the remaining oxides indicates that the steam-reforming of ethanol took place. However, all samples in Table 1 except zinc oxides, showed significant yields in the dehydration of ethanol. For V_2O_5 the production of ethylene can be related to its acidic properties.[10,11] On the other hand, the dehydration of ethanol over La_2O_3 and Sm_2O_3 has been proposed to occur over basic centres,[11] with the production of ketones from alcohols also related to basic centres in the oxides. The high conversion values and high selectivity to CO_2 and H_2 obtained over ZnO (1) and ZnO (2) is of note. Over these oxides the main reactions under the experimental conditions used were the decomposition of ethanol to acetone, the reforming of ethanol and the WGSR. The decomposition of ethanol to acetone is well documented over ZnO-based catalysts.[12,13] This takes place *via* several successive reactions such as dehydrogenation and aldol condensation over basic centres. The performance of ZnO in the steam-reforming of ethanol could be a consequence of its basic and redox characteristics. The basic properties should be related to the dehydrogenation of ethanol to acetaldehyde and then, its specific redox characteristics could help to aid the steam-reforming reaction.

The yield of acetone is expected to be affected by the contact time. A deeper study of the transformations of ethanol over ZnO (2) as a function of contact time indicated that it is possible to have a very high yield in the reforming of ethanol and to minimize the yield of all the other ethanol transformations. Table 1 also compiles some results obtained for GHSV ranging from 22 000 to 2300 h^{-1}. Different space velocities were obtained by dilution of the C_2H_5OH–H_2O mixture (1 : 13 molar ratio) with Ar, after each change the system was stabilised for 2 h and then the products were analysed. In all cases total conversion of ethanol was obtained and no CO was detected (detection limit of CO 17 ppm). When the reaction was conducted at 22 000 h^{-1}, only 2.3% of the total products were other than H_2 or CO_2. Under these conditions, values of 5.1 mol H_2 and 1.7 mol CO_2 per mol of reacted ethanol were recorded representing 85% of the theoretical values that can be obtained from ethanol reforming. This finding, together with the absence of CO production (or at least < 17 ppm) indicate that a ZnO-based catalytic system may be used for H_2 production for fuel cells. Moreover, at a practical level, bioethanol could be used as raw material.

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