

FORMIC ACID AND FORMALDEHYDE AS SPIN-OFF PRODUCTS IN Ru-EDTA-CO COMPLEX CATALYZED LIQUID PHASE WATER-GAS SHIFT (WGS) REACTION

M M TAQUI KHAN*, S B HALLIGUDI, N NAGESWARA RAO and SUMITA SHUKLA

Discipline of Coordination Chemistry and Homogeneous Catalysis, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002 (India)

(Received June 13, 1988, accepted October 7, 1988)

Summary

Liquid phase water-gas shift reaction (WGSR) experiments catalyzed by soluble Ru-EDTA-CO complex were conducted in a pressure reactor at CO pressures in the range of 7 - 34 atm and temperatures of 40 - 80 °C. Along with the formation of the usual WGSR products CO₂ and H₂ in major quantities, significant amounts of HCHO and HCOOH were obtained in the liquid phase. The rates of formation of formaldehyde and formic acid were measured and their dependence on catalyst concentration and CO pressure found to be first order. The formation of HCOOH via CO insertion into the M-OH bond has been proposed in the reaction mechanism for the first time.

Introduction

The industrial demand for hydrogen for NH₃ synthesis is largely met by the water-gas shift reaction (WGSR) [1]. The WGSR, which is the oxidation of CO by H₂O (reaction (1)), is carried out by heterogeneous catalysis, usually Fe₂O₃/MoO₃ and Cr₂O₃/MoO₃, at pressures of 200 - 300 atm and temperatures of 300 - 400 °C in the gaseous phase



The process is thus energy intensive, since it is unavoidably associated with high temperature and pressure required for the reaction. Overcoming this difficulty with the WGSR has been a challenging area of research for both chemists and technologists. There has been some degree of success in the low temperature performance of WGSR catalyzed by transition metal complexes [4 - 8]. Recent applications [9] of metal complexes in the WGSR confirm unambiguously that the equilibrium in eqn. (1) showed a large shift towards the production of hydrogen ($K_{800^\circ\text{C}} = 1.105$, $K_{25^\circ\text{C}} = 1.5 \times 10^3$); but the

* Author to whom correspondence should be addressed

rates of reaction are low. The reported [7] turnover numbers (mol CO₂/H₂ per mol catalyst per hour) for the reaction hardly exceeded 100. Recently, we reported [10] catalysis of the WGS by [Ru(EDTA-H)(CO)]⁻ in the liquid phase at a CO pressure of 15 atm and temperature 50 °C, with a turnover number of 350 mol CO₂/H₂ per mol catalyst per hour, which is the highest ever achieved.

A metal-centered pathway for the WGS may lead to the formation of other C₁ products, such as HCHO and HCOOH, in addition to CO₂ and H₂ via insertion of CO into -M-H or -M-OH bonds. The formation of free formaldehyde in metal complex (hydrido complex) catalyzed WGS was reported [11, 12], but the yields are very small. Earlier [13], using our catalyst [Ru^{II}(EDTA-H)CO]⁻, we identified small quantities of formaldehyde among the products of the reaction of CO with H₂O. In the present paper we report the formation of formaldehyde and formic acid in significant quantities in the metal complex-catalyzed WGS. To the authors' knowledge, formic acid has not been reported hitherto as a side product of the WGS. Both formaldehyde and formic acid formed in the [Ru^{II}(EDTA-H)CO]⁻-catalyzed WGS are estimated with the course of the reaction, and rate data were obtained. Probable mechanistic routes leading to HCOOH and HCHO formation are outlined.

Experimental

The water-gas shift reactions were carried out in a 300 ml stainless steel autoclave (Parr Instrument Co., USA). The autoclave has provisions for automatic temperature control accurate up to ±1 °C and mechanical stirring with speed variable from 100 - 1000 rpm.

The catalyst K[Ru^{III}(EDTA-H)Cl]·2H₂O (EDTA = ethylenediaminetetraacetic acid) was prepared by a procedure described in the literature [14]. All chemicals used were of AR grade, and water was double-distilled. High purity carbon monoxide (> 99.6%) was obtained from BOC, U.K.

Firstly, the reactor was charged with known quantities of catalyst and H₂O. After the desired temperature was attained, the reaction was started by admitting CO into the reactor up to the desired pressure limit and stirring simultaneously at 600 rpm.

Gaseous samples withdrawn at different time intervals were analyzed by an Orsat apparatus and GC (shimadzu, GC-9A). Similarly, liquid aliquots were withdrawn through sampling outlets at known intervals of time. Each aliquot was used to determine HCHO and HCOOH spectrophotometrically (UV-VIS) using the Hantzsch [15, 16] reaction and monitoring the peak at 412 nm. The NMR spectrum of the reaction solution (aliquot) was obtained in D₂O by a JEOL FX-100 FT-NMR spectrometer with DSS as reference. Kinetic and thermodynamic data were obtained by studying the rate dependence with respect to catalyst concentration, CO pressure and temperature.

Results and discussion

Figure 1 depicts the formation of formaldehyde and formic acid in a typical water-gas shift reaction (WGSR) catalyzed by $[\text{Ru}^{\text{II}}(\text{EDTA}-\text{H})\text{CO}]^-$. The concentration of both HCHO and HCOOH builds up gradually with increasing contact time, indicating that their formation is also catalyzed by $[\text{Ru}^{\text{II}}(\text{EDTA}-\text{H})\text{CO}]^-$. During the initial 6 h of contact time, the concentrations of HCHO and HCOOH increased linearly with time, however, beyond 6 h HCHO tends to saturate, whilst HCOOH shows a decay.

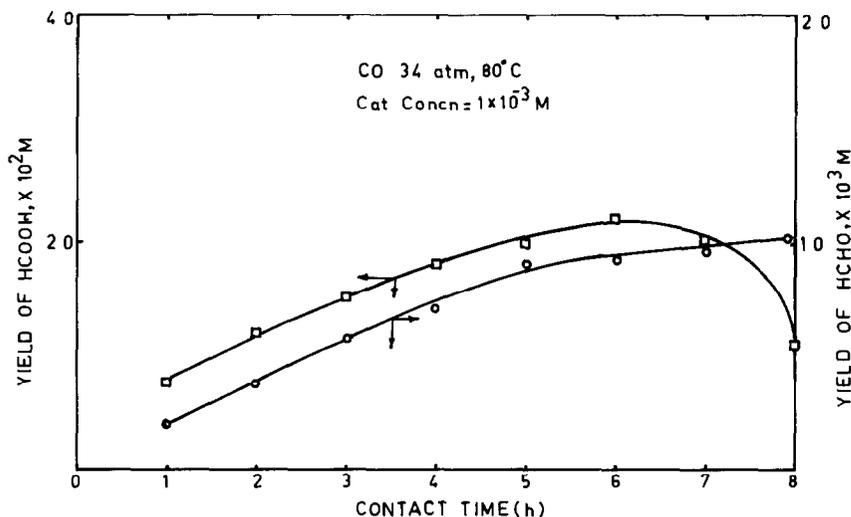


Fig 1 $[\text{Ru}(\text{EDTA}-\text{H})\text{CO}]^-$ catalyzed formation of HCOOH and HCHO

Kinetics

The reaction between CO and H_2O catalyzed by complex 1 and the rates of formation of the products were determined by varying the concentrations of catalyst, CO pressure and temperature. The rate dependences on the parameters varied are reported.

Effect of catalyst concentration

The catalyst concentration was varied between $0.5 - 2.0 \times 10^{-3}$ M, while the dissolved CO concentration, 34 atm (2.17×10^{-3} M) and temperature 80°C were maintained constant. The rate dependences of HCOOH and HCHO on catalyst concentration are shown in Figs 2 and 3, respectively. It is clearly seen from these figures that the rates of formation of HCOOH and HCHO show a first order dependence with respect to catalyst concentration.

Effect of dissolved CO concentration

The dissolved CO concentration was varied between 0.46 - 2.17×10^{-3} M (7 - 34 atm) at constant catalyst concentration 1×10^{-3} M and tempera-

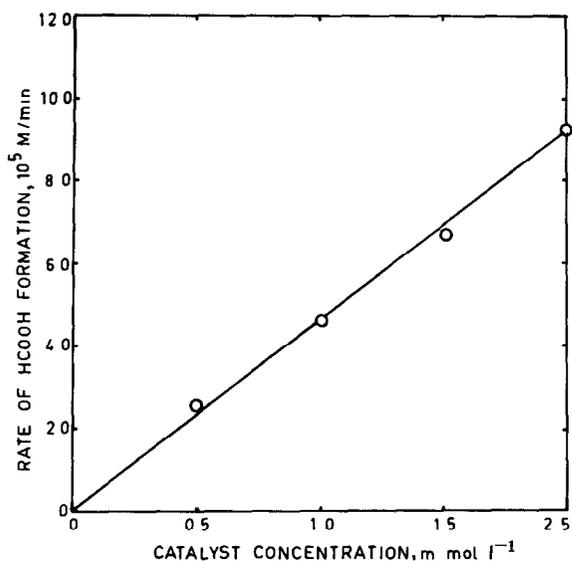


Fig 2 Effect of catalyst concentration on the rate of HCOOH formation

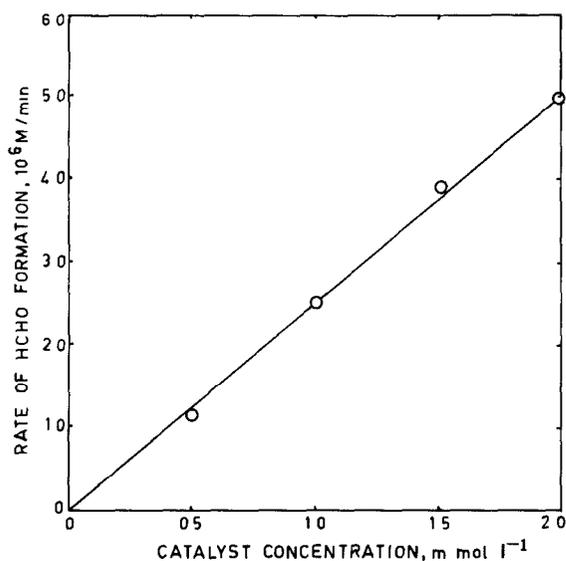


Fig 3 Effect of catalyst concentration of the rate of HCHO formation

ture 80 °C. Figures 4 and 5 illustrate the linear variation indicating first order dependence of the rates of HCOOH and HCHO formation on dissolved CO concentration.

Effect of temperature

Experiments on the carbonylation of CO and H₂O for the formation of HCOOH and HCHO in the liquid phase were conducted at catalyst concentration 1×10^{-3} M and CO partial pressure 34 atm, and the temperature

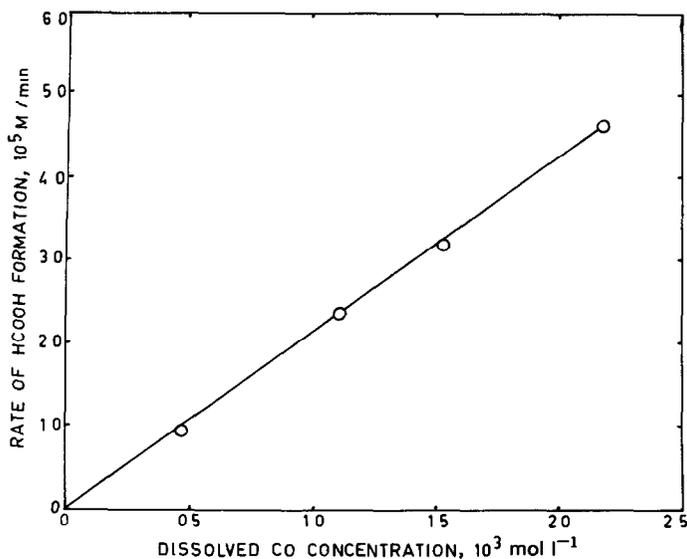


Fig 4 Effect of CO concentration on the rate of HCOOH formation

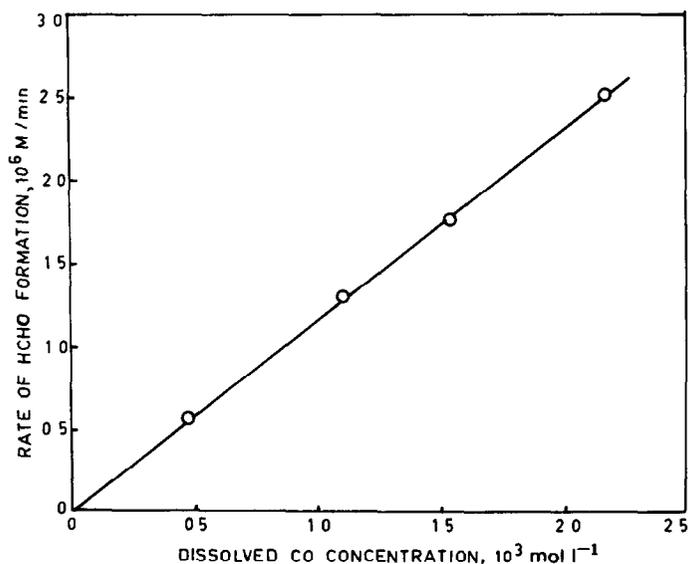


Fig 5 Effect of CO concentration on the rate of HCHO formation

was varied between 40 - 80 °C. Figure 6 shows the plot of $-\ln \text{ rate}$ vs $1/T$. From the slopes of the straight lines, the activation energies (E_a) estimated are 13.5 Kcal mol⁻¹ (HCOOH) and 6.7 Kcal mol⁻¹ (HCHO).

Mechanism

Based on the products formed and their rate dependences on kinetic parameters, a mechanism is proposed for the formation of HCOOH and

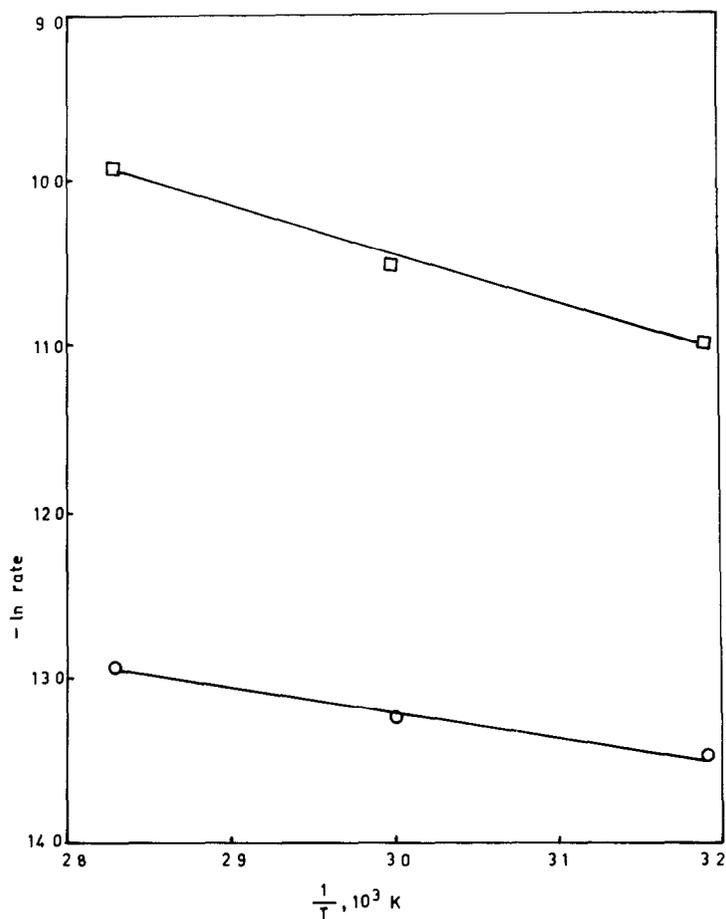
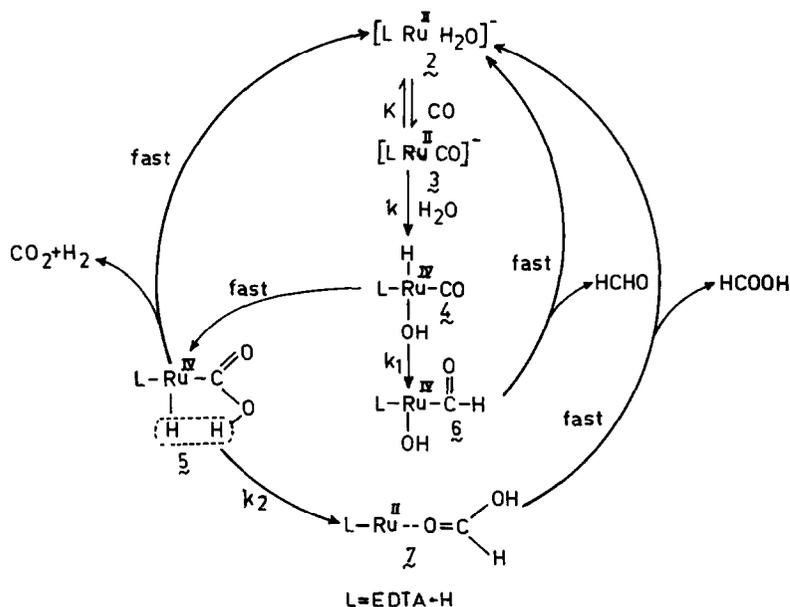


Fig 6 Effect of temperature on the rates of HCOOH \square and HCHO \circ formation

HCHO in the liquid phase during the water-gas shift reaction, as shown in Scheme 1.

In the proposed mechanism, the active catalytic species 3 is formed *in situ* via the reduction of $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{H}_2\text{O})]$ to $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{H}_2\text{O})]^- 2$ by CO. The $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{H}_2\text{O})]$ is formed in solution by rapid aquation [14] of starting material $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA-H})\text{Cl}] \cdot 2\text{H}_2\text{O}$ 1. Species 2 reacts with CO by the displacement of a water molecule to form the active catalytic species 3. In the next step, oxidative addition of H_2O to 3 takes place to form hydridocarbonyl species 4. The formation of 4 is supported [17] by the hydride proton NMR spectrum of the reaction mixture, which showed peaks at $\delta - 20.1$ and $\delta - 8.1$ ppm, for hydrides *trans* to $-\text{OH}$ and $-\text{CO}$, respectively. Subsequent to the formation of 4, through intramolecular insertion in 4, CO inserts into either the Ru-OH or Ru-H bond to give an η^1 -carboxylate 5 or formyl complex 6, respectively



Scheme 1

The metalcarboxylate species 5 is unstable and rapidly decomposes by reductive decarboxylation to form the well-known water-gas shift reaction products CO_2 and H_2 , simultaneously yielding species 2. Such η^1 -metalcarboxylate intermediates, by virtue of their lower stability, are known to decompose into CO_2 and H_2 and are currently proposed as key intermediates in transition metal-catalyzed WGS [18 - 21]. The metal formyl complex 6 readily reacts with hydrogen produced *in situ* to release a molecule of HCHO, concomitantly regenerating the aquo species 2. The formation of intermediate metal formyl complexes has been reported earlier by other investigators [22 - 25].

In an alternate pathway, species 5 may rearrange by prototropic shift from the metal ion to η^1 carbon to form an O-bonded Ru(II)-formato species 7. Species 7 rapidly decomposes to release a molecule of HCOOH and species 2. Such reductive elimination of metalcarboxylates to form formic acid has been proposed [21]. Thus species 2 once again participates in the reaction, completing the cycle.

Rate laws

From the chosen rate-determining step in Scheme 1, we could derive rate equations for the formation of HCHO and HCOOH as:

$$r_1 = \frac{kk_1K[\text{LRu}^{\text{III}}(\text{H}_2\text{O})]_{\text{T}}[\text{CO}]}{1 + K[\text{CO}]} \quad (2)$$

and

$$r_2 = \frac{kk_2K[\text{LRu}^{\text{III}}(\text{H}_2\text{O})]_{\text{T}}[\text{CO}]}{1 + K[\text{CO}]} \quad (3)$$

where r_1 = rate of HCHO formation, r_2 = rate of HCOOH formation, $[\text{LRu}^{\text{III}}(\text{H}_2\text{O})]_{\text{T}}$ = total $K[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}] \cdot 2\text{H}_2\text{O}$ concentration, $[\text{CO}]$ = dissolved CO concentration, K = equilibrium constant, k_1 = rate constant for HCHO formation, k_2 = rate constant for HCOOH formation and k = rate constant for WGSR.

Evaluation of the rate constants k_1 and k_2 was made using the known value of k , the rate constant of WGSR, and the equilibrium constant, K at 80 °C determined earlier in our studies [10]. Equations (2) and (3) can be rearranged in the slope and intercept forms as:

$$\frac{[\text{LRu}^{\text{III}}(\text{H}_2\text{O})]_{\text{T}}}{r_1} = \frac{1}{[\text{CO}]} \times \frac{1}{kk_1K} + \frac{1}{kk_1} \quad (4)$$

and

$$\frac{[\text{LRu}^{\text{III}}(\text{H}_2\text{O})]_{\text{T}}}{r_2} = \frac{1}{[\text{CO}]} \times \frac{1}{kk_2K} + \frac{1}{kk_2} \quad (5)$$

From the intercepts of eqns. (4) and (5), the values of k_1 and k_2 were obtained. The rate constants and equilibrium constants at 80 °C and 34 atm CO obtained for the reactions of CO with water leading to HCOOH and HCHO are

$$k = 90.1 \text{ min}^{-1}$$

$$k_1 = 1.39 \times 10^{-3} \text{ min}^{-1}$$

$$k_2 = 5.56 \times 10^{-3} \text{ min}^{-1}$$

$$K = 7.0 \pm 0.4 \text{ M}^{-1}$$

The value of k (the WGSR rate constant) is several orders of magnitude higher ($k/k_1 \sim 6.4 \times 10^4$, $k/k_2 \sim 1.6 \times 10^4$) than k_2 and k_1 . This confirms that the WGSR is much faster and is the predominant reaction. The rate constant k_2 (formic acid) is at least 4 times greater than that of formaldehyde (k_1). This probably indicates a facile insertion of CO into the Ru—OH rather than the Ru—H bond. It is known [2, 26] that metal formyl complexes are difficult to obtain by CO insertion into Ru—H because they are thermodynamically less stable than the corresponding hydrides [27].

Using the determined activation energies (E_a) from the slope of straight lines of Fig. 6, the other thermodynamic activation parameters for both HCHO and HCOOH formation were computed employing known expressions. These values are presented in Table 1. In the temperature range studied (40 - 80 °C), the enthalpies of activation ΔH^\ddagger for HCHO and HCOOH are 6.1 and 12.8 kcal mol⁻¹, respectively, indicating endothermic formation reactions. This is supported by other studies where HCHO formation is endothermic with $\Delta H = +5.0$ kcal mol⁻¹ [2, 26]. To the best of our knowledge, the thermodynamic data for HCOOH formation from CO under catalyzed conditions is presented for the first time in this paper.

The formation of HCOOH from CO and H₂O can be regarded as hydration of carbon monoxide. Although reports on such hydration of CO are not

TABLE 1

Thermodynamic activation parameters for WGSR-initiated formation of HCHO and HCOOH

System	E_a (kcal mol ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (e u)	ΔG^\ddagger (kcal mol ⁻¹)
HCHO	6.7	6.1	18	0.08
HCOOH	13.5	12.8	38	0.14

available in the literature, the hydration of nitrile ($-\text{C}\equiv\text{N}$) catalyzed by metal complexes has been reported [28]. Very similar to our proposal of CO insertion into the Ru-OH bond leading to the formation of HCOOH, in this work the nitrile group was likewise considered to insert into the M-OH bond, forming the corresponding amides.

The entropies of formation of HCHO and HCOOH are reported in Table 1. The entropy of formation of HCOOH, 38 e.u., is about twice that of HCHO (18 e.u.). The reason is the difference in the nature of the intermediates 6 and 7. The intermediate 7 is more of an ion pair, which is supported by the high positive value of the entropy of activation.

References

- 1 B S Kirk and D F Othmer (eds), *Encyclopedia of Chemical Technology*, Vol 23, Wiley-Interscience, New York, 1983, p 548
- 2 R P A Sneed, in G Wilkinson, F G A Stone and E W Abel (eds), *Comprehensive Organometallic Chemistry*, Vol 8, Pergamon Press, Oxford, 1982, pp 9-40 and references therein
- 3 (a) R B Anderson, in P H Emmet (ed), *Catalysis*, Vol 5, Reinhold, New York, 1957, p 1, (b) P J Denny and D A Whan, in *Catalysis*, Vol 2, The Chemical Society, London, 1978, p 46
- 4 R W Joyner, *J Catal*, 50 (1977) 176
- 5 G A Martin, M Primet and J A Dalmon, *J Catal*, 53 (1978) 321
- 6 M Primet, *J Chem Soc, Faraday Trans*, 74 (1978) 2570
- 7 A D King Jr, R B King and W B Young, *J Am Chem Soc*, 102 (1980) 1028
- 8 R B King, *Inorganic Compounds with Unusual Properties*, Vol 2, *Advances in Chemistry Series*, No 173, American Chemical Society, Washington D C 1979
- 9 P Escaffre, A Thorez and P Kalck, *J Chem Soc, Chem Commun*, (1987) 146
- 10 (a) M M Taqui Khan, S B Halligudi and Sumita Shukla, *Angew Chem Int Engl*, 27 (1988) 1735, (b) Indian Pat DEL/200/1988, to M M Taqui Khan, S B Halligudi and Sumita Shukla, CSIR, New Delhi
- 11 C P Casey and S M Neuman, *J Am. Chem Soc*, 100 (1978) 2544
- 12 H Kolbel and D Hanus, *Chem Ing Tech*, 46 (1976) 1042, D Kitzelmann, W Vielstich and T Dittrich, *ibid*, 49 (1977) 463
- 13 (a) M M Taqui Khan, S B Halligudi, S H R Abdi, *J Mol Catal*, 45 (1988) 215, (b) *ibid*, *J Mol Catal*, 48 (1988) 7
- 14 A A Diamantis and J V Dubrawski, *Inorg Chem*, 20 (1981) 1142
- 15 T Nash, *Biochem J*, 55 (1953) 416
- 16 H N Wood and H Gest, in S P Colowick and N O Kaplan (eds), *Methods of Enzymology*, Vol 3, Academic Press, New York, 1957, pp 287-289

- 17 M M Taqui Khan, S B Halligudi and S H R Abdi, *J Mol Catal*, 48 (1988) 313
- 18 R Eisenberg and D E Hendriksen, *Adv Catal*, 28 (1979) 79
- 19 D Forster, *Adv Organometall Chem*, 17 (1979) 255
- 20 M Catellani and J Halpern, *Inorg Chem*, 19 (1980) 566
- 21 N Grice, S C Kao and R Pettit, *J Am Chem Soc*, 101 (1979) 1627
- 22 W Tam, W K Wong and J A Gladysz, *J Am Chem Soc*, 101 (1979) 1589
- 23 S R Winter, G W Cornett and E A Thompson, *J Organometall Chem*, 133 (1977) 339
- 24 C P Cassey and S M Neumann, *J Am Chem Soc*, 98 (1976) 5395, also see *ibid*, 100 (1978) 2544
- 25 W K Wong, W Tam, C E Stronse and J A Galdysz, *J Chem Soc, Chem Commun*, (1979) 530
- 26 E L Muetterties and J Stein, *Chem Rev*, 79 (1979) 479
- 27 C P Casey, M A Andrews, D R McAlister, W D Jones and S G Harsy, *J Mol Catal*, 13 (1981) 43
- 28 M A Bennet and T Yoshida, *J Am Chem Soc*, 95 (1973) 3030