

NOVEL ORGANOMETALLIC INTERMEDIATES OF RUTHENIUM IN SYNTHESIS AND CATALYSIS—A CROSS ROAD OF WERNER'S COORDINATION CHEMISTRY AND ORGANOMETALLIC CHEMISTRY

M M TAQUI KHAN, FNA

*Director, Central Salt and Marine Chemicals Research Institute,
Bhavnagar 364 002, India*

(Received 5 February 1988; Accepted 19 October 1988)

Ethylenediaminetetraacetatoaquoruthenium(III) $[\text{Ru}(\text{EDTA-H})(\text{H}_2\text{O})]^-$ **1** react with CO or HCOOH to form $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{CO})(\text{H}_2\text{O})]^-$ **2** and $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{CO})(\text{OH})]^-$ **3**. The $\eta^1\text{-COOH}$ complex $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{COOH})]^-$ **3a** which is a common intermediate in both the CO and HCOOH reactions with **1**, on protonation gives formic acid and **1**. Complexes **2** and **3** are ultimately reduced to $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ which is an excellent catalyst in CO insertion reactions in M-C, M-N and M-O bonds to give a variety of products. In some of these reactions Ru(II) undergoes oxidative addition to form intermediate Ru(IV) species.

Key Words : Organometallic Intermediates; Ethylenediaminetetraacetato-aquoruthenium(III); Catalyst

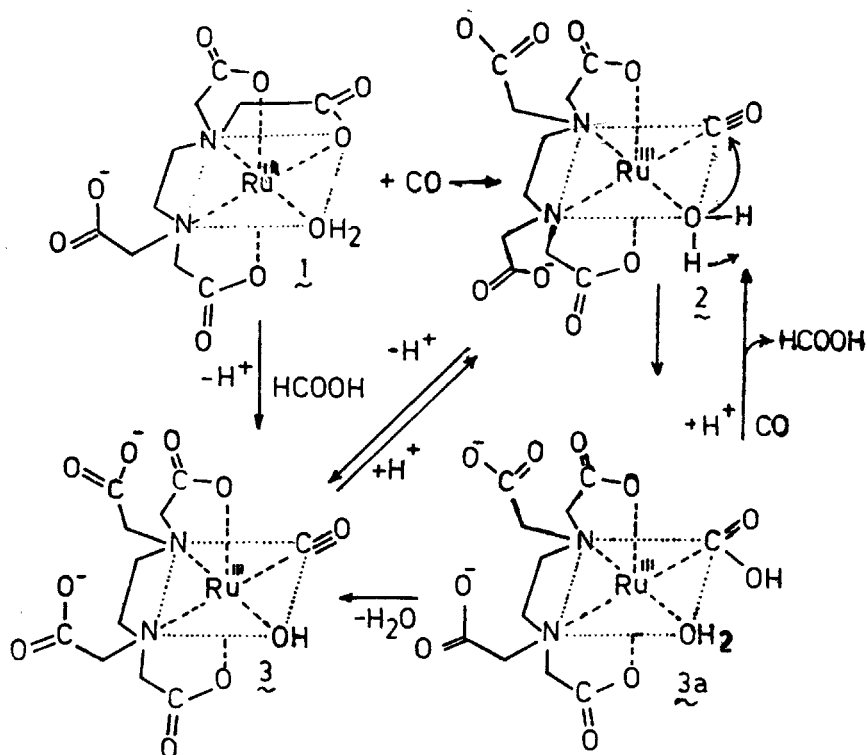
INTRODUCTION

THE complex $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{H}_2\text{O})]^-$ formed by the fast equation¹ of $[\text{Ru}^{\text{III}}(\text{EDTA-H})\text{Cl}]^-$ contains a labile H_2O group which can be substituted by hydride,² PPh_3 ,³ NO, SnCl_3^- and N_3^- and olefins.⁵ In these reactions with H^- and π -acidic ligands ruthenium behaves as a typical border line metal ion in softness, being coordinated to EDTA and the soft π -acidic ligands at the same time. Some of these complexes are excellent catalysts for homogeneous hydrogenation of substrates in mixed aqueous-organic solvents.

The reactivity of π -acidic groups on coordination to $\text{Ru}^{\text{III}}(\text{EDTA-H})$ moiety has prompted us to investigate the carbonylation of saturated and unsaturated substrates catalyzed by the carbonyl species $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{H}_2\text{O})(\text{CO})]^-$ **1** and $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ **2**. Such carbonylation reactions have a great industrial potential⁶⁻⁸ to obtain value added products. The future of homogeneous catalysis in coming decades depends on the discovery of novel reactions with low energy inputs.⁹ The carbonyl species **1** and **2** offer such routes for some important reactions such as water gas shift reaction,⁶ carbonylation of amines,⁷ and benzyl chloride⁸ and hydroformylation of allyl alcohol¹⁰ and olefins.¹¹ In the present paper these reactions are discussed. The reactions proceed under milder conditions of temperature and pressure with a high degree of specificity in most cases.

INTERACTION OF CO WITH $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{H}_2\text{O})]$

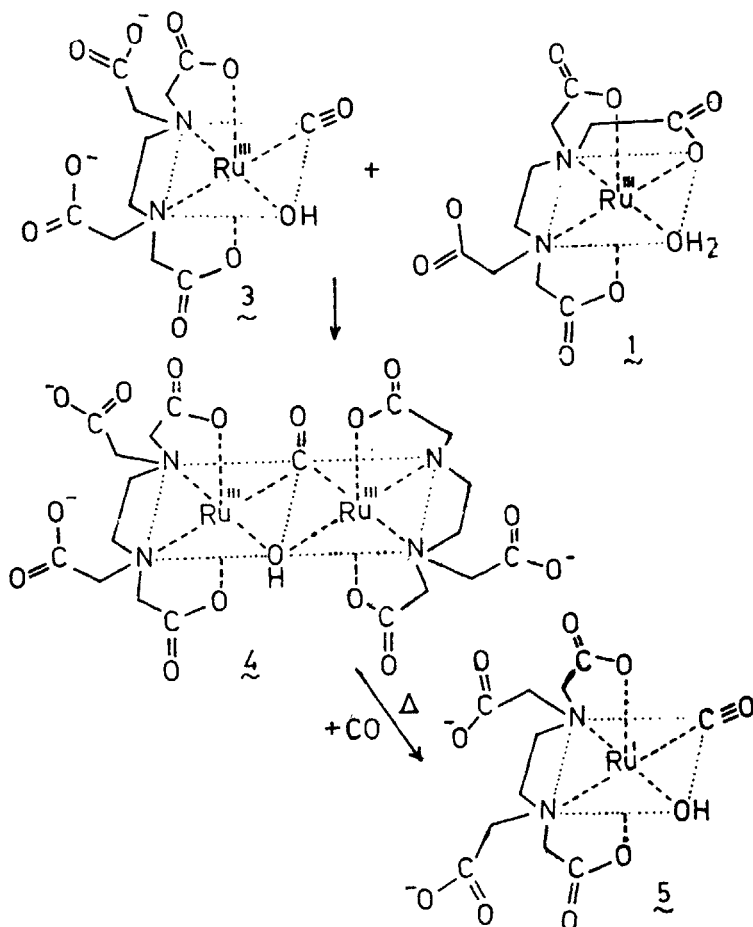
Interaction of CO with $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{H}_2\text{O})]$ 1 gives¹² an aquo carbonyl species 2 which loses a proton to form the hydroxo species 3 (Scheme 1A). The equilibrium between 2 and 3 are pH dependent. Species 3 is also formed by the direct reaction of 1 with formic acid. The reaction with formic acid may proceed through the formation of a η^1 -(COOH) species 3a which can also be obtained by the nucleophilic attack of OH^- on coordinated CO in complex 2. Complex 3a reacts with an acid (proton) to form formic acid and complex 2. The carbonylation of 1 can thus be utilized for the synthesis of HCOOH from CO which can be considered as the addition of H and OH across the triple bond. Complex 3 forms the μ -carbonyl- μ -hydroxo dimer 4 at $\text{pH} > 3.5$. Heating complexes 3 or 4 gives the stable Ru(II)-carbonyl 5 which is used as a catalyst in a number of reactions (Scheme 1B). Species 2-5 have been characterised on the basis of IR and electrochemical techniques including epr for the Ru(III) species. The dimer 4 has also been characterized by potentiometric studies.



SCHEME 1A

CATALYSIS OF WATER GAS SHIFT REACTION

The water gas shift reaction is essentially a reaction between CO and H_2O to form $\text{H}_2 + \text{CO}_2$.

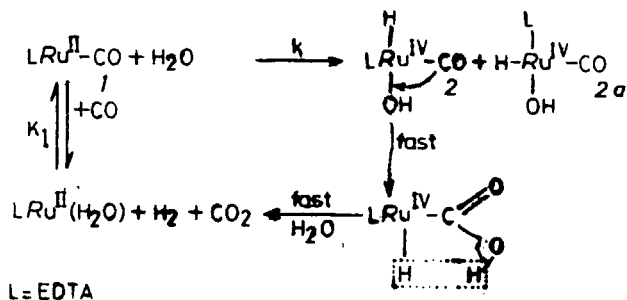


SCHEME 1B



The reaction is exothermic and acts as a source of hydrogen in ammonia plants.¹³⁻¹⁴ The source of CO is gasification of coal or natural gas. The conventional catalyst¹³ chromium activated iron oxide ($\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$) or cobalt-molybdenum catalyst (CoO/MoO_3) are used for the reaction at a temperatures of 400–460° and 200 atmosphere of CO or CO + H₂.

In view of the extreme importance of the reaction in industry as a source of H₂, we have studied the catalysis of water gas shift reaction by Ru^{II}(EDTA-H)(CO)(OH) 5 at 45–80° and 15–35atm of CO. Since the reaction is exothermic, the optimum temperature of the reaction catalyzed by 5 is about 50° at 25 atmospheres of CO. From the kinetic data the following mechanism is proposed for the water gas shift reaction catalyzed by 5.



SCHEME II

The rate determining step of the reaction has been suggested to be the oxidative addition of H_2O to $\text{Ru}^{\text{II}}\text{-EDTA}(\text{CO})$ 1 to form the hydrido carbonyl species 2 and 2a. The formation of 2 and 2a as intermediates is supported by the hydride nmr of the solution which gives peaks at -20.1 and -8.1 ppm, respectively for hydrides *cis* and *trans* to CO, respectively. Insertion of CO into $\text{Ru}^{\text{IV}}\text{-OH}$ bond in a fast-step gives the η^1 -formato intermediate 3 which dissociates in a fast step to form CO_2 , H_2 and LRu^{II} which gives 1 on reaction with CO and completes the catalytic cycle. The values of the equilibrium constants K_1 and the rate constant k at 50° and 15atm of CO are 11M^{-1} and 80.0min^{-1} , respectively with a turnover of 350 moles of CO_2/H_2 per mole of the catalyst per hour; the highest reported so far in the liquid phase. The activation energy of the reaction is 1.47kcal/mole which amounts to a decrease of about 45kcal/mole for the proposed dissociation of H_2O into H and OH in the rate determining step. The entropy and enthalpy of activation are 2.45eu and 0.83kcal/mole respectively.

CARBONYLATION OF PRIMARY AND SECONDARY AMINES

The complex $[\text{Ru}^{\text{II}}(\text{EDT A-H})(\text{CO})]$ 1 catalyzes⁷ carbonylation of diethylamine and triethylamine⁹ at a CO pressure of 5-26 atmospheres and temperatures in the range $80\text{-}100^\circ$ in aqueous medium. The products of the carbonylation of diethylamine are N,N-diethylformamide (80 per cent) and N,N-tetraethylurea (20 per cent) whereas triethylamine gave 100 per cent N,N-diethylpropionamide. The observed rates for the carbonylation of diethylamine and triethylamine have first order dependence on the catalyst, substrates and dissolved CO concentrations. The mechanism of the reaction is depicted in Scheme III.

The pre-equilibrium steps in the mechanism involve the formation of the $\text{Ru}(\text{II})$ carbonyl complex 3 and the mixed ligand diethylamine or triethylamine complex 4. The proposed rate determining step of the reaction is the CO insertion into the M-N bond of 4 to form an η^1 -amide complex 5. Alkyl migration to CO in the fast step gives the products; N,N-diethylformamide in the case of diethylamine or N,N-diethylpropionamide in the case of triethylamine. In the case of diethylamine, further reaction of the intermediate 5 with another

Rate Expressions

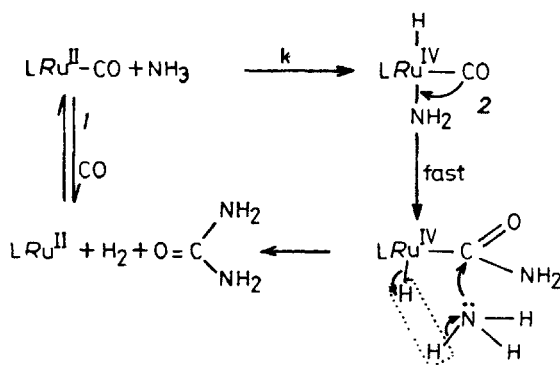
$$\frac{[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}}{\text{rate}} = \frac{1}{[S_1]} \frac{1}{kK_1K_2[\text{CO}]} + \frac{1}{k}$$

$$\frac{[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}}{\text{rate}} = \frac{1}{[\text{CO}]} \frac{1}{kK_1K_2[S]} + \frac{1}{k} + \frac{1}{K_2[S_1]}$$

S_1 = triethylamine or diethylamine

CARBONYLATION OF NH_3

The extension of the carbonylation of tertiary and secondary amines is the carbonylation of NH_3 which was conducted in a range of CO pressures from 50–80 atmospheres and temperature range 50–60°. The main product of the reaction is urea with small quantities of formaldehyde. The reaction gives a new route for urea synthesis from CO and NH_3 . The synthesis of urea through the established ammonium carbamate route requires temperatures of the order to 400–500° and a high pressure 200–300 atmospheres. The catalysis of carbonylation of NH_3 by 5 drastically reduces the input of energy for the synthesis of urea. The mechanism of the reaction is depicted in Scheme IV.



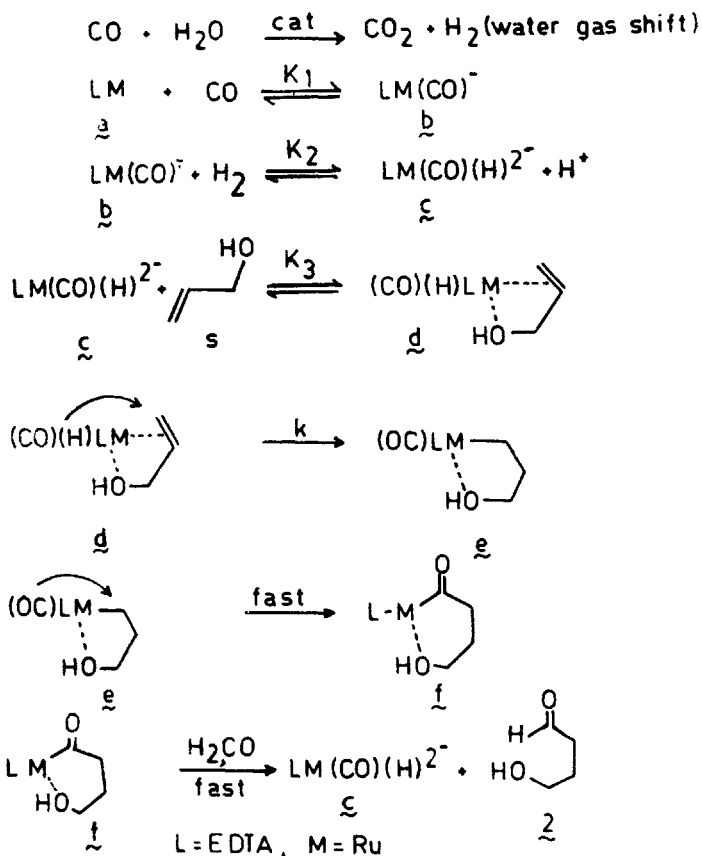
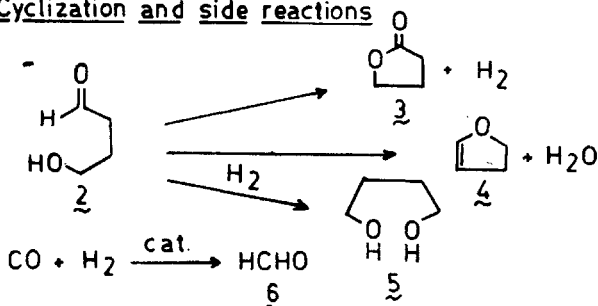
SCHEME IV

The rate-determining step of the reaction is the homolytic cleavage of NH_3 into H and NH_2 followed by the oxidative addition to $\text{Ru}^{\text{II}}(\text{EDTA})\text{CO}$ 1 to form a $\text{Ru}(\text{IV})$ hydrido imide complex 2. Insertion of CO into Ru–N bond gives the γ -formamide intermediate 3 which reacts with another molecule of NH_3 to give urea, H_2 and $\text{Ru}^{\text{II}}(\text{EDTA}-\text{H})$ to complete the catalytic cycle. The rate determining step of the reaction is the oxidative addition of NH_3 to $\text{LRu}^{\text{II}}-\text{CO}$ to give 2 (Scheme IV).

CARBONYLATION OF ARYL HALIDE

The carbonylation of benzyl chloride⁸ is catalyzed by the complex $[\text{Ru}^{\text{II}}(\text{EDTA})(\text{CO})]$ 1 at 80° and 20 atmospheres of CO in 8 : 2 ethanol-water mixture. The

Scheme - VI

Cyclization and side reactions

$$\text{Rate} = kK_1K_2K_3 [\text{ML}] [\text{CO}] [\text{H}_2] [\text{S}] \quad \dots(1)$$

$$\text{Rate} = \frac{kK_1K_2K_3 [\text{ML}] \tau [\text{CO}] [\text{H}_2] [\text{S}]}{1 + K_1 [\text{CO}] + K_1K_2 [\text{CO}] [\text{H}_2] + K_1K_2K_3 [\text{CO}] [\text{H}_2] [\text{S}]} \quad \dots(2)$$

$$\frac{[\text{MT}]_{\text{T}}}{\text{rate}} = \frac{1}{kK_1K_2K_3 [\text{CO}] [\text{H}_2]} + \frac{1}{kK_2K_3 [\text{H}_2]} + \frac{1}{kK_2} \times \frac{1}{[\text{S}]} + \frac{1}{k} \quad \dots(3)$$

$$\text{Slope} = \frac{1}{kK_1K_2K_3 [\text{CO}] [\text{H}_2]} + \frac{1}{kK_2K_3 [\text{H}_2]} + \frac{1}{kK_2} \quad \dots(4)$$

Rate

$$k = 0.57\text{min}^{-1}$$

$$K_1 = 4.9\text{M}^{-1}$$

$$K_2 = 190.6\text{M}^{-1}$$

$$K_3 = 49.2\text{M}^{-1}$$

The hydroformylation of allyl alcohol proceeds through three preequilibrium steps involving the formation of the carbonyl b the hydridocarbonyl c and the mixed ligand hydrido-carbonyl-olefin complex d. The rate determining step of the reaction involves the insertion of the hydride in the η^2 -complex d to form the complex e. Fast insertion of CO in M-C bond of e gives the intermediate f which reacts with H_2 and CO in fast steps to form the catalyst g and γ -hydroxybutyraldehyde 2 which cyclizes and takes part in side reactions as shown in Scheme VI. The percentages of the various products formed are 2 (35 per cent), 3 (25 per cent), 4 (25 per cent), 5 (1 per cent), polymeric products (\sim 14 per cent).

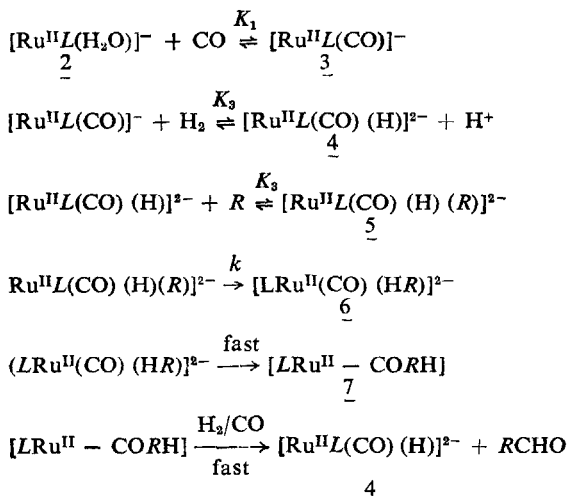
The values of the various equilibrium constants K_1 , K_2 , K_3 and the rate constant k were calculated by setting up suitable kinetic expressions (1-3) and solving them by slope intercept method. The value of the equilibrium constant K_2 is about 50 times more than K_1 which reflects on its excellent catalytic property. The value of the rate constant k of 0.57min^{-1} gives a turnover of about 86 moles of product per mole of the catalyst per hour. The activation energy of the reaction is 23 kcal/mole reflecting on the energy requirement in going from a η^2 to η^1 complex.

HYDROFORMYLATION OF 1-HEXENE

Recently, much attention has been diverted to water soluble catalysts in order to achieve a high conversion of end olefins to the linear aldehydes in oxo reaction.^{15,16} The use of the water soluble phosphine ligands especially the sulphonated phosphines^{15,16} offer a simple biphasic system where the Rh(I) catalyst is maintained in the aqueous phase, whereas the organic phase contains the reactants and products with different ligands. The use of soluble Rh(I) catalyst and 1-hexene as substrate gave a linear to branched chain aldehyde ratios ranging from 9 : 1 to 18 : 1 at 80° and CO pressure of 8 atmospheres.¹⁶ The complex Ru(EDTA) CO 3 catalyses¹¹ the hydroformylation of 1-hexene to 100 per cent 1-heptaldehyde in a homogeneous system at 130° and 80 atmosphere of syn gas in a contact time of 12 hours.

The mechanism of the reaction involves the formation of the carbonyl complex 3 and the carbonyl hydride species 4. The formation of the carbonyl hydride are established by nmr of the hydrido species 4 with hydride peaks at -24ppm and -6ppm corresponding to the formation of isomeric hydrides where H is *cis* and *trans* to CO, respectively. The hydride 4 forms the mixed ligand hydrido olefin species 5. The rate determining step of the reaction involves the transfer of H^- to coordinated olefins to form η^1 -alkyl species 6. Insertion of

CO in 6 in a fast step gives the acyl complex 7 which reacts with H₂/CO in a fast step to form the carbonyl hydride 4 and 1-aldehyde which is formed to the extent of 100 per cent. Appropriate kinetic expressions 1-4 are solved to get the values of the various equilibrium constants and rate constant *k*.



L = EDTA-H, *R* = 1-hexene

SCHEME-VI Mechanism of Hydroformylation of 1-hexene

$$\text{rate} = \frac{kK_1K_2K_3[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}} [\text{CO}] [\text{H}_2] [\text{R}]}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{H}_2] + K_1K_2K_3[\text{CO}][\text{H}_2][\text{R}]}$$

$$\frac{[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}}{\text{rate}} = \frac{1}{kK_1K_2K_3[\text{CO}][\text{H}_2]} + \frac{1}{kK_2K_3[\text{H}_2]} + \frac{1}{kK_3} \times \frac{1}{[\text{R}]} + \frac{1}{k}$$

Rate

$$K_1 = 4.9\text{M}^{-1}$$

$$K_2 = 150.6\text{M}^{-1}$$

$$K_3 = 5.33\text{M}^{-1}$$

$$k = 0.322\text{min}^{-1}$$

REFERENCES

- 1 M M Taqui Khan, Amjad Hussain, G Ramachandraiah and M A Moiz *Inorg Chem* **25** (1986) 3023
- 2 M M Taqui Khan, M R H Siddiqui and M A Samad *J mol Catal* (Submitted)
- 3 M M Taqui Khan, M R H Siddiqui, A Hussain and M A Moiz *Inorg Chem* **25** (1986) 2756
- 4 M M Taqui Khan and Z Shirin *Inorg Chem* (Submitted)
- 5 M M Taqui Khan and M R H Siddiqui (unpublished)
- 6 M M Taqui Khan, S B Halligudi and S Shukla (*Int Patent Applied*)
- 7 M M Taqui Khan, S B Halligudi and S H R Abdi *J mol Catal* (submitted)
- 8 M M Taqui Khan, S B Halligudi and S H R Abdi *J mol Catal* **44** (1988) 179
- 9 F J Waller *J mol Catal (Review Issue)* (1986) 43

- 10 M M Taqui Khan, S B Halligudi and S H R Abdi *J mol Catal (In Press)*
- 11 M M Taqui Khan, S B Halligudi and S H R Abdi *J mol Catal (in Press)*
- 12 M M Taqui Khan, A Hussain, M A Moiz and R M Naik (*Unpublished*)
- 13 R B Anderson *In Catalysis (Ed P H Emmett)* Reinhold N Y (1957) p 1
- 14 P J Denny and D A Whan *In Catalysis Vol. 2* Chemical Society London (1957) p 1
- 15 A Decbeu, P Escaffre, J M Frances, Ph Kalck and A Thorez *J mol Catal* **10** (1986) 631
- 16 P Escaffre, A Thorez and Ph Kalck *Chem Commun* **146** (1987)