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# Lewis acidity as an explanation for oxide promotion of metals: implications of its importance and limits for catalytic reactions

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Sub-monolayer quantities of metal oxides are found to influence CO hydrogenation, $CO_2$ hydrogenation, acetone hydrogenation, ethylene hydroformylation, ethylene hydrogenation, and ethane hydrogenolysis over Rh foils. The metal oxides investigated include AlOx, TiOx, VOx, FeOx, ZrOx, NbOx, TaOx, and WOx. Only those reactions involving the hydrogenation of C–O bonds are enhanced by the oxide overlayers. The coverage at which maximum rate enhancement occurs is approximately 0.5 ML for each oxide promoter. Titanium, niobium, and tantalum oxides are the most effective promoters. XPS measurements after reaction show that of the oxides studied titanium, niobium, and tantalum oxide overlayers are stable in the highest oxidation states. The trend in promotion effectiveness is attributed to the direct relationship between oxidation state and Lewis acidity. For the oxide promoters, bonding at the metal oxide/metal interface between the O-end of adsorbed CO and the Lewis acidic oxide is postulated to facilitate C–O bond dissociation and subsequent hydrogenation.

**Keywords:** oxide promotion; acidity; CO and $CO_2$ hydrogenation; Rh

## 1. Introduction

Transition metal oxides have been found to alter dramatically the catalytic behavior of group VIII metals [1–5]. Oxide promoters deposited on Rh can increase the overall activity of the metal by several orders of magnitude for reactions involving the hydrogenation of molecules such as CO, $CO_2$, and NO [4,6–14]. Several explanations for oxide promotion have been introduced. Burch and Flambard [15] have suggested that the active sites in the oxide promoted catalysts are located at the metal/metal oxide interface. Sachtler, Ichikawa and coworkers [8,16] extended this proposal by suggesting that a Lewis acid/base bonding interaction occurs between the oxygen end of the adsorbed CO and the oxide promoter at the oxide/metal interface.

The majority of investigations of oxide promotion have been performed using metals dispersed on high surface area supports. For these systems the amount of oxide promoter coverage is difficult to control and measure. In our research, a model catalyst has been designed consisting of a Rh substrate on to which known coverages of oxide promoter are deposited. The relationship between catalyst activity and composition can be rigorously determined using surface analytic tools. In this article a summary of our findings of the influence of titanium, tantalum, niobium, vanadium, iron, zirconium, tungsten, and aluminum oxide deposits on the activity of a Rh foil is presented. Reactions studied include CO hydrogenation [17–21], $CO_2$ hydrogenation [20–23], acetone hydrogenation [22], ethylene hydroformylation [24], ethylene hydrogenation [25], and ethane hydrogenolysis [25]. By relating catalytic activity to surface composition and structure using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), temperature programmed desorption (TPD), and scanning tunneling microscopy (STM), evidence is obtained which not only confirms but also expands upon explanations of oxide promotion proposed in the literature.

## 2. Experimental

A detailed description of the two UHV chambers utilized in this study is presented in refs. [20,22]. One of these is equipped with a cylindrical-mirror energy analyzer for Auger electron spectroscopy, a quadrupole mass spectrometer, a gas chromatograph, and an atmospheric-pressure isolation cell. The oxide overlayer was prepared by evaporation of the base metal and subsequent oxidation in $O_2$ at $1 \times 10^{-6}$ Torr. The oxide coverage was determined using AES and TPD. After characterization of the surface, the Rh foil was enclosed within the reaction cell, and reactant gases introduced. Product accumulation was monitored with a gas chromatograph. Additional characterization of the catalyst samples was carried out in a PHI 5300 ESCA system equipped with X-ray photoelectron spectroscopy and ion scattering spectroscopy. The PHI 5300 ESCA was also equipped with an atmospheric-pressure isolation cell. STM measurements of the surface structure of the sub-monolayer amounts of titanium oxide deposits indicate the formation of oxide islands of about 20 Å diameter that are distributed fairly uniformly over the transition metal surface [26].

## 3. Results and discussion

Titanium, tantalum, niobium, vanadium, tungsten, zirconium, iron, and aluminum oxides were deposited on a Rh foil in order to determine promoter effects for CO and $CO_2$ hydrogenation [17–23]. For titanium oxide the measure of influence on the reactivity of a Rh foil was extended to include acetone hydrogenation [22], ethylene hydroformylation [24], ethylene hydrogenation [25], and ethane hydrogenolysis [25]. For each oxide and reaction studied, the dependence of promotion on oxide coverage was investigated. Oxide coverage was calibrated using a combination of AES, ISS, and CO TPD [27]. Fig. 1 shows a typical example of the dependence of rate enhancement on promoter coverage for titanium oxide deposited on a Rh foil. Titanium oxide has a strong positive influence on the rate of methane formation from $CO_2$ hydrogenation. At a coverage of 0.5 ML the rate, which is defined as the product molecules per total surface area (oxide + metal) per second, reaches a maximum which is 15 times that measured on the clean Rh foil. However, at multilayer coverages the rate is many times lower than that measured on clean Rh foil since the oxide promoter alone has no activity for the reaction. Titanium oxide does not promote ethylene hydrogenation. The dependence of rate on titanium oxide coverage is shown in fig. 1 for ethylene hydrogenation. For reactions which are not promoted by oxide deposits (such as ethylene hydrogenation and ethane hydrogenolysis), the rate is found to decrease in proportion to the oxide coverage. This indicates that the oxide blocks catalytic sites on the Rh foil.

Table 1 shows that titanium oxide promotes only those reactions which involve hydrogenation of the polar CO bonds. The rates of CO hydrogenation, $CO_2$ hydrogenation, acetone hydrogenation, and the formation of 1-propanol from ethylene hydroformylation are enhanced by the presence of titanium oxide. Maximum rate enhancement occurs for each of these reactions at coverages of 0.5 ML.

The effect of a series of oxide deposits on CO and $CO_2$ hydrogenation over Rh

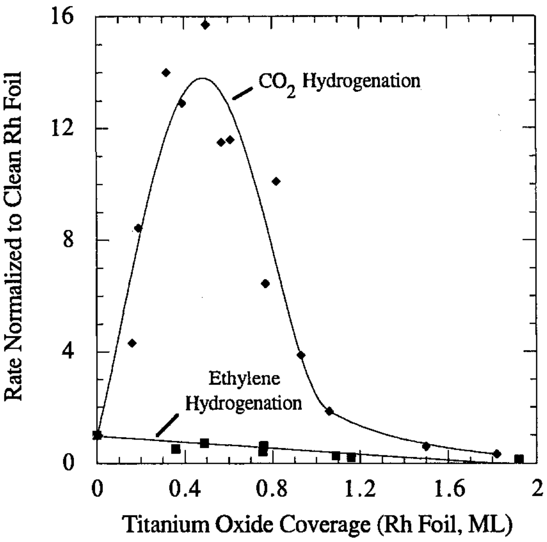

Fig. 1. Rate of methane formation from $CO_2$ hydrogenation over a Rh foil plotted as a function of titanium oxide coverage ($H_2/CO_2 = 3, P = 1$ atm, and $T = 523$ K), and rate of ethane formation from ethylene hydrogenation over a Rh foil plotted as a function of titanium oxide coverage ($H_2/C_2H_4 = 1, P = 50$ Torr, and $T = 323$ K).

Table 1
Comparison of rate enhancement of a Rh foil by titanium oxide for several reactions

| Reaction | Rate enhancement |
|---|---|
| $CO_2$ hydrogenation | 15 |
| CO hydrogenation | 3.0 |
| acetone hydrogenation | 6.0 |
| ethylene hydroformylation | 3.0 [a] |

[a] Enhancement of formation of 1-propanol.

foil is shown in table 2. Titanium, tantalum, and niobium oxides are found to have the greatest promotional effect on CO and $CO_2$ hydrogenation. Maximum rate enhancement occurs at a coverage of approximately 0.5 ML for each of the oxides. The appearance of a maximum in the catalytic activity in each case suggests that highly active sites are created at the perimeter of the deposited oxide islands. Consistent with the interpretation, simulation of the overlayer growth, assuming a finite number of nucleation sites, shows that the number of perimeter sites reaches a maximum when the overlayer coverage is $\sim$ 0.5 ML, independent of the number of nucleation sites [28]. From the computer simulation, 5–15% of the initially clean Rh sites are estimated to be located at the oxide perimeter for 0.5 ML deposits. This suggests a turnover frequency for active sites at the oxide periphery that is as much as two orders of magnitude greater than that of metallic Rh.

The oxidation states of the oxides have been determined using XPS [21,29]. Fig. 2a which is a plot of maximum rate enhancement induced by each oxide plotted versus average oxidation state after $CO_2$ hydrogenation indicates a good correlation between oxide promotion and oxidation state stable during reaction. The error bars in fig. 2a give the range in oxidation states observed after reaction and the magnitude of scatter observed in the rate measurement. Sachtler et al. [8,16] have suggested a bonding scheme for oxide promoted Rh catalysts in which

Table 2
Comparison of promotion by 0.5 ML metal oxide deposits on Rh foil

| $CO_2$ hydrogenation [a] | | CO hydrogenation [b] | |
|---|---|---|---|
| oxide | maximum rate enhancement | oxide | maximum rate enhancement |
| TiOx | 15 | TaOx | 3.9 |
| NbOx | 13 | TiOx | 3.0 |
| TaOx | 12 | NbOx | 2.5 |
| ZrOx | 5.4 | – | – |
| VOx | 5.1 | VOx | 2.1 |
| WOx | 5.0 | WOx | 2.1 |
| FeOx | 0.0 | FeOx | 1.7 |

[a] $H_2/CO_2 = 3, P = 1$ atm, $T = 523$ K.
[b] $H_2/CO = 2, P = 1$ atm, $T = 553$ K.

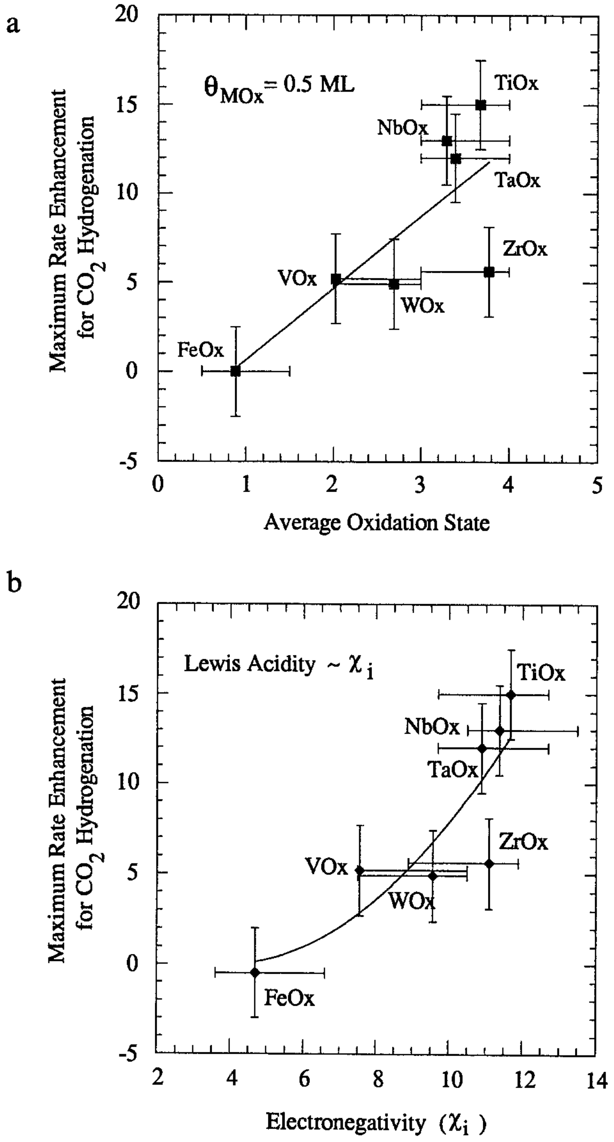

Fig. 2. Correlation of rate enhancement with (a) average oxidation state and (b) electronegativity of the oxide promoter for $CO_2$ hydrogenation over a Rh foil.

adsorbed CO at the oxide/metal interface is bound simultaneously through its carbon-end to the catalyst metal and its oxygen-end to the Lewis acidic oxide promoter in an analogous fashion to that observed in C and O bonded organo-metallic carbonyl compounds [32]. The significant weakening of the CO bond observed in these compounds, as evidenced by a lowering in CO stretching frequency of up to

500 $cm^{-1}$ [32], is postulated to enhance CO hydrogenation by facilitating CO dissociation which is considered to be the rate limiting step of the mechanism [8]. Fig. 2b shows the maximum rate enhancement induced by each oxide plotted versus the electronegativity of the metal cation of the oxide. Electronegativity of the ion ($\chi_i$) is approximately proportional to Lewis acidity and is calculated from the oxidation state of the ion ($z$) and the Pauling electronegativity ($\chi_o$) using the expression [30,31]:

$$\chi_i = \chi_o(1 + 2z) .$$

The good correlation between Lewis acidity and rate enhancement of fig. 2b demonstrates that the concept of Lewis acidity can be used to interpret differences observed in promoter effectiveness.

There are several implications resulting from the above explanation of oxide promotion of bond breaking in polar molecules. The oxidation state of the oxide, which determines promotional character through its electron acceptor Lewis acidity, is influenced by the reaction environment (the oxidizing power of the reactant mixture) as well as the redox thermodynamics of the oxide. For a given reaction the effectiveness of the oxide promoter will depend on the match of the oxidation thermodynamics of the oxide with the redox potential of the reaction atmosphere. For example, tungsten oxide which is stable in the 2+, 3+ redox pair during CO and $CO_2$ hydrogenation causes less rate enhancement than titanium, tantalum, and niobium oxides which are stable in the higher 3+, 4+ redox pair that makes them better Lewis acids. However, under reaction conditions which are more oxidizing than that during CO and $CO_2$ hydrogenation, tungsten oxide would be stable in a higher redox pair (5+, 6+, for example) and be a more effective promoter than titanium, tantalum, and niobium oxides (which have maximum oxidation states of 4+, 5+ and 5+, respectively) if a similar promotion mechanism as that proposed for CO and $CO_2$ hydrogenation is applicable. The reactions which are found to be promoted by titanium oxide deposits on Rh foil are those which involve the hydrogenation of C–O bonds. Titanium oxide has also been demonstrated by Pande and Bell [14] to promote reduction of NO by $H_2$ and CO. This suggests that a Lewis acid/base interaction with an oxide promoter requires a polar or oxygen containing bond within the molecule. Consequently other reactions with molecules having polar functional groups (such as CN, CS, and NH) may also be affected by charge transfer at the oxide/metal interface, and the scheme presented here would predict that those oxides which are present in the highest oxidation states during reaction would be the most effective promoters.

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