SOME CONCEPTUAL THOUGHTS ON THE CONVERSION OF GLYCEROL

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In recent times there are considerable efforts to value add to the products of glycerol, a conventional byproduct of the bio-diesel production. A variety of catalytic routes have been examined with the objective of generating valuable products. In the following reaction scheme we have listed a few of the value added products from glycerol.

Reaction 1 $C_3H_8O_3$ (glycerol) ----------→ $CH_2(OH)COCH_3(l) + H_2O$

$\Delta H^0_{298} = -2$ kJ/mol and $\Delta G^0_{298} = -48.2$ kJ/mol.

Reaction 2 $CH_2(OH)COCH_3 + H_2$ ----→$CH_2(OH)CH(OH)CH_3(l)$

$\Delta H^0_{298} = -57$ kJ/mol and $\Delta G^0_{298} = -14.6$ kJ/mol.

Reaction 3 $C_3H_8O_3$ (glycerol) -------→ $CH_2(OH)CH_2CHO(l) + H_2O$ (g)

$\Delta H^0_{298} = 32.30$ kJ/mol and $\Delta G^0_{298} = -16.4$ kJ/mol.

Reaction 4 $CH_2(OH)CH_2CHO(l) + H_2(g)$ ------→$CH_2(OH)CH2CH_2(OH)(l)$

$\Delta H^0_{298} = -70.50$ kJ/mol and $\Delta G^0_{298} = -42.5$ kJ/mol.

Reaction 5 $CH_2(OH)CH_2CH_2OH$ (l) $+H_2$ ----→ $CH_3CH_2CH_2OH$ (l) $+ H_2O(g)$

$\Delta H^0_{298} = -79.5$ kJ/mol and $\Delta G^0_{298} = -91,9$ kJ/mol.

It must be stated that we have chosen only a set of reactions for this discussion. There are a few other reactions possible and also there are further reactions by which one can get other value added products like acrolein. These reactions are not considered for this discussion. It may be noticed that the change of thermodynamic parameters at hypothetical condition of 298 K are also given for each of these reactions.

First some general remarks can be made on the available thermodynamic data given.

1. All the five reactions appear to be feasible reactions from the sign and values of standard free energy change.
2. Though n-propanol formation may be more favourable as seen from the free energy data the availability of hydrogen may restrict this reaction.

3. Generally it appears that the formation of 1, 2 or 1, 3 propanediol is the next set of facile reactions.

Ouyang et al., have considered these reactions in addition to various other reforming reactions and shown graphically the variation of the value of equilibrium constant with temperature. Considering the values of equilibrium constant for these five reactions at a temperature of 500 K, it can be seen that reaction 5 has the highest value ($\sim 10^{13}$) while the reaction 1 has a value ($\sim 10^{8}$) while reactions 3 and 4 have nearly the same value around ($\sim 10^{4-5}$) while the reaction 2 has the lowest value around (10^{2}). This implies in the glycerol aqueous phase reforming one can hope to get hydroxyl acetone while the production of 1,2 or 1,3 hydroxypropanediol is not that much favourable. Probably these two products are the subsequent reaction to the primary reactions from glycerol producing either hydroxyl acetone or 3-hydroxy propionaldehyde.

The main purpose of writing this note is to comment on the selectivity issue normally encountered in the catalytic studies. Even though we may be coming in the future on other aspects of glycerol conversion to value added products it is necessary at this stage to comment on the selectivity issue since this is one of the standpoints on which the investigations for new type of catalysts are being pursued.

In the aqueous reforming of glycerol, it may be necessary one has to consider the sequence of reactions and evaluate the possible selectivity. From the consideration of the values of equilibrium constants given above, it can be considered that the primary reaction can be either generation of hydroxyl acetone or 3hydroxypropanaldehyde and these primary products react subsequently to give either 1,2 or 1,3 propanediol. It is also possible under favourable conditions the most stable 1-propanol may be formed to a greater extent.

Now let us consider the selectivity aspect for the catalytic reaction. As we know the selectivity mainly depends on the values of the equilibrium constants for the coupled equilibria. For example if we are interested in 1, 2 propanediol then equilibrium one and 2 have to be combined and the net value (for the two coupled equilibria) will control the extent of formation of 1, 2 propanediol. It is therefore possible to predict the possible selectivities in any of the sequence that one considers the product of choice. However these predicated selectivities differ from the experimentally observed selectivities mainly because one does not maintain the exact experimental conditions that are governing the equilibria that have been represented by the above 5 equations.

The dehydration route as it is given in these five reactions seems to proceed either through the formation of hydroxyl acetone which yields the 1, 2 propanediol or through the aldehyde route which can give rise a variety of products including the 1,3 propanediol. Subsequent to the formation of 1, 3 propanediol one can generate either 1-propanol or other alcohols like ethanol or methanol. This reaction network that has been discussed does not consider other possible products like acrolein.

It is proposed to consider other aspects in the part 2 of this series.

Reference

1. K.Ouyang, Y.Huang, H.Chen, T.Li, F.Cao and D.Fang, Front.Chem.Eng.China, DOI 10.1007/s11705-010-0541-6.