ACTIVE SITES IN THE CARBON OXIDE HYDROGENATION ON OXIDE CATALYSTS

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Methanol synthesis by the hydrogenation of carbon monoxide or carbon dioxide has been a subject of intense research recently. Substantial amount of work has been performed on the prototype of the commercial copper-zinc oxide catalyst to address the questions of the nature of the active site and the reaction mechanism [1]. Methanol can also be produced either catalytically or by stoichiometric reactions on simple oxides. Natta has summarized the early work using various ZnO catalysts [2]. He reported that ZnO of different preparations exhibit different catalytic activities and selectivities. Unfortunately, these catalysts were not well characterized by today's standard, and they also contained impurities. Thus it was not possible to identify the importance of surface structure from those data.

Recently, the methanol synthesis reaction has been studied more extensively on a number of oxides, including ZrO_2 and ZnO. On these two oxides, one particularly interesting observation is that pretreatment of the oxides by a CO and H_2 mixture greatly enhances the methanol production rate from CO in the case of ZrO_2 [3], and from CO_2 in the case of ZnO [10]. Unfortunately, these catalysts undergo deactivation. In fact, deactivation is so severe on ZnO that methanol is considered to be produced by a stoichiometric and not a catalytic reaction.

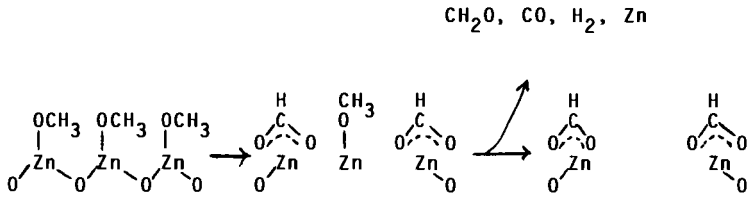
Insight into the nature of the active site on ZnO that interacts with CO or CO_2 is obtained from the study of the decomposition of methanol and 2-propanol. When methanol was decomposed on single crystal ZnO surfaces using temperature programmed decomposition technique, it was found that the Zn-polar face is the most active surface [4]. This observation has been later substantiated by the catalytic decomposition of 2-propanol on different crystal planes of ZnO [5]. The turnover frequencies at 455°C and the activation energy of this reaction are shown in the following table:

Surface	Turnover frequencies at 455 C, $X10^{-3}$ s^{-1}	Eact, kcal/mole
Zn-polar	1.5	11.7
stepped nonpolar	0.4	9.6
O-polar	0.35	8.4

Although similar catalytic measurements on methanol decomposition have not been made, the similarity in the mechanism between 2-propanol dehydrogenation to acetone and methanol dehydrogenation to CO, and the fact that a similar trend in reactivity is observed in temperature programmed

decomposition of both alcohols suggest that a similar trend should be expected in the catalytic decomposition of methanol.

On the Zn-polar surface, the decompostion of methanol proceeds in two separate pathways: a dehydrogenation pathway that leads to the production of formaldehyde, CO and H_2, and an oxidation pathway in which an adsorbed methoxy is first oxidized to formate which then decomposes to H_2, CO, CO_2, and H_2O. Recent data further show that metallic zinc is desorbed together with the dehydrogenation products [6]. It is postulated that the desorbed Zn originated from a surface site that is reduced during the oxidation of adsorbed methoxy into formate according to the scheme:



The above scheme is derived for the methanol decompostion reaction. It should be applicable to the methanol synthesis reaction because of microscopic reversibility. Both CO and CO_2 have been shown to be active in the hydogenation reaction [7], and formate has been postulated to be a reaction intermediate. Formate can be formed by the insertion of CO into surface hydroxyl, and by the hydrogenation of CO_2. There is contraversy as to the relative importance of these routes [8]. Based on the discussion above, one may postulate that the active site on ZnO composes of a region containing some reduced Zn surface ions. The reaction cycle for CO_2 hydrogenation proceeds as: (i) carbon dioxide is adsorbed on the site next to the reduced Zn ion; (ii) H_2 is adsorbed on the reduced Zn ion; (iii) the adsorbed CO_2 is hydrogenated to a formate; (iv) the reduced Zn ion is oxidized by the formate, which is hydrogenated to a methoxy; (v) the methoxy is hydrogenated to methanol; (vi) the active site is regenerated by reducing the site with CO and/or H_2.

For CO hydrogenation, the active site may be simply the reduced surface Zn ions. In this case, the reduced site or the anion vacancies associated with it acts as the CO adsorption site as well. The reaction may proceed as in the mechanism proposed earlier [9].

It is interesting to note that it has been reported on both ZnO [10] and ZrO_2 [3], pretreatment of the catalyst in a CO and H_2 mixture greatly enhances their activity in methanol production. Such pretreatment is more effective than H_2 alone. The results mentioned earlier on ZnO show that methanol is particularly effective in reducing the oxide. It becomes likely that such pretreatment serves to generate a large density of reduced surface sites, which are the active sites for methanol production.

The discussions above on the role of surface defects may be generalized to other reactions. It has been reported that mechanically polished single crystal surfaces of ZnO can be reduced by adsorbed CO much more readily than cleaved or grown surfaces [11]. Presumably, mechanical polishing introduces surface defects that are not easily removable by thermal annealing. Clearly, these defects have a different oxidizing and reducing power than ions on an atomically smooth surface. It may not be surprising that on oxides, surface imperfection is the active site for catalysis.

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