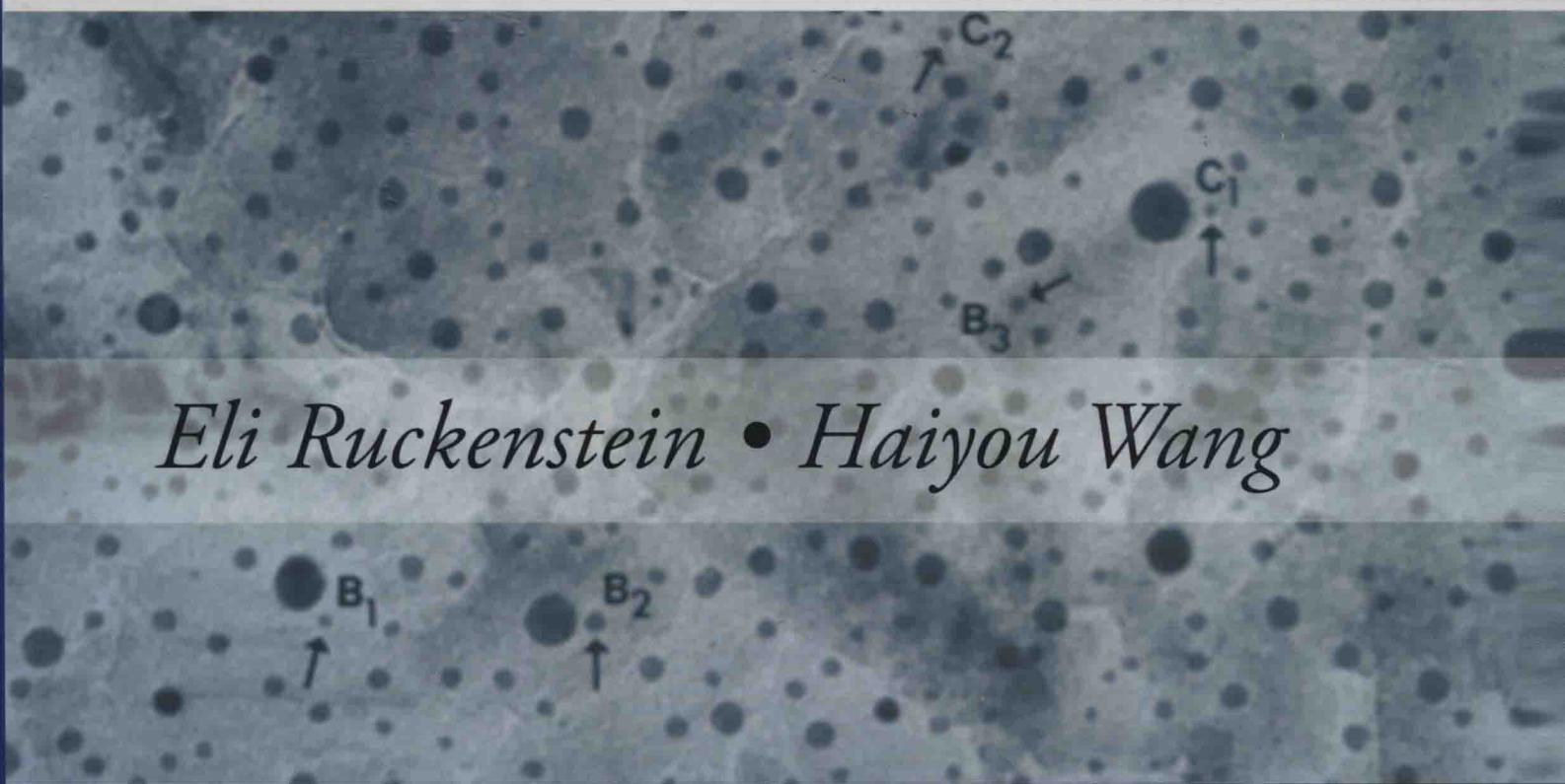


# Heterogeneous Catalysis

*Experimental  
and Theoretical Studies*

A microscopic image showing numerous small, dark, spherical catalyst particles of varying sizes. Several particles are specifically labeled with arrows and text: B1, B2, B3, C1, and C2. B1 and B2 are in the lower left, B3 is in the middle right, C1 is in the upper right, and C2 is in the upper middle.

*Eli Ruckenstein • Haiyou Wang*

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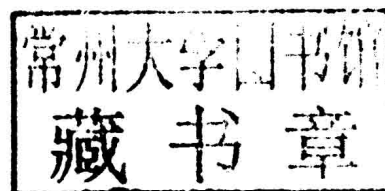
# HETEROGENEOUS CATALYSIS

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## Experimental and Theoretical Studies

ELI RUCKENSTEIN

HAIYOU WANG



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## **HETEROGENEOUS CATALYSIS**







# PREFACE

This book contains a collection of papers that Professor Eli Ruckenstein and his coworkers have published in the area of heterogeneous catalysis during the past four decades. It consists of the following eight chapters:

- 1 Catalytic conversion of methane to synthesis gas by CO<sub>2</sub> reforming
- 2 Catalytic conversion of methane to synthesis gas by partial oxidation
- 3 Catalytic combustion of clean as well as nitrogen-bound fuels over transitional metal oxides
- 4 Zeolites and their applications as catalysts and/or catalyst supports
- 5 Synthesis of mesoporous V–Mg–O oxides and their applications as catalysts
- 6 Synthesis of polymer-supported catalysts and polymer-coated silica supports and their applications in catalysis
- 7 Metal sintering during heating in various atmospheres
- 8 Heterogeneous catalysis: a theoretical approach.

Chapters 1–3 deal with a number of catalysts involved in various catalytic reactions, including, methane CO<sub>2</sub> reforming, methane partial oxidation, and catalytic combustion; Chapters 4–6 are concerned with applications of various materials, such as zeolites, mesoporous V–Mg–O oxides, polymers, and polymer-coated SiO<sub>2</sub> as catalysts or catalyst supports; Chapter 7 is devoted to theoretical and experimental investigations of metal sintering in model metal catalysts during heating in various atmospheres; and Chapter 8 deals with some theoretical approaches relevant to heterogeneous catalysis. Each chapter starts with an introduction that summarizes the papers included.

This book will be of interest to catalytic scientists and to material scientists working in universities and industry, and to graduate students.

ELI RUCKENSTEIN  
HAIYOU WANG







## ABOUT THE AUTHORS

Professor Eli Ruckenstein is SUNY Distinguished Professor at State University of New York at Buffalo and Member of the National Academy of Engineering and American Academy of Arts and Sciences. His pioneering contributions to various areas of physical chemistry and applied sciences have brought him numerous distinctions, among which are the National Medal of Science and the Founders Award of the National Academy of Engineering. In addition, from the American Institute of Chemical Engineers, he won the Alpha Chi Sigma Award for his work in transport phenomena, the Walker Award for his work in the area of catalysis, and the Founders Award for his overall contribution to Science. From the American Chemical Society, he received the Kendall Award for his contributions to colloids and interfaces, the Langmuir Lecture Award for his achievement in the area of polymers, the Schoellkopf Medal for his work in catalysis, and the Murphree Award for his work in heterogeneous catalysis. He was given the Humboldt Award by Germany for his work in surfactants and the Creativity Award by the National

Science Foundation for his work on biomolecules. He is a fellow of the American Institute of Chemical Engineers, which with the occasion of its 100th anniversary designated him as one of 50 Eminent Chemical Engineers of the Foundation Age. He is also a fellow of the American Nano Society.

Dr. Haiyou Wang was born in 1964 in Lanxi, Zhejiang Province, P.R. China. He is currently a principal engineer of Performance Materials and Technologies, Honeywell International. He was a senior scientist of Catalytic Materials LLC from 2001 to 2005, a visiting research scholar of Hong Kong Baptist University from 1994 to 1996, and a faculty member of Xiamen University from 1991 to 1997. He received a BS in 1985, a MS in 1988, and a DSc. in 1991, all in physical chemistry from Xiamen University, as well as a PhD in chemical engineering in 2001 from the State University of New York at Buffalo. He has authored or coauthored 50+ papers and 50+ patents/patent applications. He has been active within heterogeneous catalysis for over two decades.







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# CATALYTIC CONVERSION OF METHANE TO SYNTHESIS GAS BY CO<sub>2</sub> REFORMING

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## INTRODUCTION

CO<sub>2</sub> reforming of methane,



is an endothermic reaction; it produces synthesis gas with a H<sub>2</sub>/CO ratio around 1, which is suitable for the Fischer–Tropsch synthesis of long-chain hydrocarbons. In addition, this process may have important environmental implications, since it consumes CO<sub>2</sub> and CH<sub>4</sub>, two greenhouse gases. Unfortunately, no industrial technology for CO<sub>2</sub> reforming of methane has yet been developed, because no effective and commercially viable catalysts have been discovered [1]. When the conventional Ni-based catalyst for steam reforming is used for CO<sub>2</sub> reforming, it deactivates rapidly mainly because of carbon deposition on the active sites. A high molar ratio of CO<sub>2</sub> to CH<sub>4</sub> (≥3) can be used to reduce the carbon deposition, but this decreases the selectivity to synthesis gas. Therefore, the inhibition of carbon deposition without extra cost and loss of catalyst performance poses a major challenge for CO<sub>2</sub> reforming of methane.

In CO<sub>2</sub> reforming of methane, carbon formation can take place through two possible routes: CH<sub>4</sub> decomposition and CO disproportionation (Boudouard reaction). While the former is an endothermic reaction, the latter is an exothermic one. Carbon formation by CH<sub>4</sub> decomposition is a structure-sensitive reaction [2, 3]. Specifically, the Ni(100) and Ni(110) surfaces are more active in CH<sub>4</sub> decomposition to carbon than the Ni(111) surface [2]. The CO disproportionation is favored at temperatures below 973 K due to its exothermic nature. Carbon deposition with measurable rates occurs over Co, Fe, and Ni catalysts at temperatures higher than 623 K [3]. Given that CO<sub>2</sub> reforming of methane often takes place at a temperature ≥973 K, CH<sub>4</sub> decomposition to carbon constitutes the main concern. The diffusion and segregation of carbon are dependent on the structure of metal surface as well. For instance, the carbon on Ni(110) diffuses more quickly into the bulk of the metal than carbon on Ni(100) [3]. In addition, it is more difficult for the carbon adsorbed on a smaller metal particle to diffuse than on a larger metal particle [4]. The structure-sensitivity nature of carbon formation and its diffusion provides an opportunity to avoid, or at least to reduce carbon deposition through the



modification of the metal surface structure. One method is to control the size of the ensembles of metal atoms on surface since the ensembles required for carbon formation are larger than those needed for CH<sub>4</sub> reforming [5]. Accordingly, by controlling the metal particle size, one can control carbon formation. In this regard, strong adsorption of sulfur (sulfur passivation) was used to control the size of ensembles, and the degree of carbon deposition on Ni catalysts, as in the successfully commercialized SPARG process [6, 7]. Sulfur passivation is presumably responsible for the control of the size of the active metal ensembles since sulfur can preferentially eliminate the larger ensembles.

Besides the surface structure, the surface acidity of a catalyst is another major property that affects carbon deposition. It has been noted that carbon deposition can be attenuated or even completely suppressed when the metal is supported on a metal oxide with a strong Lewis basicity [8–11]. This suppression occurs because the high Lewis basicity of the support increases the ability of the catalyst to chemisorb CO<sub>2</sub> in the CO<sub>2</sub> reforming of methane and water in the steam reforming of methane, and these species react with carbon to form CO, resulting in decreased net carbon formation.

Almost all the catalysts used for CO<sub>2</sub> reforming of methane are supported metal catalysts. Based on the catalytic metal component, catalysts can be divided into two groups, that is, supported noble metal (such as Pd, Rh, Ir, Pt, Ru, etc.) catalysts and supported nonnoble metal (such as Fe, Co, and Ni) catalysts. Inui [12] and Rostrup-Nielsen [7] reported that the amount of carbon deposited on metal catalysts decreases in the order Ni >> Rh > Ir = Ru > Pt ≈ Pd at 773 K and Ni > Pd = Rh > Ir > Pt >> Ru at 923 K. Thus, noble metal catalysts, in general, provide greater likelihood of carbon-free operation than Ni and other non-noble metal catalysts. For the same metal component, the rate of carbon deposition is also dependent on the nature of the support [7, 13–16].

Among the noble metal catalysts, Pt has been the most widely studied one, probably because of its lower rate of carbon formation and its greater availability than other noble metals. Regarding the support for Pt, ZrO<sub>2</sub> has been the most widely used because of its lower rate of carbon formation compared with other supports [17–22]. Bitter et al. [20] found that the rate of carbon formation decreases in the order Pt/Al<sub>2</sub>O<sub>3</sub> > Pt/TiO<sub>2</sub> > Pt/ZrO<sub>2</sub> and that carbon deposition from methane decomposition instead of metal sintering is mainly responsible for the deactivation of supported Pt catalysts. The higher stability of Pt/ZrO<sub>2</sub> is probably due to the strong Pt–Zr<sup>n+</sup> interactions, which reduce carbon formation during reaction by promoting CO<sub>2</sub> dissociation [21]. The promoter, which can be a metal component or a metal oxide,

has a significant effect on carbon deposition as well. It was reported that the bimetallic Pt–Au/SiO<sub>2</sub>, Pt–Sn/SiO<sub>2</sub>, and Pt–Sn/ZrO<sub>2</sub> catalysts generate less deposited carbon during CO<sub>2</sub> reforming of CH<sub>4</sub> than the corresponding monometallic Pt catalysts [23], probably because of the formation of metal alloys. It was also reported that the addition of cerium or lanthanum greatly improves the stability of a Pt/ZrO<sub>2</sub> catalyst without decreasing the CH<sub>4</sub> or CO<sub>2</sub> conversions [24]. Although the total amount of carbon deposition remained comparable for a Ce-promoted Pt/ZrO<sub>2</sub> catalyst and an unpromoted Pt/ZrO<sub>2</sub> catalyst, TPO (temperature programmed oxidation) studies suggested that the carbon species on Ce-promoted Pt/ZrO<sub>2</sub> catalyst could be removed at much lower temperatures. On the other hand, the La-promoted catalyst experienced a much lower carbon deposition than the unpromoted one.

More research work has been devoted to non-noble metal catalysts, particularly Ni-based catalysts due to their low cost with comparable activity and selectivity as the noble metal catalysts. Nevertheless, thermodynamic studies indicate that Ni catalysts are prone to carbon deposition in CO<sub>2</sub> reforming of CH<sub>4</sub>, causing unstable activity [25]. Therefore, it poses an even bigger challenge to develop a stable Ni-based catalyst. Alumina is one of the most commonly used supports for Ni catalysts [10, 26–36]. The rate of carbon deposition over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts is dependent on the catalyst structure, composition, and preparation conditions [12]. Chen and Ren [37] reported that carbon deposition was significantly suppressed when NiAl<sub>2</sub>O<sub>4</sub> was formed during pretreatment. The Ni–O bond in NiAl<sub>2</sub>O<sub>4</sub> is stronger than that in NiO [38]. Consequently, it is more difficult to reduce Ni<sup>2+</sup> to Ni<sup>0</sup>, resulting in smaller nickel crystallites on the surface of catalyst. Such nickel particles, which are smaller than the size needed for carbon deposition, decrease the carbon deposition [28]. The catalyst preparation method exerts an influence on the dispersion of metal particles and ultimately on the rate of carbon deposition. Kim et al. [27, 39] and Osaki et al. [40] reported that Ni/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from aerogel alumina exhibited remarkably lower coking rates compared with alumina-supported Ni catalysts prepared by the conventional impregnation method. Osaki et al. [40] suggested that the Ni–O–Al bonds formed in aerogels are responsible for the formation of fine nickel particle after hydrogen reduction and ultimately for the high activity and low carbon deposition. A water-in-oil (w/o) micromulsion method was also found to be effective in the preparation of a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst possessing low carbon deposition and good stability [41].

Various promoters have been used to improve the performance of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. The addition of basic



oxides of Na, K, Mg, and Ca to Ni/Al<sub>2</sub>O<sub>3</sub> catalysts was found to greatly reduce carbon deposition [10, 35, 42–44]. Kinetic results indicated that these added metal oxides changed the reaction order in CH<sub>4</sub> from negative to positive and the order in CO<sub>2</sub> from positive to negative. This observation implies that the surface of a basic metal oxide doped Ni catalyst is rich in adsorbed CO<sub>2</sub>, whereas the surface of a Ni catalyst free of such a basic metal oxide is rich in adsorbed CH<sub>4</sub> [10]. The coverage of nickel with CO<sub>2</sub> is most likely unfavorable to CH<sub>4</sub> decomposition and, consequently, the carbon deposition is decreased. Choi et al. [45] examined the effect of Co, Cu, Zr, and Mn as promoters. They found that, compared with unpromoted Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, those promoted with Co, Cu, and Zr provided slightly improved activities, while the Mn-promoted catalyst exhibited a significant reduction in coke formation with only a small decrease in catalytic activity. Moreover, Seok et al. [46] found that the addition of Mn to Ni/Al<sub>2</sub>O<sub>3</sub> caused a partial coverage of the surface of nickel particles with patches of MnO<sub>x</sub>, which promoted the adsorption of CO<sub>2</sub>. Both the partial coverage of the nickel surface with MnO<sub>x</sub> and the promoted CO<sub>2</sub> adsorption appear to contribute to decreased carbon deposition on Mn-promoted Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Mo was also found to improve the stability of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst by reducing carbon deposition [47]. Rare earth metals or metal oxides were also investigated as promoters [48–50]. Nd [48] and CeO<sub>2</sub> [49, 50] were found to promote the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, by reducing carbon deposition.

Our work was mainly focused on the effect of various supports on the reactivity of supported metal catalysts and the structure–property relationships. Efforts were also made to identify the mechanism of CO<sub>2</sub> reforming of CH<sub>4</sub> to synthesis gas. In brief, Chapter 1 consists of four parts: the first is concerned with Ni-based catalysts (**1.1**, **1.2**, **1.3**, and **1.4**); the second with Co-based catalysts (**1.5**, **1.6**, and **1.7**); the third with Rh-based catalysts (**1.8**); and the fourth with mechanistic studies of CO<sub>2</sub> reforming of CH<sub>4</sub> (**1.9**).

The nature of the support was found to play a very important role in determining the performance (activity and stability) of supported metal catalysts for CO<sub>2</sub> reforming of methane (**1.1**, **1.2**, **1.5**, and **1.8**). Among all supports investigated, MgO was the best support for both Ni and Co catalysts (**1.1** and **1.5**). The reduced NiO/MgO catalyst with a NiO content in the range of 9.2–28.6 wt% prepared by impregnation provided both high CO yield (94%) and excellent stability, because it generated NiO–MgO solid solution catalysts (**1.2** and **1.3**). The strong interactions between Ni and Mg induced by the formation of a NiO–MgO solid solution help to inhibit not only the sintering of NiO, but also the formation of large clusters of Ni, which generate coke (**1.4**). Similarly,

the reduced 12 wt% CoO/MgO solid solution catalyst provided a CO yield of 93% and excellent stability (**1.5**). Since Co has two oxidation states, Co<sup>2+</sup> and Co<sup>3+</sup>, depending upon the calcination temperature and Co loading, one, two, or three Co-containing species, that is, Co<sub>3</sub>O<sub>4</sub>, MgCo<sub>2</sub>O<sub>4</sub>, and CoO–MgO solid solution, can be generated. This affects the reduction behavior and ultimately the catalytic performance of MgO-supported Co catalysts. Indeed, the Co/MgO solid solution catalysts with a loading between 8 and 36 wt%, precalcined at 500 and 800°C, respectively, provided high and stable activities; a too-high calcination temperature (e.g., 900°C) resulted in low activity, whereas too-high Co loading (e.g., 48 wt%) combined with a low calcination temperature ≤800°C, resulted in an unstable activity (**1.6**). For supported Rh catalysts, most of the reducible oxides, such as CeO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>, provided much lower yields of CO and H<sub>2</sub> than the irreducible oxides, such as γ-Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>; among the irreducible oxides, MgO and γ-Al<sub>2</sub>O<sub>3</sub> provided high and stable activities (**1.8**).

Numerous mechanistic studies have suggested that during CO<sub>2</sub> reforming of methane, CH<sub>4</sub> is decomposed on metallic sites to reactive carbon species (CH<sub>x</sub>, with  $x = 0–3$ ), which are oxidized to CO by the oxygen-containing species that originate from CO<sub>2</sub>. In this regard, a transient response analysis via a broadened pulse combined with a step change or an isotopic pulse was developed and applied to CO<sub>2</sub> reforming of methane over Ni/SiO<sub>2</sub> (**1.9**). It was found that Ni<sup>0</sup> is the active site for methane decomposition and that the reaction between C and O species on Ni<sup>0</sup> is the rate-determining step. Consequently, the rate of carbon accumulation on the catalyst surface is determined by the relative rates of formation of carbon species and their oxidative removal. When the former dominates, an excess of carbon is deposited, whereas when the latter dominates, the number of metallic sites is decreased because of their oxidation and subsequent restructuring of the catalyst. Both result in unstable activity. By optimizing the metal loading and the calcination temperature,  $T_c$ , for example, 6% wt% for  $T_c = 500^\circ\text{C}$  and 9 wt% for  $T_c = 1000^\circ\text{C}$ , highly effective and stable Co/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were obtained (**1.7**).

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