Selective Oxidation of Ethanol and 1-Propanol over V–Mg–O/TiO_2 Catalyst

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Ethanol and 1-propanol can be selectively oxidized to ethanal and propanal, respectively, by V–Mg–O catalyst supported on TiO_2 (anatase). Aldehyde yields up to 73% and 66% for ethanal and propanal, respectively, were achieved in the temperature range 573–623 K. The catalyst was rather inactive for the further oxidation of aldehyde products to carboxylic acids.

In the last decade, much attention has been devoted to produce olefins and oxygenates by direct oxidation of light paraffins. There are three main motivations behind these researches. The first one in paraffins is less toxic than aromatics. The second one is paraffins are cheaper than olefins. And the last one is the oxidation reaction is thermodynamically more favorable at lower reaction temperature than dehydrogenation reaction which requires high temperature. Only few, however, could achieve industrial application. An example is the replacement of benzene by butane in maleic anhydride production. The future of the oxidative dehydrogenation of paraffins to olefins is still in doubt since a suitable catalyst has yet to be found. The main problem is the fact that paraffin is rather inactive than its respective olefin. A catalyst capable to oxidize paraffin is usually very reactive for the olefin product formed.[1]

Using an alcohol as reactant is another alternative. C_1–C_4 alcohols can be produced by fermentation of agricultural products. Although the alcohol obtained from fermentation process has low concentration, the possibility to convert this low concentration feed to a more expansive product exists. In this study the gas phase oxidation process is selected since this process operates at low reactant concentration to avoid explosive mixture.

V–Mg–O catalyst system has found some limited success in the oxidative dehydrogenation reaction.[2-6] To the best of our knowledge, there is no published information about supported V–Mg–O catalyst. V_2O_5 has been known to have strong interaction with MgO and TiO_2(anatase). Therefore, in our research we experimentally supported V–Mg–O on TiO_2 (anatase) and applied this new catalyst system to the gas phase oxidation of alcohols.

The catalyst studied 9V2MgTi (8.7 wt% V_2O_5, 2 wt% Mg, surface area, BET method, 9.27 m^2g^{-1}) was prepared by wet impregnation method. TiO_2 was added to an aqueous solution of NH_4VO_3 and dried at 353 K until achieving a thick paste. The obtained paste was calcined in air at 823 K for 6 h to convert the paste into V_2O_5/TiO_2. Then, Mg was introduced into V_2O_5/TiO_2 by impregnation from $Mg(NO_3)_2$ solution. The suspension was dried and calcined again at the conditions mentioned above. The XRD pattern of the obtained 9V2MgTi catalyst showed only the peaks of TiO_2(anatase). Surface analysis by FT-IR spectroscopy showed three IR absorption bands around 976, 920 and 878 cm^{-1} which can be assigned to magnesium pyrovanadate species ($Mg_2V_2O_7$).[5,7]

The catalytic performance test was performed in a quartz fixed-bed reactor (6 mm i.d.) packed with 0.3 gram of catalyst (100–150 mesh). Alcohols (ethanol and 1-propanol) were fed via a saturator. Pure dry air was used as oxygen source and nitrogen was used as balancing gas. The feed contained 8 vol% alcohol and 5 vol% oxygen, total flow rate 100 mL min^{-1}. The reaction was studied in the temperature range 473–773 K. Combustion products (CO, CO_2, and H_2O) were analyzed using a gas chromatograph Shimadzu GC 8A equipped with a TCD and a MS-5A Porapak-Q column. Hydrocarbons were analyzed using a gas chromatograph Shimadzu GC 14A equipped with a FID and a VZ-10 column. Oxygenate compounds were analyzed using a gas chromatograph Shimadzu GC 14B equipped with a FID and a capillary column. Total carbon balance in product stream was with in the range 100 ± 5% The selectivity towards products was calculated from the following expression:

$$\%S = \frac{\text{mole product formed}}{\text{mole alcohol converted}} \times \frac{\text{no of C atom of product}}{\text{no of C atom of alcohol}} \times 100$$

The result obtained from ethanol oxidation is shown in Figure 1. Between 473–623 K, ethanol conversion rapidly increased up to a maximum about 86% while selectivity to ethanal was still higher than 80%. The other observed products were mainly CO_2, with traces of CH_4, C_2H_4, and C_3H_6. No CO appeared in the product stream. The maximum ethanal yield, 73%, occurred at 623 K. Beyond 623 K, both ethanol conversion and ethanal selectivity slightly decreased.

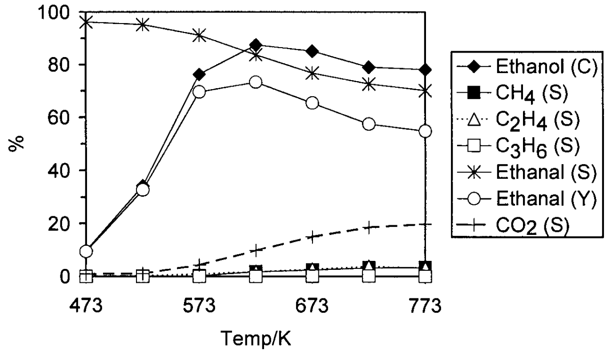

Figure 1. Ethanol oxidation: C - conversion, S - selectivity, Y - yield.

1-Propanol conversion and product selectivities are shown in Figure 2. The conversion of 1-propanol increased rapidly between 473–573 K, reaching a maximum conversion about 85%. Beyond 573 K, the conversion was quite constant. The main products observed were propanal and CO_2. Methanal, CH_4, C_2H_4, and C_3H_6 also appeared in the product stream. No CO could be detected in the product stream. The maximum propanal yield (about 66%) was achieved at 573 K.

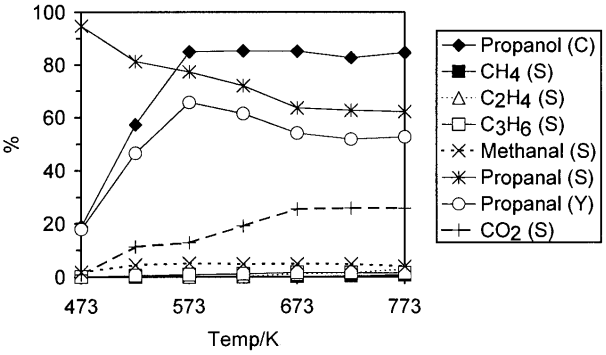

Figure 2. 1-Propanol oxidation: C - conversion, S - selectivity, Y - yield.

The mass balance of O_2 showed that O_2 was nearly completely consumed at 623 K for ethanol and 573 K for 1-propanol. This is the reason why beyond these temperatures, ethanol and 1-propanol conversions were quite constant. For ethanol oxidation, the slight decrease of ethanol conversion when the reaction temperature was higher than 623 K was the result of the competitive reaction between ethanol/ethanal with O_2. At high temperature, part of oxygen reacted with ethanal rather than ethanol. This reaction caused the decrease in ethanal selectivity as well as ethanol conversion.

1-Propanol seems to be oxidized faster than ethanol. In addition, the oxidation of 1-propanol produces small molecule products (formaldehyde, methane, and ethene) more than the ethanol oxidation. These differences can be explained by considering the structure of both alcohols.

The difference between ethanol (CH_3–CH_2OH) and 1-propanol is 1-propanol has an methylene group (CH_3–$\mathbf{CH_2}$–CH_2OH). The C–H bond of the methylene group is easier to be broken than the C–H bond of the carbon atoms at both ends of the carbon chain. 1-Propanol can react via its hydroxyl group or the methylene group. While ethanol can react mainly through its hydroxyl group. Therefore, 1-propanol has more chance to react with the catalyst surface than ethanol.

The reaction via the methylene group of a C_3 molecule may cause the breaking of the C_3 molecule, resulting in the formation of formaldehyde and small molecules. Selectivity to formaldehyde up to 5% at 573 K (Figure 2) was observed. No formaldehyde was detected during the oxidaiton of ethanol.

It is known that when vanadium oxide forms a new compound with MgO, vanadium ion can form bridging oxygen structure, V–O–V, apart from V=O species. This V–O–V species plays role as selective oxidation site. For the oxidation of ethanol, the reaction mechanism shown in Figure 3 is purposed.

The selective oxidation mechanism shown in Figure 3 was modified from that proposed in literature.[8,9] Ethanol is adsorbed on a V–O–V site via the H atom of the hydroxyl group (step 1) to produce an adsorbed alkoxide species (step 2). The H-atom of the alcohol hydroxyl group is eliminated in the form of hydroxyl group by an O anion on the catalyst surface. The surface hydroxyl group further subtracts an H atom of the C atom attaches to the O atom to form water and an aldehyde product. Desorption of water causes a vacant oxygen site, V–□–V, on the catalyst surface (step 3). Finally, the V–□–V site is reoxidized by an oxygen molecule from the gas phase to form V–O–V again (step 4). 1-Propanol is believed to react in the same way as ethanol.

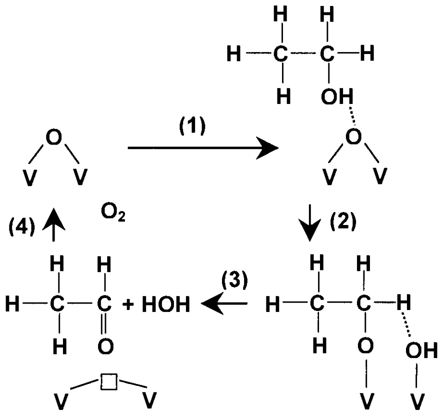

Figure 3. Proposed scheme for ethanol oxidation to ethanal.

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