From glycerol to allyl alcohol: iron oxide catalyzed dehydration and consecutive hydrogen transfer†

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Using iron oxide as catalyst, glycerol can be converted to allyl alcohol through a dehydration and consecutive hydrogen transfer.

Due to decreasing petroleum reserves and increasing energy demand, biomass, as a sustainable and renewable alternative source, has attracted great interest.[1] Biodiesel is one of the few examples to have been produced on a large scale and production will continue to increase in the coming years.[2] Thus, as the byproduct of biodiesel production, glycerol is considered as a potential biorefinery feedstock. To date, various processes have been developed to obtain valuable chemicals from glycerol, such as reforming,[3] oxidation,[4] hydrogenolysis,[5] etherification,[6] and dehydration.[7] For the selective dehydration of glycerol to acrolein, catalysts with strong acidity are commonly used and acrolein yields of up to 75% can be obtained. However, the catalysts often suffer from fast deactivation.[7]

The selective hydrogenation of acrolein to allyl alcohol is of great interest from both the industrial and academic point of view.[8] However, since the hydrogenation of the C=C double bond is strongly favored over hydrogenation of the C=O double bond, only in a few cases could allyl alcohol be highly selectively produced by the hydrogenation of acrolein. One possibility to selectively hydrogenate the C=O double bond is the use of supported silver[9] or gold[10] catalysts; another possibility is to go through a gas-phase hydrogen transfer reaction which is similar to the Meerwein–Ponndorf–Verley reduction.[11] Recently, we reported the pseudomorphic transformation of mesoporous Co_3O_4 and ferrihydrite to CoO and Fe_3O_4.[12] Now we have studied this system from the catalytic point of view, and discovered that both materials can catalyze not only the dehydration of glycerol to acrolein, but also consecutively the transfer hydrogenation to allyl alcohol, albeit presently still in only moderate yields. While this observation alone is interesting, the mesostructured oxides are obtained only after a complex synthesis sequence, and thus alternative, cheaper catalysts would be needed. Iron oxide would be preferred over cobalt oxide, since it is less toxic and cheaper. In addition, a simpler synthetic access to an active catalyst is required. Herein we report a simple synthesis of iron oxide with high surface area, over which almost full conversion of glycerol and 20–25% yield of allyl alcohol could be achieved. The selectivity in the second step, the transfer hydrogenation to allyl alcohol, is close to 100%, and only slight deactivation was observed after 72 h.

Phosphorus containing Fe_2O_3 nanoparticles were synthesized through a very simple procedure by adding a small amount of $Al(H_2PO_4)_3$ to diluted $Fe(NO_3)_3$ aqueous solution and then heating the mixture up to 380 °C for 1 h (experimental details are available in the Supporting Information†) until dryness. Afterwards Fe_2O_3 nanoparticles with a nearly amorphous structure and a surface area of 164 $m^2 g^{-1}$ could be collected (ESI†, Fig. S2 and S3). The addition of $Al(H_2PO_4)_3$ is necessary to obtain high surface areas; without phosphate addition Fe_2O_3 materials with much lower and poorly reproducible BET surface areas (varying between 47 and 85 $m^2 g^{-1}$ in three different batches) were obtained. The catalytic performance of phosphate containing Fe_2O_3 with high surface area in glycerol conversion was tested, and the result is shown in Fig. 1a. It can be seen that at a space velocity (GHSV) of 96.4 h^{-1}, full conversion of glycerol could be achieved in the first 6 h, and after 24 h the conversion still remains at around 95%, which is quite remarkable compared with former reports. However, even more interesting is the fact that allyl alcohol was formed as the main product, besides acrolein and hydroxyacetone, although no molecular hydrogen was present in the system. The unusually high and unexpected yield of allyl alcohol is very interesting, because allyl alcohol is the product of the selective hydrogenation of the C=O double bond of acrolein, while propanal or even propanol would be expected to form as the product of C=C double bond hydrogenation. Acrolein, hydroxyacetone and allyl alcohol were quantitatively analyzed, and the results are shown in Fig. 1b. It can be seen that the distribution of the products is quite stable over reaction time and 6–9% of acrolein, 18–20% of hydroxyacetone, and 20–25% of allyl alcohol could be obtained, which add up to 50–60% of the total carbon balance. Trace amounts of

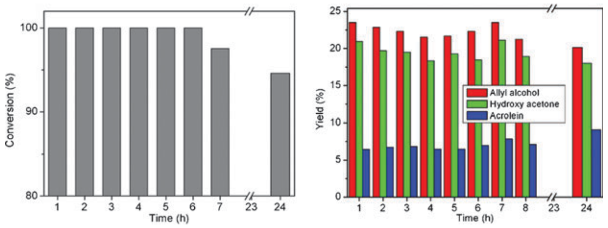

Fig. 1 (a) Glycerol conversion and (b) product distribution at 320 °C with a space velocity of 96.4 h^{-1}.

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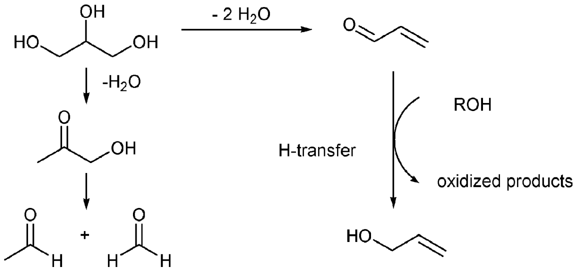
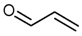
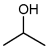
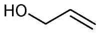
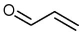
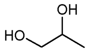
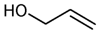
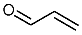
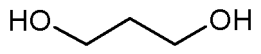
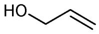
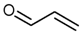
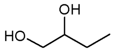
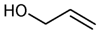
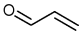
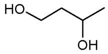
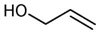
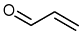
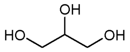
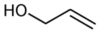
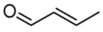
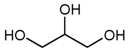
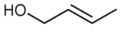
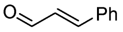
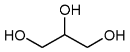
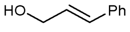


Scheme 1 Possible reaction pathways from glycerol to allyl alcohol.

Table 1 Yields of hydrogen transfer reactions between different α,β-unsaturated aldehydes and alcohols catalyzed by iron oxide

Entry	Substrate	H-donor	Product	Yield [%][a]
1[b]				1.57
2[b]				1.36
3[b]				4.50
4[b]				2.18
5[b]				6.50
6[c]				16.90
7[d]				1.72
8[d]				3.87

[a] All yields are based on GC results with quantification. [b] Acrolein was premixed with the corresponding alcohol at a molar ratio of 1 : 1 and then pumped through the reactor at the same temperature, catalyst amount and flow rate. [c] Glycerol : acrolein molar ratio = 2.4 : 1, allyl alcohol yield was calculated based on the amount of glycerol. [d] Crotonaldehyde and cinnamaldehyde were mixed with 50 wt% glycerol by a supersonic bath since they are not miscible with glycerol (detailed procedures are given in ESI†).

propanal, acetone and acetaldehyde were also detected by GC-MS. However, since the signal intensities are very low, these species were not calibrated (detailed discussion about the total carbon balance is available in the ESI†). Since only a very small amount of propanal was formed and propanol was not detected at all, it can be concluded that iron oxide can not only catalyze the dehydration of glycerol to acrolein, but also consecutively the selective hydrogenation of acrolein to allyl alcohol.

Studies on the possible mechanism for the formation of allyl alcohol were then carried out. Bergman *et al.* recently reported the preparation of allyl alcohol *via* a formic acid-mediated deoxygenation of glycerol.[13] However, stoichiometric amounts of formic acid are needed in that case, and this mechanism is highly unlikely for the current system, since formic acid was never detected in our experiments. The probable reaction sequence is shown in Scheme 1. Hydroxyacetone and acrolein are both products of the dehydration of glycerol, and allyl alcohol could be obtained either through the direct hydrogenation of acrolein with molecular hydrogen, or through a hydrogen transfer reaction with an alcohol (glycerol or some intermediates in this case) as hydrogen donor. The possibility of direct hydrogenation was excluded by two facts. Firstly, no molecular hydrogen was supplied to the system; secondly, pure acrolein instead of glycerol was pumped through the reactor under the same conditions with and without hydrogen, and no allyl alcohol was detected in either case.

Catalysts such as MgO, ZrO_2 and $MgAl_2O_4$ are known to be active for hydrogen transfer reactions,[11] while iron oxide has never been reported for this type of reaction. Therefore, several reactions between different alcohols and α,β-unsaturated aldehydes were carried out and the results are shown in Table 1. It can be seen that hydrogen transfer reactions can indeed take place in all cases, although the yields of the allylic alcohols are considerably lower than for the iron oxide–glycerol system. It seems that the hydrogen transfer does not only include the reaction between glycerol and acrolein. Instead, probably intermediates with hydroxy groups forming during the reaction play an important role, and these intermediates together with glycerol then react as hydrogen donor with acrolein. Further research on a more detailed mechanism is still ongoing in our laboratory, although this is rather difficult due to the complexity of the system. However, it is clear that iron oxide plays a rather unique role, even when compared with the already known hydrogen transfer catalysts. For comparison, MgO and $MgAl_2O_4$ with high surface areas were synthesized and used for both glycerol conversion and the reaction between glycerol and acrolein. In all cases, the yield of allyl alcohol was below 1% (the preparation procedures and properties of the MgO and $MgAl_2O_4$ materials are supplied in the ESI†).

To better understand the system, studies on the structure and components of the catalyst before and after the reaction were carried out. The catalyst used in the current system is quite complicated. On the one hand, according to our previous report, the catalyst should be reduced from Fe_2O_3 to Fe_3O_4 during the reaction.[12] On the other hand, to obtain high surface area, $Al(H_2PO_4)_3$ was added which probably leads to the formation of Al_2O_3 and phosphates. As far as the structural change of the catalyst during the reaction is concerned, XRD analysis showed that the reduction of Fe_2O_3 to Fe_3O_4 also took place in the current system during reaction (ESI†, Fig. S4) and further studies confirmed that the catalyst reduction procedure was already finished after 6 h. The broadening of the XRD reflections indicates that the size of the catalyst is still very small. However, nitrogen sorption measurements showed that after 24 h, the BET surface area of the catalyst had dropped significantly from 164 to 16 $m^2\ g^{-1}$. This could be caused by the carbon depositions on the surface of the catalyst. High glycerol conversion was observed before and after the reduction of Fe_2O_3 to Fe_3O_4, however one cannot compare the activities of Fe_2O_3 and Fe_3O_4 based on the data given in Fig. 1a, since at 100% conversion no difference could be seen any more. The experiment was then carried out at the same temperature (320 °C) but at increased GHSV of 413 h^{-1} instead of 96.4 h^{-1}, and the results are shown in ESI†, Fig. S5. It can be seen that the glycerol conversion dropped to 30–40%. However, no deactivation could be observed over 24 h, which indicates that the catalyst has very good stability and both Fe_2O_3 and Fe_3O_4 can effectively catalyze this reaction. To further confirm this, the catalyst after the reaction (already reduced to Fe_3O_4) was reused at 320 °C with a GHSV of 96.4 h^{-1}. Glycerol conversions of 80–90% were reached over 24 h and no deactivation was observed (ESI†, Fig. S6). In the solid acid catalyst catalyzed glycerol dehydration to acrolein, the deactivation of the catalyst is usually attributed to carbon deposition on the surface of the catalyst.[7] For the catalyst system described here, thermogravimetric (TG) analysis of the catalyst after 24 h reaction time (320 °C, GHSV 96.4 h^{-1}) revealed a weight loss of 22.8% (ESI†, Fig. S7a). In interpreting this result, one also needs to take into account that the catalyst which was collected after reaction had already been reduced to Fe_3O_4. During the TG measurement, it would be re-oxidized to γ-Fe_2O_3 (as also confirmed by DSC results). Taking the 3.7% weight gain resulting from the oxidation into account, a total weight loss of 26.5% can be calculated. This might partly explain why the nitrogen sorption measurements showed that after 24 h, the BET of the catalyst dropped significantly from 164 to 16 $m^2\ g^{-1}$. The broadening of XRD reflections of the material (ESI†, Fig. S4b) indicates that the particle size is still small, and the reduction in surface area is thus probably caused by pore blocking. When the reaction time was further prolonged to 72 h (320 °C, GHSV 96.4 h^{-1}), the weight loss increased to 31.6% (ESI†, Fig. S7b), and accordingly a reduced glycerol conversion of 90.4% and allyl alcohol yield of 16.3% were observed.

As far as the presence of Al_2O_3 and phosphates is concerned, one would expect that their acidity would have an effect on the formation of acrolein and consequently on the whole reaction, since the dehydration of glycerol to acrolein is normally catalyzed by catalysts with strong Brønsted acidity. To confirm this, another method was used to synthesize Fe_2O_3 nanoparticles with reproducible BET surface area (85 $m^2\ g^{-1}$) without the addition of $Al(H_2PO_4)_3$ (detailed synthesis procedure is available in the ESI†). Glycerol conversion and product distribution are shown in ESI† Fig. S8 and Fig. S9, respectively. Glycerol conversions of close to 100% and allyl alcohol yields of around 25% could be observed in the first 6 h, indicating that iron oxide is the active species and the addition of $Al(H_2PO_4)_3$ in principle does not play a crucial role. The Brønsted acidity needed for the glycerol dehydration could then come from both the hydroxy groups on the surface of iron oxide and the autoprotolysis of water on the surface defects of iron oxide at a temperature as high as 320 °C. Since the Brønsted acid sites are not as strong as in typical solid acid catalysts such as zeolites and sulfated zirconia, the conversion of glycerol is also lower. This lower activity is actually advantageous for this system since unreacted glycerol may be needed as the hydrogen donor in the following hydrogen transfer reaction. However, it is noteworthy that without the addition of $Al(H_2PO_4)_3$, a more significant deactivation of the catalyst was observed (glycerol conversion dropped to 80% after 24 h and allyl alcohol yield decreased to 20%). However, the reason for the better stability of the phosphorus containing sample is still not clear.

In summary, a process for the conversion of glycerol to allyl alcohol over an iron oxide catalyst was discovered. A dehydration and consecutive hydrogen transfer mechanism is proposed, although the details of how the hydrogen transfer takes place are still under investigation. The iron oxide catalyst shows high activity and good stability, and due to its low price, easily tunable structures and morphologies, further improvements can be expected which may even open the route to practical applications.

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