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SOLID-STATE, SURFACE, AND CATALYTIC PROPERTIES OF OXIDES

Progress Report

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Introduction

Transition metal oxide catalysts, although generally less active than transition metals in reactions such as hydrogenation, combustion and hydrogenolysis, have the properties of being very selective in a number of reactions. Notable examples of high selectivies can be readily found in various selective oxidation reactions, in methanol synthesis from syn-gas, and dehydration reactions. As high selectivity has always been greatly desirable, it is important to understand its origin. More broadly, it is important to obtain fundamental understanding of catalysis by transition metal oxides. Our effort has been towards this goal. In the past year, our effort has been concentrated in two directions: to elucidate the relationship between surface structure and surface chemical properties, and to investigate the effect of crystallite size. Briefly, by comparing the decomposition reactions of methanol, formaldehyde, and formic acid on the nonpolar and the Zn-polar surfaces of ZnO, it was found that the Zn-polar surface was more metallic-like than the nonpolar surface. On the nonpolar surface, defects always make the surface more reactive. In the study of the crystallite size effect, it was found that the selectivity for butadiene production in the oxidative dehydrogenation of butene on iron oxide increases with decreasing crystallite size, ranging from about 40% for very large crystallites to about 80% for very small crystallites. It is believed that this is the first documentation of crystallite size effect in transition metal oxide catalysis. The details of these and other investigations are described below.

Relation between surface structure and surface chemistry of ZnO:

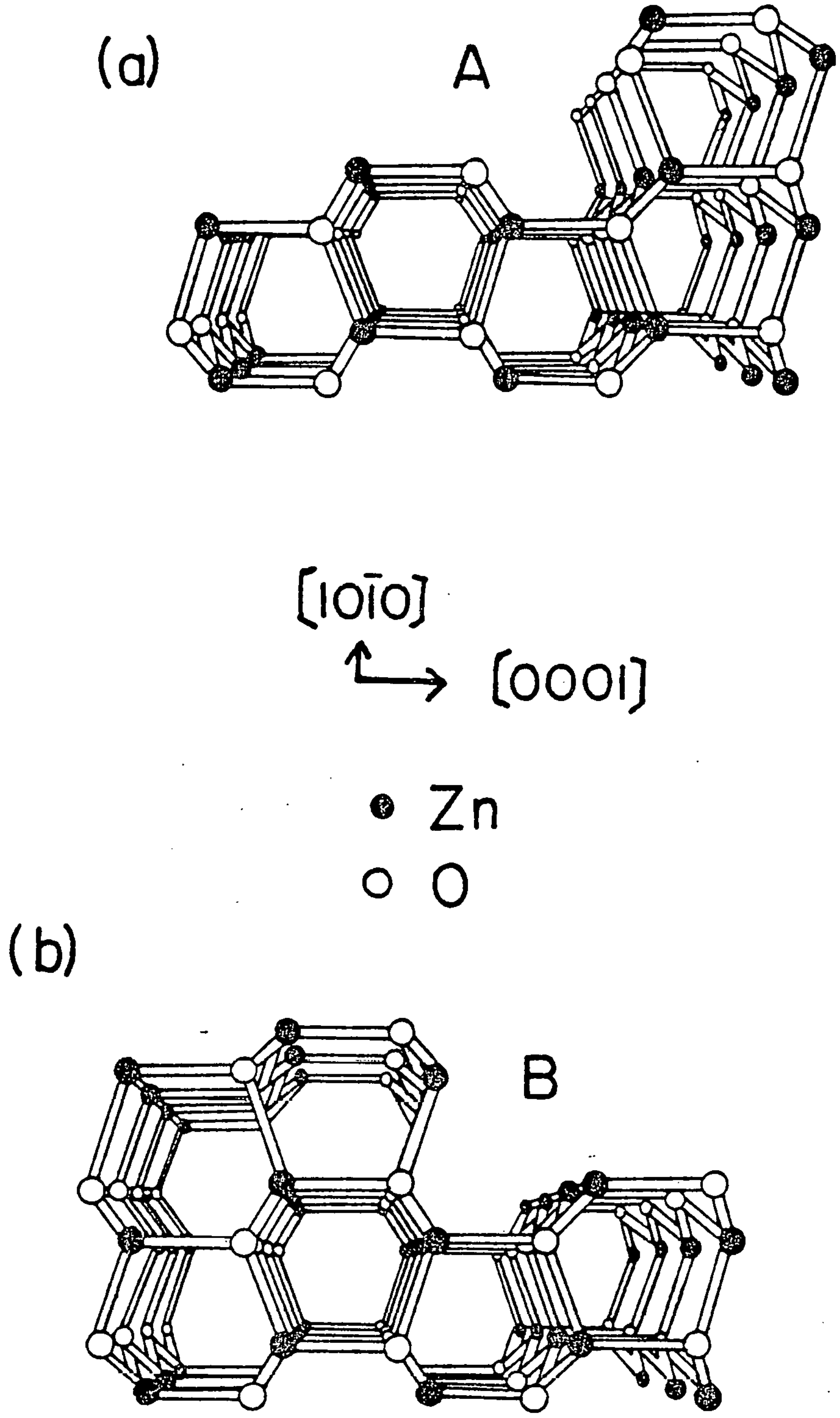
In the last annual progress report, characterization of the nonpolar $(10\bar{1}0)$, the stepped $(40\bar{4}1)$ and $(50\bar{5}1)$, and the Zn-polar (0001) surfaces of ZnO by LEED, Auger spectroscopy, and temperature programmed desorption/decomposition (TPD) of CO, CO_2, O_2, and CH_3OH were described. The TPD results showed that the interaction of CO and CO_2 on the $(10\bar{1}0)$ and the (0001) surfaces are different (see Fig. 1 for a schematic representation of these surfaces), and the stepped surfaces behave like the Zn polar surface in CO adsorption, but like the nonpolar surface in CO_2 adsorption. In the TPD of methanol, the stepped surfaces were like the nonpolar surface except for the higher activity in decomposition of methanol, and were very different from the polar surface. Details of these results have been published.

The different product distributions in methanol decomposition in TPD suggested the possibility of a reaction mechanisms for the Zn-polar surface that is different from the other surfaces (collectively referred to as nonpolar surfaces). Effort was spent to elucidate the reaction mechanisms by comparing the TPD results of methanol, formaldehyde, and formic acid on these surfaces. Details of the results can be found in the manuscript submitted for publication in the Journal of Catalysis. The important conclusions are summarized as follows:

1) On the nonpolar (which includes the $(10\bar{1}0)$ and the stepped $(50\bar{5}1)$) surfaces, and the Zn-polar surface, there are two reaction pathways for methanol decomposition as studied by TPD. The nonpolar and the polar surfaces differ in one pathway, but are the same for the other. The common pathway is the oxidation of methanol by lattice oxygen to a surface formate which decomposes at high temperature to CO, CO_2, H_2, and H_2O. This decomposition occurs at a higher temperature on the polar surface suggesting that the formate is more stable on this surface. Formaldehyde decomposition also proceeds via this formate pathway. Thus the decomposition products of methanol (via oxidation), formaldehyde, and formic acid are all similar.

2) For methanol decomposition, there is a second pathway of dehydrogenation on the Zn-polar surface to yield formaldehyde, CO, and H_2. The dehydrogenation and the oxidation pathway compete, and their relative importance depends on the coverage of methanol. Oxidation is more favored at low coverage while dehydro-

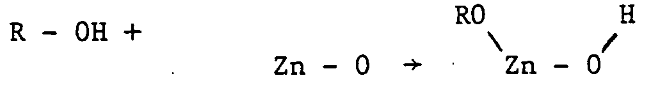
FIG. 1



genation is favored at high coverage. Within the dehydrogenation pathway, the ratio of CO/formaldehyde increases steadily with increasing coverage. This was interpreted as an indication of the presence of metallic properties on the Zn-polar surface in addition to its oxidic properties which give rise to the oxidation pathway.

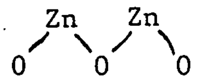
3) The second pathway for methanol decomposition on the nonpolar surfaces is the hydrogenation of surface methoxide (or methyl group) to form methane. Isotopic studies using CH_3OD showed the absence of D in the oxidation products. This suggests that the methyl group is intact in the production of methane.

4) Comparison of the desorption temperature of H_2O, isopropanol, methanol, formaldehyde, formic acid, acetone, and acetaldehyde reviewed the following pattern (table 1). On the Zn-polar surface, desorption of these molecules (in the undecomposed form) occurs at about the same temperature. On the nonpolar surface, acetone, formaldehyde and acetaldehyde desorb at a temperature slightly lower than hydroxyl-containing molecules of H_2O, isopropanol, formic acid, and methanol. This difference was interpreted as an indication that these molecules adsorb molecularly on the Zn-polar surface via the electron lone-pair at the oxygen atom of the molecules. On the nonpolar surface, dissociative adsorption occurs for the -OH containing molecules, while molecular adsorption takes place for the others.



$$\mathrm{R-OH} + \mathrm{Zn-O} \rightarrow \mathrm{\overset{RO\ \ }{Zn}-\overset{\ \ H}{O}}$$

The atomic structure of the Zn-polar surface, where all the coordination unsaturation bonds are associated with the Zn atom, makes dissociative adsorp-



tion energetically less favorable. Dissociation of the adsorbed molecules still occurs at higher temperature, probably when oxidative dehydrogenation by lattice oxygen takes place. This represents the first definitive differences observed

Table 1: Desorption Temperatures of Undecomposed Adsorbates on ZnO(a).

	Surface	
Adsorbate	$(10\bar{1}0),(50\bar{5}1)$	(0001)
H_2O	135±5	230±10(d)
CH_3OH	150±5	220±5
C_2H_5OH	130(b)	240±5(c)
i-C_3H_7OH	150±5(c)	240±5(c)
CD_2O	125±5	225±5
CH_3CHO	105(b)	-
$(CH_3)_2CO$	105±5(c,e)	250±10(c)

Footnotes:

a) All temperatures are in °C for a heating rate of 10 C sec^{-1} except those indicated.

b) These are taken from ref. 29. The heating rate was 11 C sec^{-1}.

c) Unpublished results from this laboratory.

d) This temperature is for saturation coverage. It is for the lower temperature peak.

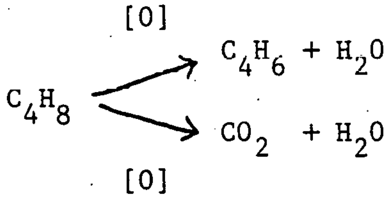
e) This is the lower temperature peak.

for structural effect in oxide surface chemistry.

Thus far, our effort has been on the nonpolar and the Zn-polar surfaces. Other surfaces will be studied in the future.

Crystallite size effect in transition metal oxide catalysis

While crystallite size effect in metal catalysis has been extensively studied, corresponding study in oxide catalysis is rare. We have been studying it in the selective oxidative dehydrogenation of butene to butadiene on iron oxide catalysts. This reaction is schematically represented as:



Crystallite size effect if present can affect the conversion of butene and/or the selectivity for butadiene.

Two series of catalysts were studied. One was supported on SiO_2, and showed an average crystallite size ranging from 2.5 to 8.5 nm (as determined by X-ray line broadening). The other was unsupported and showed an average size of 13 to >61 nm. These samples were subjected to various characterizations including steady-state reactivity measurement, X-ray diffraction, X-ray line profile analysis, Mössbauer spectroscopy, and magnetization measurements. Detailed results can be found in the manuscripts submitted for publication. The important results are as follows:

1) There is a definite general trend that the selectivity for butadiene decreases with increasing crystallite size (see Fig. 2). However, the trend is not monotomic in that there appears to be some differences between supported and unsupported samples. Furthermore, the change in selectivity is temperature dependent such that over the temperature range studied (300 to 375 C), the trend is most obvious at 300 C, and becomes less and less obvious with increasing temperature.

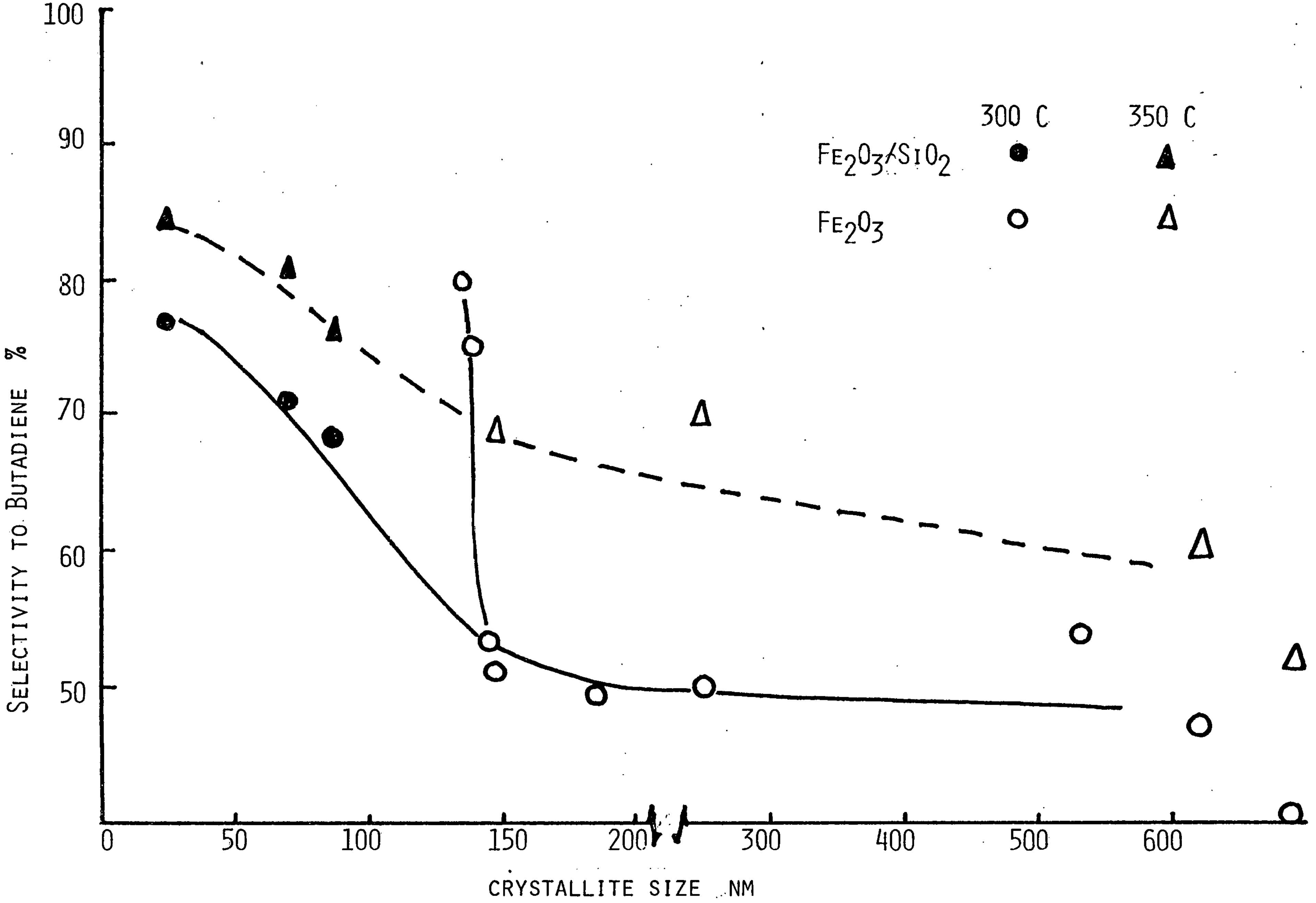

100
90
80
70
60
50
Selectivity to Butadiene %
300 C
350 C
Fe2O3/SiO2
Fe2O3
0
50
100
150
200
300
400
500
600
CRYSTALLITE SIZE NM

FIG. 2

2) For the three supported samples, Mossbauer, X-ray, and magnetization characterizations of the two larger crystallite size samples indicated the presence of only the alpha crystallographic phase of Fe_2O_3. Characterization of the smallest size sample is less definitive. Mössbauer and magnetization data were consistent with α-Fe_2O_3, but the X-ray diffraction data was inconclusive.

3) For the unsupported samples that were calcined in air or oxygen at high temperature (>350 C), various characterizations indicated the presence of only α-Fe_2O_3. For samples calcined at lower temperatures, the presence of a second phase identifiable as iron hydroxide was detected. The amount of hydroxide increased with decreasing calcination temperature.

4) X-ray Fourier line shape analysis showed that the supported iron oxide has a much narrower crystallite size distribution than the unsupported samples. It also showed that the α-Fe_2O_3 phase in the unsupported samples calcined at low temperature contained a relatively large amount of strain. The supported samples and the unsupported samples calcined at high temperatures are rather strain free.

5) Taking all the characterization data together, it was conclued that the differences in selectivity for butadiene production is indeed a crystallite size effect and not due to the presence of other iron oxide phases. This then represents the first documented crystallite size effect in oxide catalysis.

6) Within the uncertainty in determining the surface area of iron oxide, the turnover number of butene was roughly the same independent of crystallite sizes. There are a number of possible explanations for this crystallite size effect. First, the reaction may be crystal face specific. If the ratios of exposed crystal planes depend on the crystallite size, the selectivity changes accordingly. Second, the production of butadiene may require a specific site, such as anion or cation vacancies. The density of such defect sites may be higher for smaller crystallites. Third, the reaction mechanism has been pro-

posed to involve an oxidation-reduction cycle. Since it has been established that smaller oxide crystallites are harder to reduce, this can cause a change in selectivity. Finally, it has been found that the degradation to CO_2 is due to the vulnerability of adsorbed butadiene precursors to weakly adsorbed oxygen. It is possible that the activation of such active oxygen on α-Fe_2O_3 is crystallite size dependent. At present, there is no direct evidence to distinguish these possibilities. More work is needed to elucidate the origin of the effect.

The meaning of equilibrium exchange rates in nonelementary reactions:

Although not in the original proposal, we became interested in investigating the use of postulates in nonequilibrium thermodynamics to study kinetics of catalytic reactions. An example of the application of this approach is the methanol synthesis reaction from syn-gas. In the reactant mixture of CO, CO_2 and H_2, three reactions are potentially important:

$$CO + 2H_2 = CH_3OH$$

$$CO_2 + 3H_2 = CH_3OH + H_2O$$

$$CO + H_2O = CO_2 + H_2$$

However, the individual rates of these three reactions cannot be determined uniquely in a conventional reactor because of the five chemical species, only two are truly independent. The other three are related to these two through mass conservation equations.

Based on nonequilibrium thermodynamic theories, the flux of each reaction can be written as linearly proportional to the sum of the deviation from equilibrium of the individual species weighed by the appropriate stoichiometric coefficient. The proportionality factor for each reaction i, X_i is known as the equilibrium exchange rate. If the reaction i as written is an elementary reaction, then X_i is the rate in one direction at equilibrium.

When applying this concept to determine the X_i's of a series reaction, such as a catalytic reaction, it was not clear what is the meaning of the equilibrium exchange rate X_o for the overall reaction, and what is the relationship between X_o and the X_i's of the elementary steps. To answer these questions, we performed a mathematical analysis for both a batch reactor system in which the system is relaxing towards equilibrium, and a steady-state flow reactor system. The result is that as long as the concentrations of the intermediate species are low such that the quasi-steady state assumption holds well, X_o is related to the X_i's by

$$\frac{1}{X_o} = \sum_i \frac{1}{X_i}$$

In other words, the reaction system behaves like an electrical circuit when close to chemical equilibrium, and when the quasi-steady state assumption holds. Thus, if there is a rate limiting step in the series, the overall exchange rate is that of the rate limiting step. This result is being reported in a manuscript accepted for publication in the AIChE Journal. In that manuscript, the conditions for the determinability of the exchange rates were also presented.

This approach has now been used to find the rates of the three reactions in methanol synthesis. Results thus far show that at 15 atm, 250°C over a Cu/Zn/O catalyst, the equilibrium exchange rates of CO_2 hydrogenation $\gtrsim$ CO hydrogenation $\gtrsim$ water-gas shift reaction. Thus, contrary to what most people believe, CO_2 hydrogenation is actually a dominant pathway for methanol production, especially at high conversions.

Publications resulted from this work:

1) "Study of Iron Oxide Surface by Adsorption and Temperature programmed Desorption," M.C. Kung, W.H. Cheng and H.H. Kung, J. Phys. Chem., 83, 1737(1979).

2) "Surface Composition of a Solid Solution of Monovalent Ionic Compounds of NaCl Structure," W.H. Cheng and H.H. Kung, Surface Sci., 88 (1979) 153.

3) "Selectivity in the Oxidative Dehydrogenation of Butene on Zinc Iron Oxide Catalyst," H.H. Kung, B. Kundalkar, M.C. Kung and W.H. Cheng, J. Phys. Chem. 84, (1980) 382.

4) "Methanol Syntheis," H.H. Kung, Catal. Rev., 22, (1980) 235.

5) "Chemical Properties of Anion Vacancies on Zinc Oxide," W.H. Cheng and H. H. Kung, Surface Sci., 102, (1981) L21.

6) "The Surface Cation Densities of Iron Oxide-Chromium Oxide Solid Solutions," M.C. Kung and H.H. Kung, Surface Sci., 104, (1981) 253.

7) "The Effect of Additives on Iron Oxide in the Selective Oxidative Dehydrogenation Reactions," H.H. Kung, M.C. Kung, and B. Yang, J. Catal., 69, (1981) 506.

8) "The Surface Cation Ratios of Mixed Cubic Oxides," G. Liu and H.H. Kung, Surface Sci., 110 (1981) 504.

9) "Catalytic Behavior of a Transition Metal Ion in a Solid Solution--an Electrostatic Potential Approach," H. H. Kung, J. Catal., 73 (1982) 387.

10) "Oxygen on Iron Oxide: Kinetic Evidence of an Atomic Species," B.L. Yang and H.H. Kung, J. Catal., 75 (1982) 329.

11) "Oxygen on Iron Oxide: Effect on the Selective Oxidation of Butene," B.L. Yang and H.H. Kung, J. Catal., 77, 410 (1982).

12) "Interaction of CO, CO_2 and O_2 with Nonpolar, Stepped, and Polar Zinc Surfaces of ZnO," W.H. Cheng, S. Akhter, and H.H. Kung, Surface Sci., 122, 21 (1982).

13) "Structure Sensitivity in Methanol Decomposition on ZnO Single Crystal Surfaces," W.H. Cheng, S. Akhter, and H.H. Kung, J. Catal., accepted.

14) "The Interpretation of Equilibrium Exchange Rates for Nonelementary Reactions," D. Willcox, and H. H. Kung, AIChE Journal, accepted.

15) "Decomposition of Methanol, Formaldehyde, and Formic Acid on Nonpolar ($10\bar{1}0$), stepped ($50\bar{5}1$), and Zn Polar (0001) Surfaces of ZnO by Temperature Programmed Decomposition," S. Achter, H.H. Kung, W.H. Cheng, and K. Lui, J. Catal., submitted.

16) "Crystallite Size Effect in the Selective Oxidation of Butene to Butadiene on Iron Oxide. I: Mössbauer, X-ray and Magnetization Characterization of the Catalysts," F. Hong, B.L. Yang, L.H. Schwartz, and H.H. Kung, J. Phys. Chem., submitted.

17) "Crystallite Size Effect in the Selective Oxidation of Butene to Butadiene on Iron Oxide. II: Reaction Studies," B.L. Yang, F. Hong, H.H. Kung, J. Phys. Chem., submitted.

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