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A GORDIAN KNOT?



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# UNTANGLING THE WATER GAS SHIFT FROM FISCHER-TROPSCH:

## A GORDIAN KNOT?

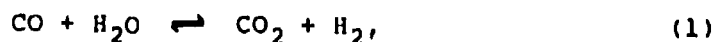
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### ABSTRACT

The water gas shift reaction is an integral part of the Fischer-Tropsch synthesis. Although it may appear convenient to consider the water gas shift a separate reaction in some cases, a detailed examination of the mechanism indicates that the water gas shift and other synthesis gas reactions share several elementary reactions. Experimental support for the relevant elementary reactions for the water gas shift on metals, metal oxides, and in homogeneous solution is examined, from both surface and complex chemistry. Multiple paths leading to a net water gas shift reaction may be available; oxygen transfer and reaction through C-H-O intermediates may take place.

### INTRODUCTION

The water gas shift reaction is catalyzed by numerous metals and oxides. Thus, in any environment containing CO and H<sub>2</sub>O, or CO<sub>2</sub> and H<sub>2</sub>, the water gas shift reaction,



or its reverse, the water gas reaction, may occur. The water gas shift is used to regulate H<sub>2</sub> and CO concentrations in synthesis gas, and it occurs as part of synthesis gas reactions such as the Fischer-Tropsch synthesis, in

which CO and H<sub>2</sub> are starting materials, and CO<sub>2</sub> and H<sub>2</sub>O may be products. At typical synthesis gas reaction temperatures, the equilibrium constant for the water gas shift is close enough to unity and the reaction proceeds rapidly enough that all four species can be expected to be present. The economics of synthesis gas reactions usually require that oxygen rejection be via H<sub>2</sub>O rather than CO<sub>2</sub>; therefore, control of the oxygen-carrying product through the water gas shift may be desirable.

Although the water gas equilibrium is sometimes conceptually separated from other synthesis gas reactions, it probably shares elementary reactions with them and thus cannot be separated either in a theoretical or practical way. This is an important point; if the water gas shift itself is considered an elementary step (which it cannot be in a heterogeneously catalyzed system), its function in a synthesis gas reaction such as Fischer-Tropsch cannot be understood. It is tautological to attribute, for example, the production of H<sub>2</sub>O as the oxygen-carrying product for an iron-catalyzed Fischer-Tropsch system to iron's activity in the water gas shift reaction. The differences between H<sub>2</sub>O- and CO<sub>2</sub>-producing catalysts are rather within some subset of elementary reactions occurring under Fischer-Tropsch conditions to give an effective water gas shift. Identification of these

elementary reactions will allow the design of improved Fischer-Tropsch catalysts.

In the conventional phenomenological approach to catalytic kinetics, a mechanism is found that gives orders of reaction similar to those in the empirical rate equation. The approach I will take in this paper is complementary to the phenomenological approach, but it is seldom used.<sup>1</sup> Studies of elementary reactions will be emphasized in order to provide a basis for suggesting their participation in the water gas shift.

Increasing availability of experimental data and of computer calculational capability makes this approach more useful than it has been in the past. A calculational analysis of the mechanism built up from the elementary reactions is not possible within the scope of this paper, but work is in progress on estimating (or obtaining from the literature) rate constants for elementary reactions of interest and combining them to give overall reaction rates.

The organization followed in this paper will be similar to that in my analysis of the Fischer-Tropsch synthesis.<sup>1</sup> The same notation will be used. However, because the water gas shift reaction takes place with metal, metal oxide, and homogeneous catalysts, those subdivisions will be used. Relevant material will be evidence for intermediates or reactions on (1) the metals in the catalysts used

industrially, and to other metals. Direct observation of intermediates or reactions will be preferred to inference from kinetics, and systems in which elementary reactions are isolated will be preferred to systems of complex reactions. The literature has been covered from 1960 through mid-1982, with emphasis since 1970.

#### WATER GAS SHIFT REACTION ON METALS

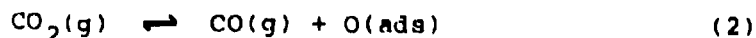
Metal catalysts are of particular interest for understanding the relation of the water gas shift reaction to the Fischer-Tropsch synthesis, because of the reduced nature of the Fischer-Tropsch catalysts under reaction conditions. The evidence for the relevant elementary reactions has been reviewed.<sup>1</sup> Publications since that time have generally supported those reactions. Deuterium adsorbs dissociatively on Rh(100);<sup>2</sup> potassium on iron surfaces increases the adsorption energy of hydrogen.<sup>3</sup> Adsorption of hydrogen is hindered by adsorbed electronegative atoms, such as oxygen,<sup>4</sup> carbon,<sup>4,5</sup> and nitrogen.<sup>5</sup> Several techniques have given more detail on the adsorption of CO on nickel,<sup>6</sup> alumina-supported cobalt,<sup>7</sup> platinum,<sup>8</sup> copper,<sup>8</sup> and rhodium.<sup>2</sup> The degree of dissociation of CO on rhodium is subject to differing interpretations,<sup>9</sup> and CO is reported to dissociate on stepped nickel surfaces,<sup>10</sup> but not on kinked platinum surfaces.<sup>11</sup> The presence of adsorbed

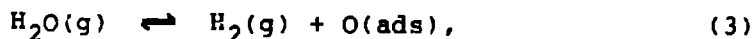
potassium on platinum strengthens the adsorption of CO,<sup>12</sup> as do sodium, potassium, and cesium on nickel, in addition to inducing CO dissociation.<sup>13</sup> Conversely, an oxygen adlayer on Cu-Ni surface alloys weakens CO adsorption.<sup>14</sup> These effects on CO adsorption are generally interpreted to mean that the alkali metals increase backbonding from the metal to CO, and electronegative elements decrease the backbonding.

A thermal desorption study of CO and H<sub>2</sub>O adsorbed on Ru(001) shows that the presence of water induces a strongly-bound state of CO, possibly dissociated.<sup>15</sup> CO<sub>2</sub> dissociates on alumina-supported rhodium to CO and adsorbed O, although the details of this interaction, and the effect of hydrogen on it, are not clear.<sup>16</sup> Coadsorption of CO<sub>2</sub> and H<sub>2</sub> on alumina-supported rhodium gave adsorbed formate, as observed by infrared spectroscopy.<sup>17</sup>

The overall kinetics of the water gas shift reaction have been studied on unsupported iron<sup>18</sup> and platinum,<sup>19</sup> on alumina-supported Group 7B, 8, and 1B metals, some of which were also supported on silica and carbon,<sup>20</sup> on zeolite- and alumina-supported rhodium,<sup>21</sup> and on zeolite-supported ruthenium.<sup>22</sup>

For unsupported iron at high temperatures, an oxygen transfer mechanism,





was deduced.<sup>18</sup> However, this is in conflict with findings that CO adsorbs readily on metals and H<sub>2</sub> adsorbs dissociatively. (See discussions in Ref. 1, and references therein.) For unsupported platinum, the stoichiometric number method<sup>23</sup> was used to interpret overall kinetics and isotopic labeling experiments. The proposed mechanism<sup>19</sup> is given in Table I. The adsorbed intermediate was not identified.

For supported metals, the situation appears to be more complex. Because the commonly-used supports, such as alumina, can adsorb water significantly and the other components of the water gas shift equilibrium to lesser degrees, the catalyst may be bifunctional, with some processes taking place on the metal surfaces, some on the support surfaces, and some at the interface between the metal and the support. A comparative study<sup>20</sup> of the water gas shift reaction on rhenium, cobalt, iron, nickel, rhodium, ruthenium, palladium, iridium, osmium, platinum, copper, and gold showed activities ranging over three orders of magnitude for the metals supported on alumina. Platinum and rhodium were found to be most active on alumina supports, of intermediate activity on silica, and least active on carbon. A mechanism was proposed for a bifunctional catalyst. This mechanism is given in Table II, where M indicates a site on the metal,

and MO a site on the support. However, the activity of a bifunctional catalyst should be strongly dependent on the dispersion of the metal, and no such dependence was found.

Methane was a significant product in the water gas shift reaction over zeolite- and alumina-supported rhodium, and both methane and ethane were observed in small amounts over the alumina-supported catalyst.<sup>21</sup> The activity of alumina alone for the reaction was two orders of magnitude less than for the alumina-supported rhodium. Zeolite-supported ruthenium also produced methane in addition to the water gas shift reaction, but the support seems to have less effect than for rhodium.<sup>22</sup> The occurrence of methanation greatly complicates the interpretation of these results.

A set of elementary reactions describing the water gas shift reaction on most metals is given in Table III. This table includes the reactions of Table X in Ref. 1, with all adsorption-desorption steps made explicit, and nucleophilic attack of adsorbed OH on adsorbed CO added, partly because of more recent studies,<sup>17,20</sup> and partly because of evidence on the homogeneously catalyzed reaction, to be discussed later in this paper. Hydroxycarbonyl is given as the product of nucleophilic attack, rather than formate, because several reactions can be written for formate formation and decomposition, none of which have significant support from surface studies. Although inclusion of formate at this time



would be both speculative and lengthy, it may be justified with further study.

#### WATER GAS SHIFT REACTION ON OXIDES

The water gas shift catalysts used industrially have been iron and chromium oxides (high-temperature catalyst) and copper, zinc, chromium, and aluminum oxides (low-temperature catalyst). Limited information is available on the adsorption of  $H_2$ ,  $H_2O$ ,  $CO$ , and  $CO_2$  on these oxides. However, many of the elementary steps of the water gas shift are adsorption-related: adsorption and dissociation, or their reverse, association and desorption.

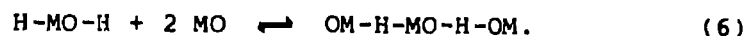
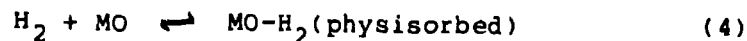
#### $H_2$ Adsorption

At least three, and as many as seven types of hydrogen have been identified as adsorbed species on zinc oxide.<sup>24-32</sup> Infrared spectroscopy has identified three species: a heterolytically dissociated species,  $Zn-H$  and  $OH$  on adjacent sites, that appears to be active in hydrogenation;<sup>24-27</sup> a low-temperature molecularly adsorbed species that participates in  $H_2-D_2$  exchange;<sup>28,29</sup> and a species inactive for hydrogenation that appears to be bridged,  $Zn-H-Zn$  or  $O-H-O$ .<sup>26</sup> Temperature-programmed desorption (TPD) studies and conductivity studies seem to indicate the presence of greater numbers of hydrogen species,<sup>30-32</sup> but

these have not all been identified with infrared species. At least two TPD peaks appear to represent different reaction paths to desorption for the species identified in the infrared studies.<sup>33</sup>

Although zinc oxide is considered the hydrogen activation component in methanol and water gas shift catalysts, other components of the catalysts can also adsorb hydrogen. TPD results<sup>34</sup> show five different types of hydrogen adsorbed on gamma-alumina between -196 and 450 C. Chromia and chromia-silica adsorb hydrogen, although to a lesser extent than zinc oxide. A very low-temperature form of hydrogen adsorbed on chromia appears to be molecular, analogous to the low-temperature form on zinc oxide.<sup>35</sup> A heterolytic dissociative adsorption of hydrogen is reported at intermediate temperatures, and transformation of the Cr<sup>3+</sup> bonded to H to Cr<sup>2+</sup> and OH is reported to take place at higher temperatures.<sup>36</sup>

The reactions producing the various forms of hydrogen adsorbed on oxides are likely to be



Other routes are possible, and diffusion on the surface may be important, as indicated by the TPD results. Reactions 4-6 account in a simple way for relationships among the three

species observed by infrared spectroscopy, but the reactions themselves have not been observed directly.

### H<sub>2</sub>O Adsorption

The adsorption of water onto metal oxides gives hydroxyl groups, intermediates also formed by the adsorption of hydrogen. In the case of water, dissociation is to a hydrogen that adds to an oxide oxygen and a hydroxyl that adds to a metal ion. Hydrogen bonding with the oxide oxygens and hydroxyl groups also causes molecular adsorption of water.

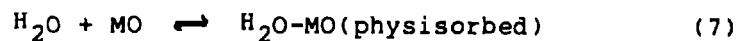
On iron oxide, adsorption isotherms<sup>37</sup>, dielectric relaxation,<sup>38</sup> infrared spectroscopy,<sup>39</sup> and ultraviolet photoemission spectroscopy<sup>40</sup> have shown both molecularly adsorbed and dissociated water. Water is physisorbed onto surface hydroxyls. Physisorbed water was observed by infrared spectroscopy on an iron-chromium catalyst; dissociative chemisorption was also deduced.<sup>41</sup>

Water adsorption on zinc oxide has been studied by adsorption isotherms<sup>42</sup> and a combination of thermogravimetry and infrared spectroscopy;<sup>43</sup> again, molecular adsorption and dissociation were both observed. Water adsorbs dissociatively onto oxygen-treated copper and zinc,<sup>44</sup> although it adsorbs poorly onto clean copper and zinc surfaces. For a low-temperature shift catalyst, both hydroxyls and undissociated water have been observed by infrared spectroscopy.<sup>45</sup>

Dissociation increases with the degree of reduction of the catalyst. Molecularly adsorbed water appears to be present on both catalyst and support.

On alumina, as determined by microcalorimetry and infrared spectroscopy,<sup>46</sup> water is physisorbed, then molecularly chemisorbed and dissociated. Silica<sup>47</sup> and chromia<sup>48</sup> behave similarly. The processes of water adsorption on silica-alumina appear to be similar to those on silica and alumina, but the combination has a greater capacity for water adsorption than what would be extrapolated by a linear combination of the two.<sup>49</sup>

The reactions of water adsorption on oxides can be summarized:



There appear to be two kinds of water chemisorbed molecularly: one in which the oxygen is bonded to the metal ion (reaction 8), and one in which the water is hydrogen bonded to the oxygen or hydroxyl groups of the oxide (reaction 9).

### CO Adsorption

CO adsorption on oxides has been less studied and therefore is not as well understood as CO adsorption on metals. Infrared spectroscopy has been the method of choice for examining CO adsorption on metal oxides; few other methods have been used. In general, a low-frequency group of bands (1100 to 1800  $\text{cm}^{-1}$ ) is attributed to carbonate, bicarbonate, formate, and carboxyl or hydroxycarbonyl, and a higher-frequency group of bands (2000 to 2250  $\text{cm}^{-1}$ ) is attributed to a weakly adsorbed species, in which the carbon is sigma-bonded to the metal ion with no backbonding or the interaction is primarily electrostatic. Carbonyl bands (1900 to 2000  $\text{cm}^{-1}$ ) are sometimes observed. Interpretation of some of the bands is not unambiguous. Harrison and Thornton<sup>50</sup> have concluded that the weakly bonded CO is adsorbed, carbon down, perpendicular to the surface, as in carbonyls, but the bonding is primarily electrostatic. Copper is an exception to this, in that significant pi bonding appears to be present, and this model is not completely consistent with other data, suggesting the possibility of some pi bonding for other metals. Infrared absorption frequencies for CO adsorbed on transition-metal ions on silica<sup>51</sup> appear to be consistent with this model, and a simple correlation between heat of adsorption and CO frequencies for several oxides<sup>52</sup> also argues for a simple bonding model. The C-O bond for

this type of CO adsorption is strengthened relative to its gas-phase value.

Conductivity data suggest a partly cationic CO adsorbed on the  $\text{Fe}^{2+}$  ions of  $\text{Fe}_2\text{O}_3$ ,<sup>53</sup> although the charge of the CO changes from partially positive to partially negative with increasing reduction of the oxide.<sup>54</sup> CO was adsorbed onto a reduced iron-chromium catalyst with apparent formation of carbonates and carbonyls;<sup>41</sup> however, one of the bands attributed to a carbonyl ( $2095\text{ cm}^{-1}$ ) is in the range usually considered to belong to a weakly-bound species. On FeO, CO appears to be adsorbed at a metal ion, although the ultraviolet photoelectron spectrum cannot be fully interpreted.<sup>55</sup> With potassium on FeO, the CO is adsorbed more strongly, probably as a carbonyl.<sup>55</sup>

Adsorption on copper oxide gives a weakly bound species,<sup>56,57</sup> carbonyls,<sup>56-62</sup> and carbonates, bicarbonates, and formates;<sup>56,58,59</sup> in addition, if another component, such as alumina, silica, or other metal oxide, is present, bicarbonate and formate concentrations will be increased. A large range of frequencies is observed for carbonyls ( $2000\text{--}2200\text{ cm}^{-1}$ ); apparently differences in the preparation of the catalyst affect the relative amounts of copper in the three oxidation states. It has not been possible to relate frequencies unambiguously to oxidation states because of the lack of appropriate model compounds. Copper carbonyls that

may simulate surface compounds have been synthesized only recently.<sup>63</sup>

Zinc oxide shows bands in the weakly bound region<sup>61,64-66</sup> and the carbonate region<sup>64-66</sup>, but none that have been identified as carbonyls. Other surface diagnostics tend to confirm these identifications.<sup>67</sup> Angle-resolved photoelectron spectroscopy shows the CO to be adsorbed, carbon end down, on the zinc ions.<sup>68</sup>

Both pure and supported chromia show bands indicating a weakly adsorbed species,<sup>48,69-73</sup> a carbonyl,<sup>71</sup> and carbonates.<sup>69,72,73</sup> Transient response techniques have given results consistent with these interpretations.<sup>74</sup> However, for a copper chromite catalyst, it was concluded that carbonyls formed only on copper.<sup>56</sup>

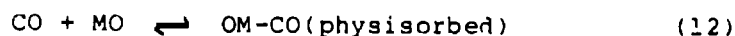
Alumina is reported to form one<sup>69,75</sup> or two<sup>76</sup> weakly adsorbed species and carbonates. Kinetic data support the presence of two types of adsorption, but these cannot be correlated readily with those identified by infrared spectroscopy.<sup>77</sup> A potassium promoter on alumina results in carboxylate and carbonate upon adsorption of CO and CO<sub>2</sub>.<sup>78</sup>

Adsorption of CO on silica is not observed at temperatures above 75 C.<sup>58</sup>

Magnesia forms a weakly adsorbed species and carbonates,<sup>59,79</sup> and there is some evidence for a species

containing an unpaired electron. This species has been identified as a carbonyl radical<sup>80</sup> or a polymeric radical anion.<sup>81</sup> These species participate in the disproportionation of CO, forming carbonates and carbon. A similar species is formed on calcium and strontium oxides.<sup>82</sup>

The probable reactions representing CO adsorption on metal oxides, are then



Distinctions will not be made here between unidentate and bidentate species. The formation of bicarbonates and formates from CO must involve interactions with hydrogen or hydroxide and will be discussed later. The stoichiometries and structures of the polymeric radical anions formed on alkaline earth oxides are not known, so reactions cannot be written for their formation and eventual disproportionation to carbonates and carbon. Therefore, these reactions will be neglected at this time, but they should be considered for catalysts containing the alkaline earth metals.

#### CO<sub>2</sub> Adsorption

Carbon dioxide initially physisorbs on metal oxide surfaces and then chemisorbs in three ways: with the carbon bonded to metal to give a carboxyl group, with an oxygen



bonded to metal, or with the carbon bonded to oxygen to give a carbonate. Relatively little evidence exists, however, for the M-OCO species.

$\text{Fe}_2\text{O}_3$  adsorbs  $\text{CO}_2$  to give a weakly adsorbed species and possible carbonates, bicarbonates, and carboxyls.<sup>83,84</sup> Chromia and chromia-silica give species similar to those on  $\text{Fe}_2\text{O}_3$ .<sup>69,85</sup>

Copper oxide adsorbs  $\text{CO}_2$  weakly,<sup>58</sup> with possible formation of carbonates and carboxyls.<sup>86</sup> Zinc oxide forms carbonates and a carboxyl upon  $\text{CO}_2$  adsorption.<sup>64,83,87</sup> The carboxyl group probably does not carry a full negative charge.<sup>67</sup>

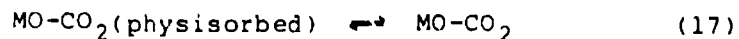
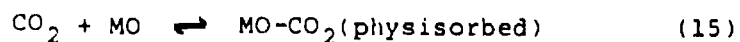
Two weakly adsorbed species have been identified on silica by infrared spectroscopy,<sup>88</sup> but this observation is in contradiction to the observation of carboxyl groups on silica exposed to  $\text{CO}_2$  by electron spin resonance<sup>89</sup> and adsorption-desorption techniques.<sup>90</sup>

On alumina, carbonates and bicarbonates<sup>69,91-96</sup> and one,<sup>91</sup> two,<sup>92</sup> or three<sup>93</sup> weakly bonded species have been observed. No carboxyls have been reported. An adsorption isotherm study generally supports the carbonate identifications.<sup>97</sup> The species and their relative concentrations are strongly influenced by heat treatment and the crystal structure of the alumina.<sup>94</sup>

On magnesia, carbonates are formed,<sup>79b,92b,95</sup> and a weakly-bound species has been observed.<sup>79b</sup>

Soluble CO<sub>2</sub> complexes of cobalt and alkali metal cations have been characterized.<sup>98</sup> The carbon is bonded to the cobalt, and the oxygens to the alkali metal cations. The infrared C-O frequencies are in the range of those observed for carboxyls on surfaces.

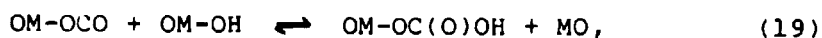
The reactions for adsorption of CO<sub>2</sub> on metal oxides can be summarized:



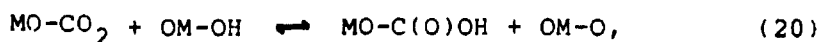
#### Interactions Among Adsorbed Species

The major interactions appear to take place among adsorbed species, rather than between adsorbed and gas-phase species. However, information about these steps is incomplete and sometimes contradictory.

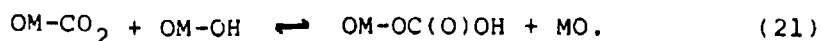
The presence of hydroxyl groups on the surface of several of these oxides appears to promote CO<sub>2</sub> adsorption, although this effect has not been studied in detail. Water interacts with adsorbed CO<sub>2</sub> on magnesia to produce bicarbonate.<sup>99</sup> This could come about by nucleophilic attack on the carbon by hydroxyl,



hydrogen transfer,

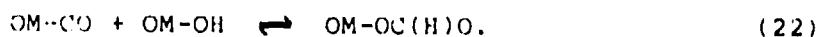


or oxygen insertion,

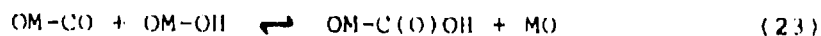


In a relevant solution reaction,  $\text{Cu}^{2+}$  has been found to catalyze the nucleophilic attack of water at a carbonyl carbon.<sup>100</sup>

$\text{CO}$  and  $\text{H}_2\text{O}$ , and  $\text{CO}_2$  and  $\text{H}_2$ , have been coadsorbed on zinc and magnesium oxides and the surface intermediates observed by infrared spectroscopy.<sup>101</sup> Formate ions were the predominant species observed. Formate,<sup>102,103</sup> acetyl and acetate,<sup>102</sup> and carbonate and bicarbonate<sup>103</sup> intermediates have been trapped during  $\text{CO-H}_2$  and  $\text{CO}_2\text{-H}_2$  reactions on copper-zinc catalysts. Water and  $\text{CO}$  adsorbed on an iron-chromium catalyst interact to produce formate.<sup>41</sup> A possible reaction producing formate is



This is an oxygen insertion into the  $\text{M-C}$  bond (or carbon migration to oxygen) with hydrogen transfer. It may be broken down into



Hydrogen addition to adsorbed  $\text{CO}_2$  will also give formate: